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Cheng, Hongyuan; Stenby, Erling Halfdan; Kontogeorgis, Georgios

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Hongyuan Cheng

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Ph.D. Thesis

DTU

TECHNICAL UNIVERSITY OF DENMARK
DEPARTMENT OF CHEMICAL ENGINEERING

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Hongyuan Cheng

2003

Department of Chemical Engineering
Technical University of Denmark
DK-2800 Kongens Lyngby, Denmark

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Preface

This thesis is submitted as a partial fulfilment of the Ph.D. degree at the Technical University of Demark.

The project, granted by the Danish Environmental Research Programme, has been carried out from January 2000 to June 2003 at the Department of Chemical Engineering, Technical University of Denmark under the supervision of Professor Erling Stenby and associate Professor Georgios Kontogeorgis. I wish to thank my supervisors for their guidance, their ideas, and their ability to encourage me.

My thanks also extend to Professors Peter Rasmussen, Jørgen Mollerup, Michael Michelsen, Simon Andersen and Kaj Thomsen in IVC-SEP for discussions on the new research topic.

I would also like to thank Dr. Chau-Chyun Chen for our many discussions on matters of modelling surfactant solutions through email and during his visit in Denmark.

My thanks also give to my family, my wife Hongwen Li and my son Fan Cheng for their support and understanding during the past years.

Finally, I wish to thank all members of the IVC-SEP for making the past years so successful.

Hongyuan Cheng

Kongens Lyngby, October 2003

Summary

In this work, the key physical properties of non-ionic and ionic surfactant solutions, such as the critical micelle concentration (CMC) and the octanol-water partition coefficient (*K*ow), are studied by molecular thermodynamic methods based on UNIFAC. The mean activity coefficients of the aqueous electrolyte and organic electrolyte solutions are modelled by a modified Achard's UNIFAC model proposed in this work. Some of important properties in the surfactant solutions, such as the hydrophilic-lipophilic balance (HLB), the Krafft point (KP), the cloud point (CP), the aggregation number (n_g), the toxicity (EC50) and the bio-concentration factor (BCF) are also investigated. And suitable correlations have been developed.

Surfactant solutions are unique systems because the surfactant molecules form micelles in aqueous and non-aqueous solvents by self-assembly under the hydrophobic interaction with solvent molecules. Surfactant solutions have attracted much attention from academia and industry because they play important role in different industrial areas, e.g. chemical and oil industry, pharmaceutical and bio-industries, paper, food and film industries.

In this work, different thermodynamic frameworks for the micelle formation of surfactant molecules in aqueous solution are systematically reviewed and compared. The method proposed by Chen et al. (Chen, C.-C., *AIChE J.*, **42**, 3231, 1996; Chen, C.-C., C. P. Bokis, and P. Mathias, *AIChE J.*, **47**, 2593, 2001) is selected for studying the micelle formation of surfactant molecules in aqueous solutions.

Based on the method of Chen (1996), the CMC of non-ionic surfactant solutions is correlated and predicted successfully with the UNIFAC method. In this step, a new UNIFAC functional group is introduced. The necessary interaction parameters for the new group are obtained from vapour-liquid equilibrium data.

In order to correlate the CMC of ionic surfactant solutions, an electrolyte UNIFAC model proposed by Achard et al. (Achard C., C. G. Dussap, and J. B. Gros, *AIChE J.*, **40**, 1210 , 1994a; Achard C., C. G. Dussap, and J. B. Gros, *Fluid Phase Equilibria*, **98**, 71, 1994b) is modified and used to correlate the mean ionic activity coefficient of aqueous electrolyte and organic electrolyte solutions. It was found that the structural parameters (Q,

R) of ions used in the work of Achard and others do not follow Flory-Huggins assumption ($Q/R \leq 1$). Thus, a new method is developed to calculate the Q, R of ions from ionic radii using the condition $Q/R<1$. The mean activity coefficients of some aqueous electrolyte solutions are correlated with the modified Achard method and compared with the electrolyte NRTL and the extended UNIQUAC models. The mean activity coefficients of five sodium carboxylate systems are correlated simultaneously with the modified Achard model. The correlation results show a good agreement with the experimental values.

Based on the work of Chen et al. (2001), the CMC of sodium alkyl sulphates, sodium alkyl sulfonates and potassium carboxylates are successfully correlated using the modified Achard model.

Furthermore, the *K*ow of phthalates and non-ionic surfactants are predicted with different UNIFAC methods and commercial software. The prediction results are compared with the few experimental data available.

Finally, some correlations for properties of surfactant solutions, i.e. HLB, KP, CP, n_g, EC50 and BCF are presented.

Summary in Danish – Resume på dansk

I Ph.D arbejdet er de vigtige fysiske egenskaber af ikke-ioniske og ioniske surfaktantopløsninger, så som kritisk micelle koncentration (CMC) og oktanol-vand fordelingskoefficient (*K*ow), undersøgt ved molekylære termodynamiske metoder baseret på UNIFAC. Middel-ion-aktivitetskoefficienter for vandige elektrolytopløsninger og organiske elektrolytopløsninger er modelleret vha. en modificeret Achard's UNIFAC model foreslået i denne afhandling. Nogle vigtige egenskaber for surfaktantopløsninger, som hydrofil-lipofil balance (HLB), Krafft punkt (KP), "cloud"-punkt (CP), aggregationstal (n_g), toksisitet (EC50) og bio-koncentrationsfaktor (BCF) er ligeledes bestemt og passende korrelationer er udviklet.

Surfaktantopløsninger er unikke systemer, fordi surfaktantmolekyler i vandige og ikke-vandige opløsningsmidler danner miceller ved selvorganisening ved hydrofob vekselvirkning med solventmolekyler. Surfaktantopløsninger har fået megen akademisk og industriel opmærksomhed, fordi de spiller en vigtig rolle på forskellige industrielle områder, f.eks. olie- og kemisk-industri, farmaceutisk- og bio-industri, papir, fødevare og film industri.

I Ph.D. arbejdet, er forskellige termodynamiske metoder for micelledannelse af surfaktantmolekyler i vandig opløsning systematisk undersøgt og sammenlignet. Metoden foreslået af Chen et al. (Chen, C.-C., *AIChE J.*, **42**, 3231, 1996; Chen, C.-C., C. P. Bokis, and P. Mathias, *AIChE J.,* **47**, 2593, 2001) er udvalgt for yderligere at undersøge micelledannelse af surfaktantmolekyler i vandige opløsninger.

Baseret på Chens metode (1996), er CMC af ikke-ioniske sufaktantopløsninger korreleret og forudsagt med succes ved anvendelse af UNIFAC metoden. I dette trin er en ny funktionel gruppe introduceret i UNIFAC. De nødvendige interaktionsparametre for denne nye gruppe er hentet fra damp-væske ligevægtsdata.

For at korrelere CMC for ioniske surfaktantopløsninger, er en elektrolyt UNIFAC model, foreslået af Archard et al. (Achard C., C. G. Dussap, and J. B. Gros, *AIChE J.*, **40**, 1210 , 1994a; Achard C., C. G. Dussap, and J. B. Gros, *Fluid Phase Equilibria*, **98**, 71, 1994b), blevet modificeret og anvendt til at korrelere middel-ion-aktivetetskoefficienten af vandige elektrolyt- og organiske elektrolytopløsninger. Det viste sig, at ion strukturparametrene (Q,R) brugt i Achards og andres arbejde ikke følger Flory-Hugggins antagelse (Q/R≤1). Derfor er

en ny metode udviklet til at beregne Q, R ud fra ionradiier ved brug af antagelsen ($Q/R<1$). Middel-ion-aktivitetskoefficienterne for nogle vandige elektrolytopløsninger er korreleret med den modificerede Achard metode og sammenlignet med elektrolyt NRTL og Extended UNIQUAC modellen. Middel-ion-aktivitetskoefficienterne for fem natriumcarboxylat-systemer er korreleret samtidig med den modificerede Achard model. Korrelationsresultaterne viser god overensstemmelse med eksperimentelle data.

Baseret på Chen et al.'s arbejde (2001), er CMC af natriumalkylsulfater, natriumalkylsulfonater og kaliumcarboxylater, korreleret med succes ved brug af den modificerede Achard model.

Ydermere, er Kow for phthalater og ikke-ioniske surfaktanter forudsagt ved anvendelse af forskellige UNIFAC metoder og kommercielt software. De forudsagte resultater er sammenlignet med de få eksperimentelle data, der er til rådighed.

Sluttelig er nogle korrelationer for surfaktantopløsningers egenskaber, f.eks. HLB, KP, CP, n_g, EC50 and BCF, præsenteret.

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Chapter 1 Introduction

Surfactants

Surface-active compounds (surfactants) are chemicals that show ability to adsorb at interfaces. The surfaces (interfaces), at which surfactants adsorb, can be between two immiscible liquids, the liquid-gas (air) surface or between a solid and a liquid. The surfactants are also often called amphiphiles, surface-active agents or "soft-matter". Surfactant molecules have two parts: a hydrophilic (polar) part which likes water, and a hydrophobic (non-polar) part which does not. The hydrophobic part of a surfactant molecule is soluble in oil (non-polar solvents) but is not very soluble in water and other polar solvents. The hydrophilic part, on the other hand, has a great affinity to water but is not very compatible with non-polar solvents. The amphiphilic nature of these molecules results in many unique phenomena when surfactants are dissolved in aqueous or non-aqueous solutions. Although surfactants are often present in very small amounts in solution, they do affect the overall properties of the system greatly, such as surface tension, osmotic pressure, solubility, etc., because of their ability to adsorb at surfaces and to form micelles in the solutions. The characteristics of solutions containing surfactants, such as detergency, wetting, emulsification, dispersion and foaming, have been known for a long time and have many practical applications in daily life and industry. Many industrial products, like soap, shampoo, washing powders, etc. contain surfactants. The characteristics of surfactants have attracted huge attention from the scientific community. For example, in 1991, de Gennes's Nobel Lecture was on "Soft Matter", i.e. polymers, surfactants and liquid crystals.

When surfactants are dissolved in aqueous solutions, the surfactant solution has a completely different behaviour. In the aqueous surfactant solution, at fairly well defined concentration, abrupt changes occur in several physical properties, such as osmotic pressure, electrical conductance and surface tension. This anomalous behaviour could be explained in terms of formation of organised aggregates of the surfactant molecules (the micelles) in which the hydrophobic hydrocarbon chains are orientated towards the interior of the micelle, leaving the hydrophilic groups in contact with the aqueous medium. The concentration above which micelle formation becomes appreciable is termed critical micelle concentration (CMC).

Thermodynamic Modelling of the Surfactant Solutions

Understanding and modelling the surfactant solutions are focused on some suitable properties. These are, for surfactant solutions, the surface tension, the aggregation number, the CMC, the Krafft temperature, the cloud point, etc., all of which have been studied by both experimental and theoretical methods. In surfactant solutions, the micelle formation (also called self-association or self-assembly) is a unique phenomenon. All properties in surfactant solutions are related to the micelle formation of surfactant molecules. Among these properties, the CMC and the aggregation number are possibly the most important properties for surfactant solutions. The CMC gives the condition of micelle formation. The aggregation number, which is the number of surfactant molecules making up a micelle, describes the initial 'size' of a micelle, the growth of the micelle and the phase separation of the surfactant solution.

Many experimental and theoretical publications about micelle formation in surfactant solutions are presented in the literature. Although great progress has been made in experimental and theoretical aspects of surfactant solutions, there are still gaps between understanding of surfactant solutions and practical applications. Research work on surfactant solutions is somewhat limited to experimental study and documentation of the observed behaviour (Hines, 2001). The theoretical understanding is still rather poor. A complete thermodynamic or physical framework has not been established.

Several thermodynamic treatments or frameworks have been proposed for the micelle formation in aqueous surfactant solutions. In these frameworks, the micelle formation is treated as a pseudo-phase formation, a mass-action process, etc. in solution. These treatments capture at least partly the phenomena of the micelle formation.

Working Strategy

The main purpose of this research project is not to set up a completely new thermodynamic theory for micelle formation. Rather, the objective of this work is to develop a thermodynamic method for the micelle formation and use it to correlate or predict the important properties of surfactant solutions. The CMC of surfactant solutions is the main property studied by molecular thermodynamic methods.

Recently, a thermodynamic framework was proposed by Chen et al. (1996, 2001) to describe the micelle formation of non-ionic and ionic surfactant solutions. In Chen's work, the activities of components or ionic species are combined with a thermodynamic expression for the micelle formation. A local composition based activity coefficient model, the NRTL (nonrandom, two-liquid) equation, is used to calculate the activities.

From an industrial application viewpoint, it would be convenient to develop structure activity models possibly based on group contributions, which can predict the important properties of surfactant solutions. The universal functional activity coefficient (UNIFAC) model is such a group contribution method for the estimation of activity coefficients. Comprehensive studies of UNIFAC have been presented by several researchers (see Appendix A), but not for the surfactant solutions until very recently (Cheng, et al. 2002, Flores, et al. 2001). Several versions of UNIFAC with different group interaction parameters are readily available in the literature. Due to the extensive use of UNIFAC in the chemical industry and its large amount of group parameters, it is interesting to explore its applicability to surfactant solutions. Therefore, the UNIFAC model will be used in this work to study the CMC with the thermodynamic treatment of Chen et al. (1996, 2001).

Another property studied in this work is the octanol-water partition coefficient (*K*ow). The *K*ow is a widely used property for assessing the hydrophobic and hydrophilic tendencies of molecules in environmental and pharmaceutical applications. However, it is difficult to measure for surfactants. Alternatively, *K*ow can be predicted from thermodynamic methods such as UNIFAC and empirical correlations for these difficult chemicals.

Some special properties are often applied to surfactant solutions, e.g. the cloud point, the Krafft point, the hydrophilic-lipophilic balance (HLB), the aggregation number (n_g), phase inversion temperature (PIT). Some of them, e.g. HLB, are not strictly defined, but are convenient for certain practical applications and are widely used in practice to describe the specific surfactant characteristics, such as emulsification, solubility, wetting, dispersing, foaming, and detergency. These properties often provide a fast way to classify the abilities of surfactants. For example, many producers report the HLB values for surfactant-based products.

Some of these empirically-based properties, e.g. HLB and n_g can be correlated with CMC and *K*ow which can be measured and/or calculated from thermodynamic models. Such correlations are useful in surfactant development and choice of new materials. Some relevant correlations of this type are collected from the literature, and others are developed in this work.

As part of cleaning products (detergents), Europe consumes more than 1 million tons surfactants in 1997 (Morse, 1999). Most of these consumed surfactants will finally enter the natural ecosystem. The environmental effects of surfactants have been brodly discussed. In this work, correlations between *K*ow and environmental effects are also developed. Figure 1.1 summarizes the working strategy followed in this research project.

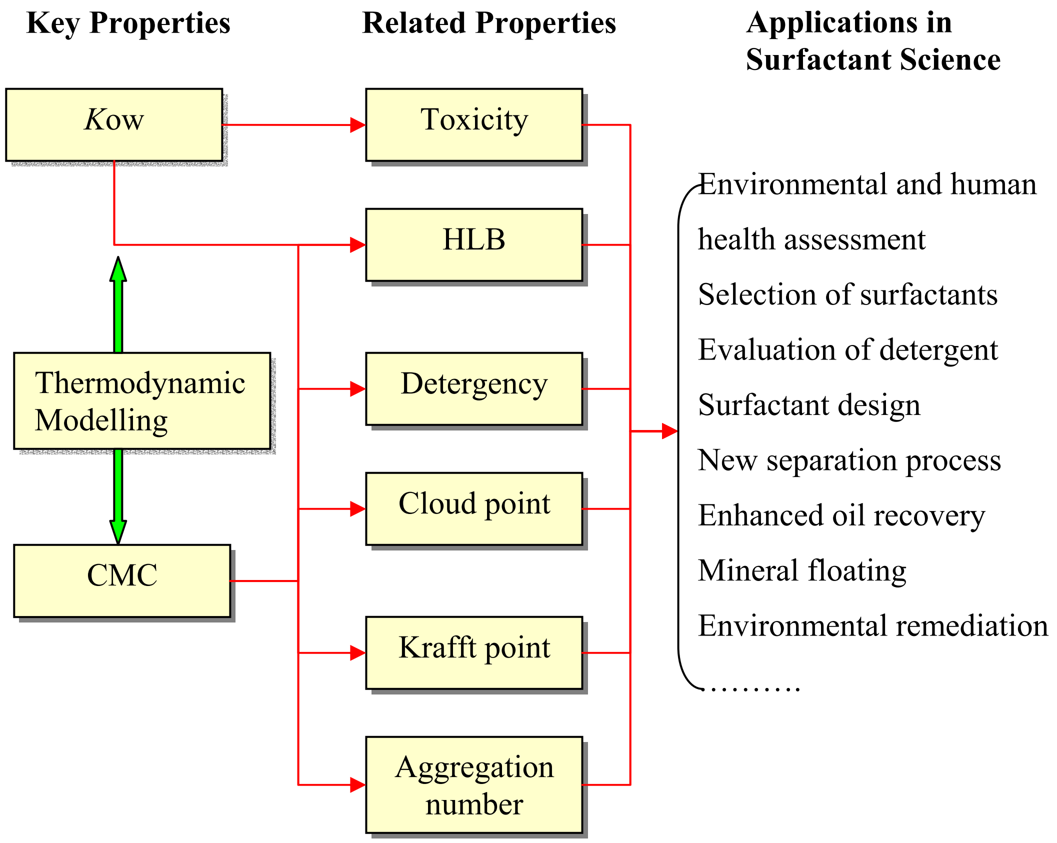

Figure 1.1 Working strategy of this research project

Priority Surfactants

Following the guidelines of the Danish environmental research programme (AMI report, 2000, Madsen, et al. 2001, Danish EPA web page: www.mst.dk), the priority surfactant families which were chosen for further studying in this work are sodium alkyl sulphates, sodium alkyl ether sulphates and alcohol ethoxylates. Meanwhile, the octanol-water partition coefficient of phthalates has been also studied as part of this environmental program.

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Morse, P. M. “Soaps & Detergents”, *Chemical & Engineering News*, **77**, 35, Feb. 1, (1999).

Chapter 2 Surfactant Solutions

In this chapter, some basic characteristics of surfactant molecules and solutions are briefly described. The environmental and health assessment of surfactants is discussed. The micelle formation and phase diagrams of surfactant solution are outlined.

2.1 Surfactants and Classification

Surfactant Molecules

Surfactant molecules have a dual nature. One part of the molecule is soluble in water (the hydrophilic part or "head"), while the other part is not water-soluble (the hydrophobic part or "tail"), as shown in Figure 2.1. The hydrophobic part is commonly a hydrocarbon chain (branched or linear) that may contain aromatic structures. This part of the surfactant is soluble in oil (non-polar solvents) but only sparingly soluble in water and other polar solvents. The hydrophilic part on the other hand has a great affinity to water but is not very soluble in non-polar solvents (oil). The hydrophilic part can be an ionic or strongly polar group (such as ethylene oxide).

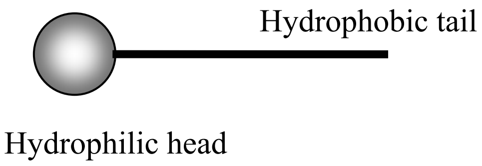


Figure 2.1 Structure of surfactant molecules

Despite being called the head-group, the hydrophilic part is not necessarily placed at the end of the hydrocarbon chain. More than one hydrophilic or hydrophobic group can be present in a surfactant molecule. A surfactant molecule is not fully compatible with either a non-polar or a polar medium. There is always a conflict between the affinity of the headgroup and the tail. Their amphiphilic nature forces the surfactant molecules to adopt unique orientations in an aqueous medium and to form suitably organized aggregates.

Classification of Surfactant Molecules

Surfactants are typically classified according to the nature (charge) of their head-group. Four main types of surfactants exist: anionic, cationic, non-ionic and zwitterionic (or amphoteric) surfactants, as shown in Figure 2.2 (Porter, 1994). The ionic surfactants carry a net charge (positive or negative) located on the head-group, whereas the non-ionic surfactants are neutral, but have polar head-groups e.g. ethylene oxide (EO). Zwitterionic surfactants can be either anionic or cationic depending on the pH value of the solution.

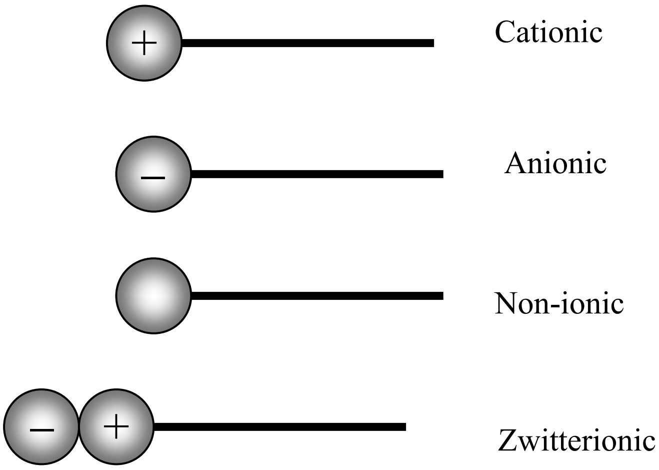


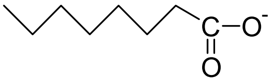
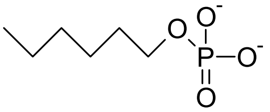
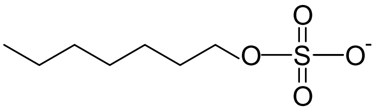
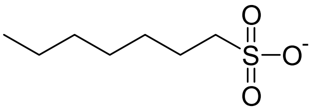
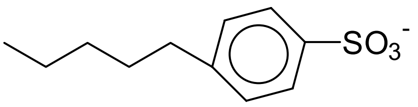
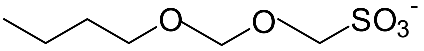
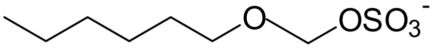
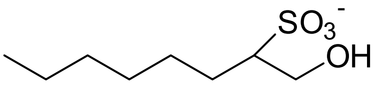
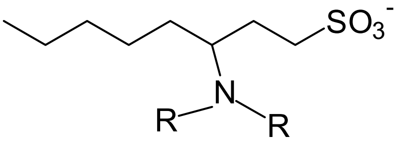
Figure 2.2 The four different main types of surfactants

Examples and Chemical Structures of Surfactant Molecules

Anionic Surfactants

Anionic surfactants are the most common surfactants in cleaning products with 0.6 million tons consumed in the U.S. in 1997. Anionics are the least expensive surfactants, at 0.6 cents to $2.00 per kg, and prices are generally stable (Morse, 1999). The hydrophilic part of the molecules can be a carboxylate, sulphate, sulfonate or phosphate. Some examples are given in Table 2.1 (de Guertechin, 1999, Huibers et al. 1997).

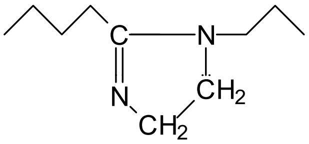
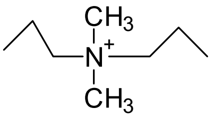
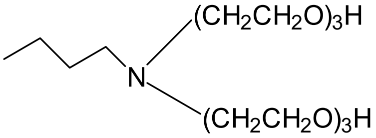
Table 2.1 Examples and chemical structures of anionic surfactants

Carboxylates $CH_3CH_2\ldots CH_2\text{-}COO^-$ 	Phosphates $CH_3CH_2\ldots CH_2\text{-}PO_4^-$ 
Alkylsulfates $CH_3CH_2\ldots CH_2\text{-}OSO_3^-$ 	Alkyl sulfonates $CH_3CH_2\ldots CH_2\text{-}SO_3^-$ 
Alkylbenzenesulfonates $CH_3CH_2\ldots CH_2\text{-}C_6H_4\text{-}SO_3^-$ 	Alkylethersulfonates $CH_3CH_2\ldots CH_2\text{-}CHO\text{-}SO_3^-$ 
Alkylethersulfates $CH_3CH_2\ldots CH_2\ CHO\text{-}OSO_3^-$ 	Others  

Cationic Surfactants

Typical cationic surfactants are alkyl amines, alkylimidazolines, quaternary ammonium compounds, ethoxylated alkyl amines and esterified quaternaries, as shown in Table 2.2. The alkyl amines are not strictly cationic surfactant because they are uncharged in solution (de Guertechin, 1999). Only a small amount of cationic surfactants are consumed per year compared to anionic and non-ionic surfactants. Cationics are remain a small, specialized part of cleaning product market (Morse, 1999).

Table 2.2 Examples and chemical structures of cationic surfactants

Alkyl amine $CH_3CH_2\ldots CH_2\text{-}NH_2$ 	Alkylimidazolines $CH_3CH_2\ldots CH_2{=}CH_2CH_2N_2CH_2..CH_2CH_3$ 
Quaternary ammonium compounds $CH_3CH_2\ldots CH_2(CH_3)\text{-}$ $N^{+}(CH_3)CH_2\ldots CH_2CH_3$ 	Ethoxylated alkyl amines $CH_3CH_2\ldots CH_2N[(CH_2CH_2O)_3H]_2$ 

Non-ionic Surfactants

Typical non-ionic surfactants are alkyl ethoxylates, alkylphenyl ethoxylates, alkanediols, alkyl mon- and disacchardes, ethoxylated alkylamines, ethoxylated alkylamides, fluorinated linear alkyl ethoxylates, fluorinated ethoxylated amides, as shown in Table 2.3 (Huibers et al. 1996). Anionics are gradually replaced by milder non-ionic surfactants in detergent products (milder to environment). As the large laundry products change from powders to liquids, nonionic surfactants offer greater stability and formulation flexibility than many anionics.

Zwitterionic (or Amphoteric) Surfactants

Zwitterionic surfactants carry a positive charge on a cationic site and a negative charge on an anionic site. The charge of the molecule changes with the pH value of the solution and show a zwitterionic form around the isoelectric point. Normal zwitterionic surfactants are acyl ethylenediamines, alkyl amino acids or imino diacides, as shown in Table 2.4 (de Guertechin, 1999). Zwitterionic surfactants are growing the most rapidly in using for all cleaning products, but from a very small base, benefiting from a trend toward milder surfactants.

Table 2.3. Examples and chemical structures of non-ionic surfactants

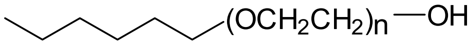
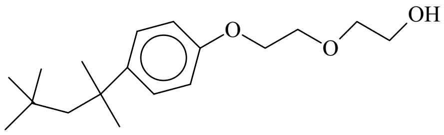
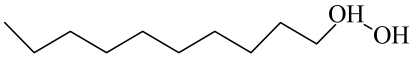
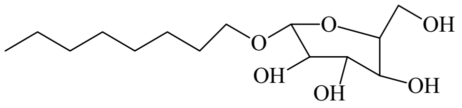
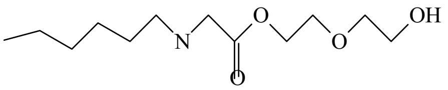
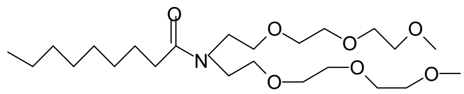
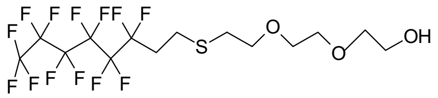
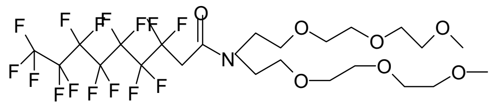
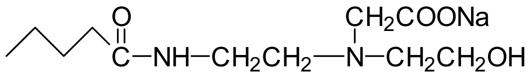
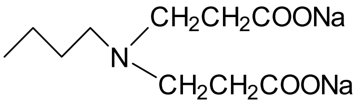
Alky ethoxylayes $CH_3CH_2\ldots CH_2(OCH_2CH_2)_nOH$ 	Alkylphenyl ethoxylates $CH_3CH_2\ldots CH_2C_6H_4(OCH_2CH_2)_nOH$ 
Alkanediols $CH_3CH_2\ldots CH_2OHOH$ 	Alkyl mono-and disaccharides $CH_3CH_2\ldots CH_2O_2(OH)_4$ 
Ethoxylated alkylamines 	Ethoxylated alkylamides 
Fluorinated linear alkyl ethoxylates 	Fluorinated ethoxylated amides 

Table 2.4. Examples and chemical structures of zwitterionic surfactants

Acyl ethylenediamines 	Alkyl amino acids 

2.2 Consumption, Application, Environmental and Health Assessment of Surfactants

Consumption

The high volume consumption of surfactant is mostly due to their use in detergents and other cleaning products. In Europe, around 2 million tons surfactants are consumed in 1997 (Morse, 1999). The content and type of surfactants may differ in various detergents and other products. A liquid product may contain about 50% surfactant compared to less than

25% in powders. The consumption of various household detergents is given in Table 2.5 (Madsen et al., 2001).

Although new types of surfactants and products appear often, the mildness (mild to enviroment) is an important role to use surfactants in the product. Today, anionic surfactants are used in the largest amount in the household products. However, the growth of anionic surfactants is expected to be slow in the future because they are gradually replaced by milder non-ionic and zwitterionic surfactants. The trend towards milder surfactant has already favoured the use of specific surfactant types, such as the zwitterionic surfactants: alkyl betaines and alkylelamido betaines; the anionic surfactant: α-olefin surfonates (AOS). The consumption of different surfactant types is given in Table 2.6 and figure 2.3 (Madsen, et al., 2001).

Table 2.5 Estimated annual consumption of household detergents (Madsen et al., 2001)

Product	Annual consumption (tons)	
	Denmark (1997)	Europe (1998)
Laundry detergents, powders	28,700	3,100,000
Laundry detergents, liquids	4,900	560,000
Laundry detergents, special	3,200	--
Fabric softeners	9,100	1,000,000
All-purpose cleaning agents	5,100	950,000
Toilet cleaning agents	2,300	400,00
Hand dishwashing agents	6,000	800,000
Machine dishwashing agents	3,800	500,000
Personal care products	14,200	1,900,000
Total	77,300	3,200,000

Table 2.6 Estimated annual consumption of surfactants in 1998 (tons) (Madsen et al., 2001)

Surfactant	Denmark	Europe
Anionic	10,100	908,000
Nonionic	7,100	626,000
Cationic	1,400	115,000
Zwitterionic	540	47,000
Total	19,140	1,696,000

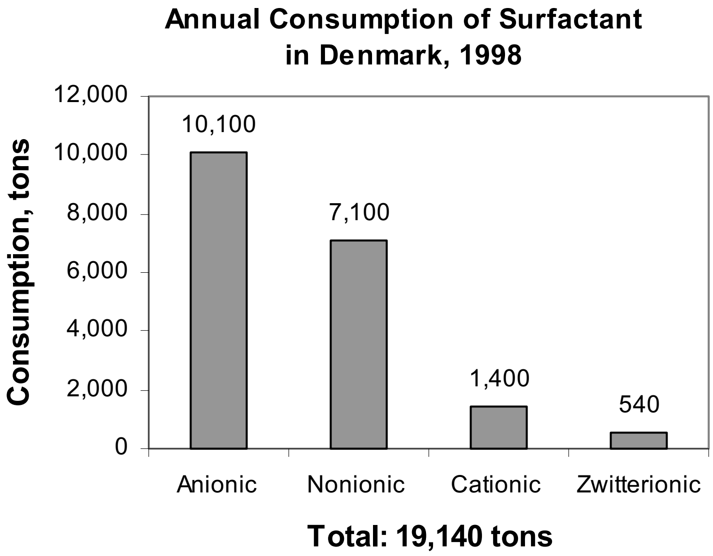


Figure 2.3 Annual consumption of anionic, non-ionic, cationic and zwitterionic surfactants in Denmark, 1998 (Madsen et al., 2001).

Application in Household Detergents

The main types of surfactants in household detergents are given in Table 2.7. The exact amount used depends on specific products.

Environmental and Health Assessment

The commonly used surfactants in household detergents and cosmetics, such as those listed in Table 2.7, have been assessed by The Danish Environmental Protection Agency (Miljøstyrelsen) in the Environmental Project No. 615, 2001 (Madsen et al., 2001). In this assessment, the environmental factors include biodegradation pathways, aerobic biodegradability, anaerobic biodegradability, effects on algae, invertebrates, fish, etc. The evaluations of human health hazard effects are toxicity effects, skin and eye irritation, reproductive toxicity, etc. More than 50 different surfactants are ranked by the environmental and human health hazard factors. The ranking of surfactants can be used to indicate cases for a more detailed risk assessment or potentially hazardous chemicals that may be considered for substitution. The assessment report (Madsen et al., 2001) can also be found in The Danish Environmental Protection Agency webpage: www.mst.dk.

Table 2.7 Overview the contents of household detergents (Morse, 1999)

Household detergent	Surfactant contents*
Heavy-duty laundry powders	Linear alkylbenzene sulfonates α- Sulfomethyl esters Alkyl polyglucosides Alcohol sulfates Linear alcohol ethoxylates
Heavy-duty laundry liquids	Linear alkylbenzene sulfonates Linear alcohol ethoxylates
Light-duty liquid detergents	Linear alkylbenzene sulfonates
Light-duty liquid dish detergents	Secondary alkane sulfonates α-Olefin sulfonates Fatty amine oxides Fatty alkanolamides Alkyl polyglucosides Linear alcohol ethoxylates
Liquid hand soaps	α-Olefin sulfonates,
Shampoos	α-Olefin sulfonates Fatty amine oxides Fatty alkanolamides Alcohol sulfates Linear alcohol ethoxylates
Toilet soaps	Alkyl glyceryl ether sulfonates
Specialty cleansers	Linear alkylbenzene sulfonates Fatty amine oxides

*It is not necessary to have all the contents in one product.

2.3 Micelle Formation

When surfactants are dissolved in water, they are forced to adopt unique orientations in the water medium because of their dual nature. The surfactant molecules become adsorbed at an air-water or oil-water interface. They are able to locate their hydrophilic head groups in the aqueous phase and allow the hydrophobic hydrocarbon chains to escape into the vapour or oil phases, as shown in Figure 2.4. This situation is energetically more favourable than complete solubilization in either phase. The strong adsorption of such molecules results in the formation of an orientated mono-molecule layer at surface or interface. This surface activity is a dynamic phenomenon, since the final state of a surface or interface represents a balance between the tendency towards adsorption and the tendency towards complete mixing due to the thermal motion of the molecules.

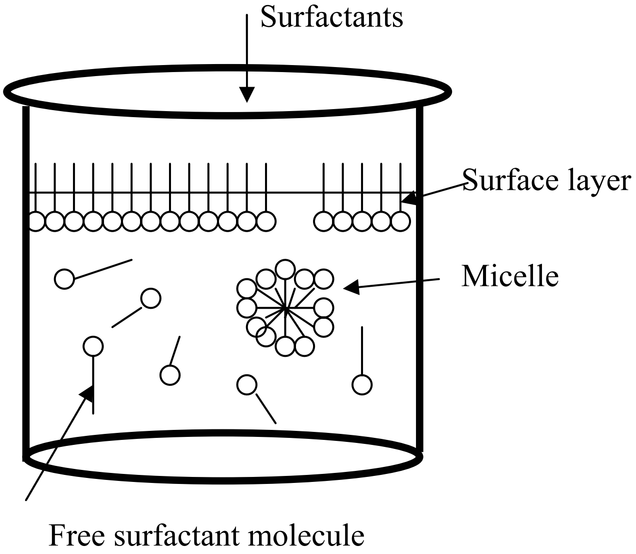


Figure 2.4 Surface adsorption and micelle formation

The tendency of surfactants to pack into an interface favours an expansion of the interface. Therefore, this must be balanced against the tendency for the interface to contract under normal surface tension forces. The surface tension is thus lowered. If the interfacial tension between two liquids is reduced to a sufficiently low value with the addition of a surfactant, emulsification will readily take place, because only a relatively small increase in the surface free energy of the system is involved (Shaw, 1992).

At fairly well defined concentrations, several physical properties (e.g. osmotic pressure, electrical conductivity, surface tension, etc.) abruptly change their values in aqueous surfactant solutions, as schematically shown in Figure 2.5. McBain and Swain (1936) suggested that this seemingly anomalous behaviour could be explained in terms of the formation of organised aggregates of the surfactant molecules, the micelles. The concentration above which micelle formation becomes appreciable is termed “critical micelle concentration (CMC)”. However, the CMC is a narrow concentration range, not a fixed value as shown in figure 2.5. When the hydrophobic part of the surfactant is a hydrocarbon chain, the micelle will consist of a hydrocarbon core, with hydrophilic groups at the surface serving to maintain solubility in water. In such micelles, the hydrophobic core is, in effect, a small volume of liquid hydrocarbon because the hydrocarbon chains are generally regarded as disordered (Tanford, 1980).

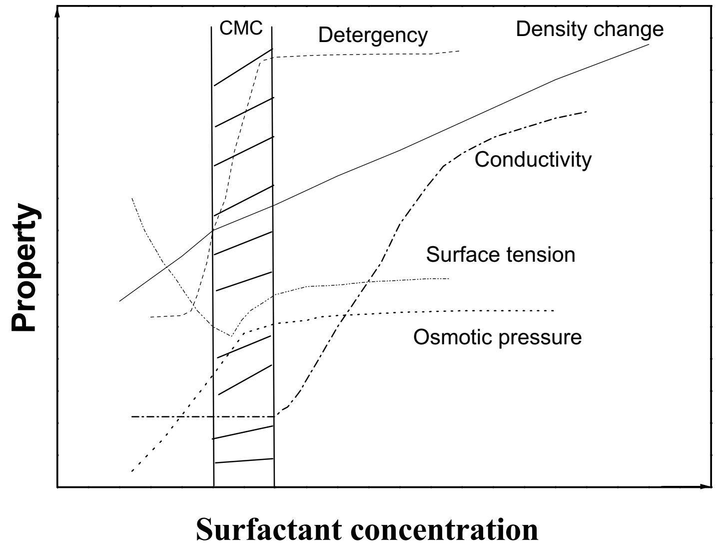


Figure 2.5 Variation of various properties with surfactant concentration

2.4 Phase Behaviour of Surfactant Solutions

The phase behaviour of surfactant solutions is a basis to understand the properties of these systems and is important for the numerous industrial applications of surfactants. However, the phase diagram of surfactant solution is very complex because the surfactant molecules undergo many different metastable states with changing temperature and concentration. The metastable phases are characterized as irreversible colloid particles. Many research aspects in phase studies of surfactant systems are summarized in book of Laughlin (1994) and in some reviews (Chernik, 2000, Khan, 1996).

The basic phase behaviour of surfactant solutions and the commonly encountered phase regions are shown in Figure 2.6 (Holland and Rubingh, 1992). In the temperature vs.

concentration phase diagram, there is a plateau line between the two-phase region and the homogenous solution. This flat line is the crystal solubility boundary of some surfactants and is called “Krafft boundary” (Laughlin, 1994). Below the Krafft boundary is the solid + liquid region in which surfactants precipitate from solution. Above the Krafft boundary, there is a dashed line dividing the solution into a monomer (free surfactants) and a micelle solution. This line is not a real phase boundary and terminates at the Krafft point.

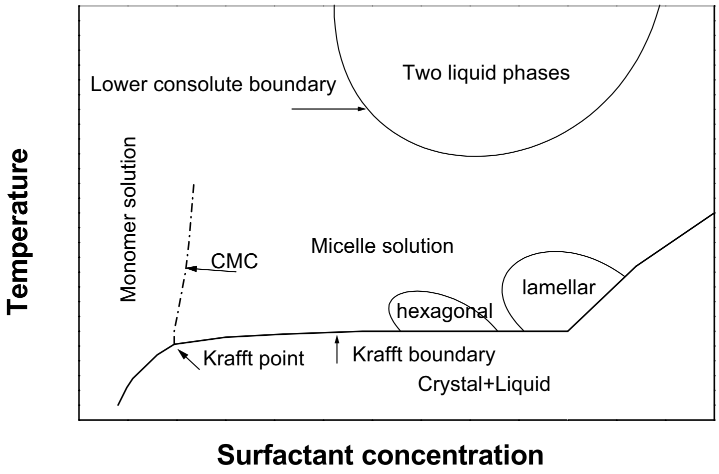


Figure 2.6 Schematic phase diagram for surfactant solutions

If the phase rule was truly obeyed for micelles, i.e. micellization could be treated as the formation of a separate phase, the Krafft boundary above the Krafft point should occur at constant temperature. The Krafft boundary is indeed relatively flat for most surfactants (figure 2.6). Krafft temperatures of surfactants are sometimes considered to be a unique characteristic of each surfactant, although in reality they slowly change with the surfactant concentration.

In the two-liquid phase region (as shown in figure 2.6), generally, one of the two phases is a surfactant rich region, while the other is a surfactant poor region. For example, the alkyl ethoxylate non-ionic and semi-polar surfactants exhibit phase separation upon heating around the lower consolute boundary. In addition, certain zwitterionic surfactants yield two phases upon cooling.

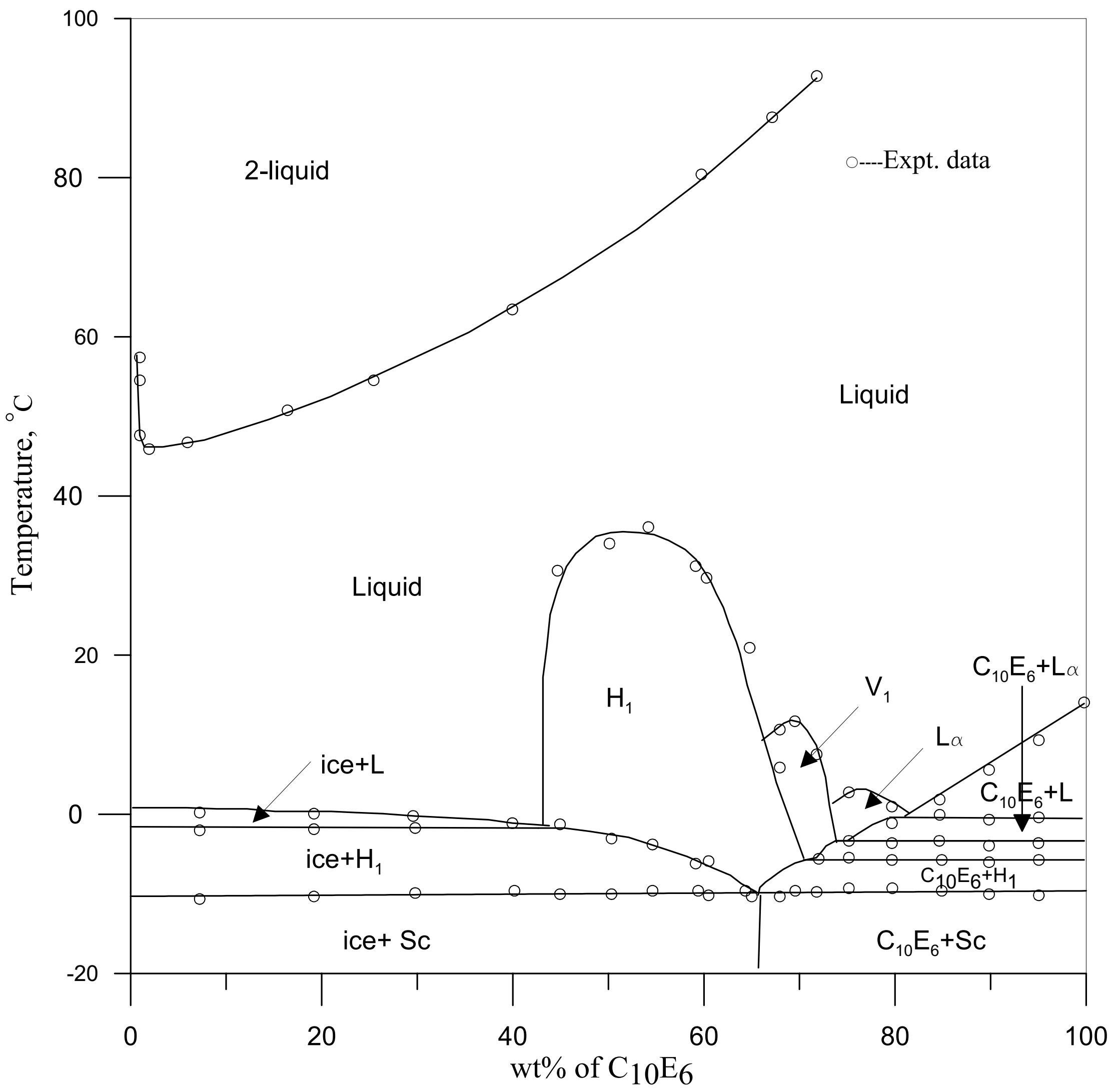


Figure 2.7 Phase diagram for $C_{10}E_6$+H_2O mixture (Nibu et al., 1998, Laughlin, 1994). ○ is experimental data. “Liquid” and “L” represent surfactant solution. “H_1”, “L_α” and “V_1” represent the hexagonal phase, lamellar phase and bi-continuous cubic phases, respectively. “$C_{10}E_6$” and “Sc” represent the solid of pure $C_{10}E_6$ and hydrated compound formed in a solid phase. “ice” is the solid water.

In the hexagonal and lamellar regions, these are two liquid crystal phases. They are commonly found in the middle composition range of the phase diagram and for practically all surfactant-water systems. The hexagonal phase consists of rod-shaped micelles packed in a hexagonal array. The lamellar phase consists of infinite continuous bilayers separated by water layers. In some systems a variety of phases have been reported to exist between the hexagonal and lamellar phases (Fontell, 1992), such as bi-continuous cubic and the so-called intermediate phases (Holmes, 1998). An example of phase diagram for hexaethylene glycol decyl ether is given in figure 2.7.

Figure 2.7 shows a phase diagram for hexaethylene glycol decyl ether ($C_{10}E_6$) and water system (Nibu, et al., 1998, Laughlin, 1994). In figure 2.7, “2-liquid phase” represents a two liquid phase region. H_1 and L_α represent the hexagonal and the lamellar phases, respectively. $C_{10}E_6$ and Sc represent the solid of pure $C_{10}E_6$ and the hydrated compound formed in a solid phase, respectively. V_1 represents a bi-continuous cubic phase. Ice represents the solid water. Liquid and L represent the $C_{10}E_6$+H_2O solution.

Chapter 3 Thermodynamics of Surfactant Solutions

In this chapter, different thermodynamic treatments for micelle formation in surfactant solutions are discussed. Although many efforts have been made towards theoretical understanding of surfactant solutions, capturing the nature of such solutions is still considered rather difficult. In contrast to the rigorous universal thermodynamic treatment of fluid phase equilibrium, many thermodynamic formulations have been proposed for micelle formation.

In this study, two types of thermodynamic methods are discussed: i) phenomenological models, such as the pseudo-phase separation model and the mass-action model and ii) molecular thermodynamic methods, such as those proposed by Tanford (1980), Israelachvili (1992), Nagarajan (1991, 1997a), Blankschtein (1986), and Chen et al. (1996, 2001).

3.1 Outline

The majority of research in the area of surfactant science focuses on experimental studies and documentation of behaviour. The theoretical understanding is rather limited (Hines, 2001). Blandamer et al. (1995), Blankschtein et al. (1997), Hines, (2001), Nagarajan (1997b), and Zana (1995) have reviewed the theories for surfactant solutions. Laughlin (1994) reviewed phase behaviours of surfactant solution and the history of surfactant science. These reviews include many different theories and models for surfactant solutions. However, only few of them have been applied to practice.

Theoretical approaches for surfactant solutions may be classified into molecular thermodynamic and phenomenological methods (empirical, semi-empirical methods). The molecular thermodynamic methods describe the physical properties of surfactant solutions using molecular thermodynamic principles and molecular structure characteristics. Empirical relations correlate experimental results via statistical methods. The semi-empirical methods follow an intermediate road, employing empirical rules and combining databases of physical properties with quantum chemical or topological descriptors. An important limitation of the semi-empirical and empirical approaches is that their implementation relies exclusively on the availability of experimental data. In phenomenological methods, the pseudo-phase separation models consider the micelle formation is a new macroscopic phase formation and use concepts and method of phase equilibrium calculation. The mass-action models treat the micelle formation as a chemical equilibrium and calculate the chemical equilibrium constant. An overview of these methods is given in figure 3.1.

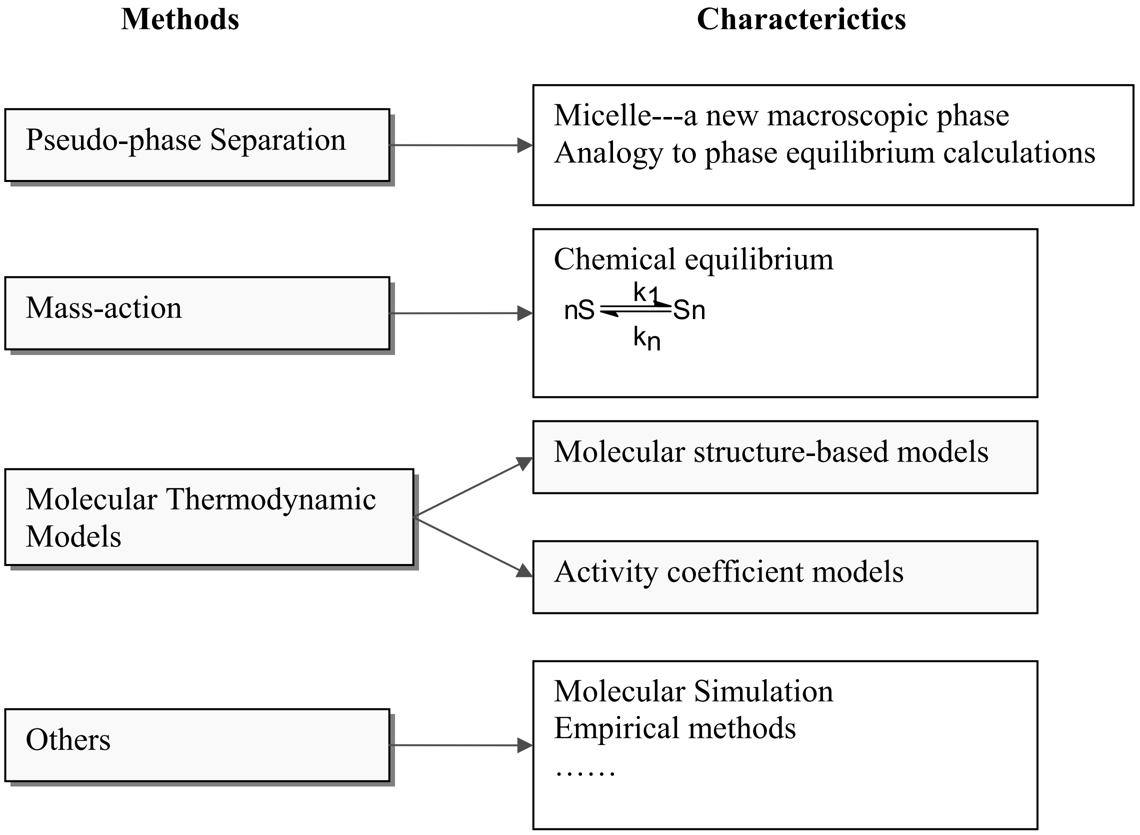


Figure 3.1 An overview of different methods for micelle formation

An application of pseudo-phase separation model can be found in the work of Flores et al. (2001) and Voutsas et al. (2001). In their work, the micelle formation is assumed to result in a second liquid phase. Micelle formation is calculated as liquid-liquid equilibrium.

Desnoyers and co-workers (1997) applied the mass-action approach to non-ionic surfactants and extended it to ionic systems by correlating the data for the monomers with the Debye-Hückel limiting law.

Two different methods are used in the molecular thermodynamic models: one is based on detailed molecule structure information to calculate the properties of micelle formation; the other depends on activity coefficient models.

The objective of molecular thermodynamic theories is to relate the chemical potential of surfactant molecules in the micelle state to the chemical potential of the free surfactant molecules in solution. These theories provide a way of relating the molecular geometry, size and chemical nature of the hydrophilic and hydrophobic groups in surfactant molecules to both macroscopic properties of the solutions and the size of the aggregated micelles. Fundamental contributions in this area are the work by Tanford (1980) and Israelachvili (1992).

Nagarajan (1991, 1997a), and Blankschtein (1997, 1998) developed two similar molecular thermodynamic methods for surfactant solution (“molecular structure” branch in figure 3.1). Detailed molecular and micelle structures descriptions are used to build up the properties of micelle formation and surfactant solution. They have used their methods to calculate CMC and other properties for nonionic, anionic, pure and binary surfactant mixtures (Zoller, 1996).

Recently, Chen et al. (1996, 2001) proposed a thermodynamic framework for the micelle formation combined with conventional local composition activity coefficient models, such as NRTL (“activity coefficient” branch in figure 3.1). This method has been applied to calculate CMC of non-ionic and ionic surfactant solutions. Based on Chen’s proposal, Li et al. (1998, 2000) used UNIQUAC and SAFT equations to calculate CMC of non-ionic and ionic surfactant solutions.

Some of these methods are briefly presented in following sections.

3.2 The Pseudo-phase Separation Model

The pseudo-phase separation model suggests that the micelles form an independent phase, and can be treated as a phase-separation phenomenon similar to vapour-liquid phase equilibrium of air-water system or to liquid-liquid phase equilibrium of aqueous-organic mixtures. The process of forming micelles as surfactant concentration reaches CMC is treated similarly to the formation of liquid droplets as the dew point pressure of a vapour is reached, as illustrated in figures 3.2 and 3.3.

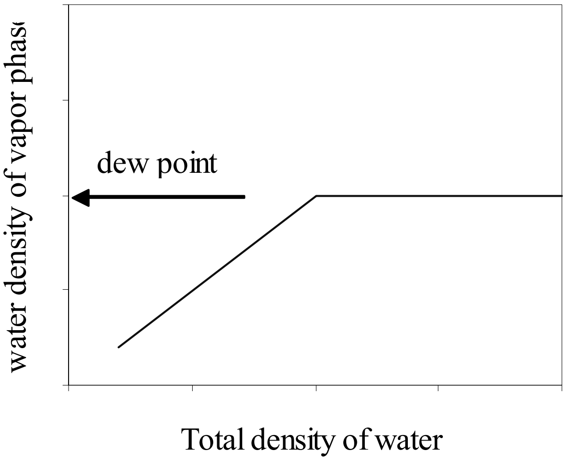


Figure 3.2 Illustration of the liquid droplets formation

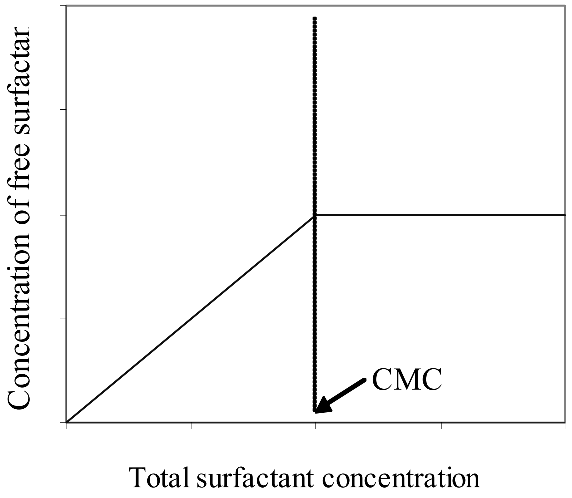


Figure 3.3 Illustration of the micelle formation

As water molecules are added to an empty volume at constant temperature, the density of vapour phase (water molecules) increases steadily until the dew point pressure is reached. At the dew point, any added molecules would not contribute to the vapour density. The sharp transition at the dew point, as shown in figure 3.2, is very similar to the transition at the CMC for surfactant solutions forming large micelles, as shown in figure 3.3. Due to the near-constancy of the free surfactant concentration above CMC, the surfactant solutions can be compared to a phase transition. Several methods have been proposed to give the expressions of the pseudo-phase separation model, as discussed following.

The Analogy Method (Cox and Benson, 1986)

Using the similarity of micelle formation to vapour-liquid equilibrium, an analogy method is used to an equation of micelle formation. For a multi-component system at low pressures, the vapour-liquid equilibrium is described as

$$\left(y_i P\right)_{vapour} = \left(x_i \gamma_i P_i^0\right)_{liquid} \tag{3.1}$$

where subscripts 'vapour', 'liquid' represent the vapour phase and the liquid phase, respectively, γ_i is the activity coefficient of component *i* in the liquid phase, P_i^0 and P are the vapour pressure of pure component *i* and the total system pressure, respectively, x_i and y_i denote to the mole fraction of the liquid and vapour phase, respectively.

For a micelle-forming surfactant system, the analogy to equation (3.1) is

$$\left(y_i \mathrm{CMC}\right)_{aq} = \left(x_i \gamma_i \mathrm{CMC}_i^0\right)_{micelle} \tag{3.2}$$

where subscripts '*aq*' and '*micelle*' represent the aqueous phase and the micelle pseudo-phase, respectively, γ_i is the activity coefficient of component *i* in the micelle pseudo-phase, CMC_i^0 is the critical micelle concentration of pure component *i*, CMC is the concentration of free surfactants (monomer) in the equilibrium with the micelles, i.e. the CMC of the mixed surfactant system, in analogy to the total pressure of vapour-liquid equilibrium system, x_i and y_i denote to the surfactant mole fraction in the micelle pseudo-phase and the bulk aqueous phase, respectively.

Equation (3.2) uses a molecular density (CMC in moles per liter) while equation (3.1) uses pressure (pure component vapour pressure or system pressure). The key assumption of this approach is that CMC has the same effects as the total pressure in a vapour-liquid equilibrium system, since the pressures in equation (3.1) are directly proportional to densities under ideal gas conditions (low pressures), where equation (3.1) is valid.

The Flores and Voutsas Approach (Flores et al., 2001, Voutsas et al., 2001)

In this approach, micelles are assumed to form a new macroscopic phase, i.e. a second liquid phase. Liquid-liquid equilibrium is assumed between water and micelle. Two phases coexist: one solvent (water)-rich phase where the surfactant concentration is the CMC, and one surfactant-rich phase approximated by the micelle phase. At CMC (equilibrium) the activities of both solvent and surfactant are the same in the two phases.

Flores et al., (2001) and Voutsas et al., (2001) used the UNIFAC method for describing liquid-liquid equilibrium. The CMC of non-ionic surfactants in aqueous and non-aqueous solvent is predicted. The reported average deviation between predicted and experimental values was about 0.1 log units.

Many researchers have used the “pseudo-phase separation” approach to calculate CMC in different surfactant solutions, such as non-ionic, ionic, anionic and cationic surfactant solutions (Cox and Benson, 1986; Hall, 1987; Holland and Rubingh, 1992; Ogino and Abe, 1993).

From a thermodynamic point of view, however, the formation of micelles is not a true phase transition, because the micelle formation does not create a new macroscopic phase in solution. The sharp changes in properties occur over a range of concentration. The “pseudo-phase separation” approach represents the case when the aggregation number in the micelles is assumed to approach infinity. In practical, the aggregation number falls down in the range of 20 to 2000 in surfactant solutions. Thus, the pseudo-phase model cannot describe the size of micelles (aggregation number).

3.3 The Mass-action Model

In the mass-action model, the micelle formation is considered as a chemical equilibrium between free surfactant and micelle. At low concentrations, the micelle solution is the formation of aggregates from free surfactant, as shown in equation (3.3).

$$\mathrm{nS} \rightleftharpoons \mathrm{Sn} \tag{3.3}$$

where n free surfactant molecules (S) form a micelle (Sn) having an aggregation number of n_g. Both micelles and free surfactants are treated as solutes in an aqueous solution. In the mass-action model, the thermodynamic formulations are slightly different for nonionic and ionic surfactant solutions. One of the formulations (nonionic surfactant) is described as follows (Blandamer et al. 1995):

For nonionic (neutral) surfactant solutions, at chemical equilibrium, we have:

$$n_g \mu_{i,mon} = \mu_{i,micelle} \tag{3.4}$$

where $\mu_{i,mon}$ is the chemical potential of monomeric (free) surfactant *i*, $\mu_{i,micelle}$ is the chemical potential of surfactant *i* in the micelle form, n_g is the aggregation number. The chemical potentials of monomeric surfactant and surfactant in micelle are given as:

$$\mu_{i,mon} = \mu^0_{i,mon} + RT \ln x_{i,mon}\gamma_{i,mon} \tag{3.5}$$

$$\mu_{i,micelle} = \mu^0_{i,micelle} + RT \ln x_{i,micelle}\gamma_{i,micelle} \tag{3.6}$$

Using equation (3.4), we have

$$\Delta_{mic} G_i^0 = \frac{1}{n_g}\mu^0_{i,micelle} - \mu^0_{i,mon} = RT \ln x_{i,mon}\gamma_{i,mon} - \frac{1}{n_g} RT \ln x_{i,micelle}\gamma_{i,micelle} \tag{3.7}$$

where $x_{i,mon}$ and $x_{i,micelle}$ are the mole fraction of monomeric surfactant and surfactant in micelle, respectively, $\gamma_{i,mon}$ and $\gamma_{i,micelle}$ are the activity coefficient of monomeric surfactant and surfactant in micelle, respectively, $\mu^0_{i,mon}$ and $\mu^0_{i,micelle}$ are the standard state chemical potential for monomeric surfactant and surfactant in micelle, respectively, and $\Delta_{mic} G_i^0$ is the difference of Gibbs energy.

For a dilute solution, the activity coefficients of monomeric surfactant and surfactant in micelle are set equal to 1.0. Then equation (3.7) becomes

$$\Delta_{mic} G_i^0 = RT \ln x_{i,mon} - \frac{1}{n_g} RT \ln x_{i,micelle} \tag{3.8}$$

In surfactant solution, CMC is the total concentration of surfactant (x_{tot}), which is a sum of free surfactant ($x_{\mathrm{i,mon}}$) and surfactants in micelles ($x_{\mathrm{i,micelle}}$). Assuming a sufficiently high value for n_g, the second term in the above equation become very small and can be neglected. Then $x_{\mathrm{i,mon}}$ can be approximated to CMC.

Based on the mass-action model, Amos et al. (1998) proposed a model for the distribution of micelle sizes. The model of Amos et al. includes micelle-micelle interactions as a function of the size for a multi-component solution consisting of micelle aggregates, monomer, counterions, and added electrolytes. Surfactant solutions of sodium dodecyl sulphate and cetylpridinum chloride with 0.01M NaCl are studied in their work.

3.4 Molecular Thermodynamic Models

3.4.1 Tanford's Approach

The work of Tanford (1980) systematically investigated the micelle formation using molecule thermodynamic method. In Tanford's theory, the hydrophobic effect of molecules in aqueous solutions provides the driving force for aggregation, whereas the repulsion between head (hydrophilic) groups limits the size that a micelle can attain. However, both factors vary with the micelle size. It is therefore evident that a theoretical treatment without containing the size dependence may account for the occurrence of surfactant aggregation, but it cannot explain why micelles are the statistical aggregates with a broad size distribution.

Since at equilibrium, a mixture will normally contain micelles with a range of different aggregation numbers n_g, it is necessary for a rigorous approach to account for the size dependent contributions in the chemical potential. The simplest procedure is to consider micelles of different size as distinct components of the solution, each characterized by the number n_g of constituent monomer molecules and by a distinct value of the standard potential. The dependence of the standard potential on the value of n_g arises from the dependence of surface area with micelle size.

A chemical potential expression, equation (3.9), is often expressed as a sum of a standard state chemical potential, μ_i^0, and the part including the mole fraction x_i and the activity coefficient γ_i:

$$\mu_i = \mu_i^0 + RT \ln x_i \gamma_i \tag{3.9}$$

Tanford suggests that the second part ($RT \ln x_i \gamma_i$) contribution to the chemical potential per mole of micelle of size n_g is RTln(mole fraction of micelles of size n_g), assuming a sufficiently dilute solution in micelles, thus neglecting nonideality. Thus, the second part of equation (3.9) becomes $RT \ln x_{n_g} / n_g$, and the contribution per mole of surfactants is $1/n_g$. Based on this analysis, Tanford formulated the conditions for micelle formation with the chemical potential of free monomeric surfactants and the surfactants in the micelle state.

Thermodynamic Formulation of Micelle Formation

In a solution of a single surfactant, the chemical potential of a surfactant in a micelle of size n_g, μ_{mic,n_g} , is given by

$$\mu_{mic,n_g} = \mu^0_{mic,n_g} + \frac{RT}{n_g} \ln \frac{x_{n_g}}{n_g} \tag{3.10}$$

where μ^0_{mic,n_g} is the standard state chemical potential of a surfactant in the micelle state, x_{n_g} is the mole fraction of surfactant inside the micelle of size n_g.

The chemical potential of free monomeric surfactant in aqueous solutions, μ_{mon}, is:

$$\mu_{\mathrm{mon}} = \mu^0_{\mathrm{mon}} + RT \ln x_{\mathrm{mon}} \gamma_{\mathrm{mo}n} \tag{3.11}$$

where μ^0_{mon} is the standard state chemical potential of the free monomeric surfactants in aqueous solutions, x_{mon} is the mole fraction of free monomeric surfactants in aqueous solutions, and γ_{mon} is the activity coefficient of free monomeric surfactants in aqueous solutions.

At equilibrium:

$$\mu_{mic,n_g} = \mu_{mon} \tag{3.12}$$

then

$$\mu^0_{mic,n_g} + \frac{RT}{n_g} \ln \frac{x_{n_g}}{n_g} = \mu^0_{mon} + RT \ln x_{mon} \gamma_{mon} \tag{3.13}$$

We assume that all micelles have the same size n_g in the surfactant solutions, and introduce a new standard state chemical potential μ^0_mic (without subscript n_g) for surfactant in any micelle. Thus, equation (3.13) becomes

$$\ln x_{n_g} = -n_g \frac{\mu^0_{mic} - \mu^0_{mon}}{RT} + n_g \ln x_{mon}\gamma_{mon} + \ln n_g \tag{3.14}$$

Critical Micelle Concentration (CMC)

Tanford says that the concept of a "critical concentration" for the formation of micelles from free surfactant is, rigorously speaking, inexact but convenient. It would be exact if micelle formation could be regarded as separation of a distinct phase, and free surfactant in solution could coexist with the micelle phase at only a fixed concentration. An important feature of micelle formation is that the free monomeric surfactant concentration in equilibrium with micelles changes only slowly with the concentration of micelles.

By defining a parameter $\sigma = x_{n_g} / \mathrm{CMC}$, then

$$x_{mon} = (1-\sigma)\mathrm{CMC} \tag{3.15}$$

Here the CMC is the total concentration in the micelle solution as follow:

$$x_{total} = \mathrm{CMC} = x_{mon} + x_{n_g} \tag{3.16}$$

Thus, at CMC, equation (3.14) gives:

$$\frac{\mu^0_{mic} - \mu^0_{mon}}{RT} = \left(\frac{n_g - 1}{n_g}\right)\ln \mathrm{CMC} + \ln \gamma_{mon} + \ln(1-\sigma) + \frac{1}{n_g}\ln\left(\frac{n_g}{\sigma}\right) \tag{3.17}$$

The exact choice of σ varies from 0.01 to 0.10.

The Tanford's method and analysis for the hydrophobic effect in aqueous solutions have been widely used in research related to biological lipids, proteins, serum lipoproteins, and biological membranes. This method has been extended to large lipid aggregates such as bilayers, vesicles, other micelle phases and microemulsion droplets by Nagarajan and Rukenstein (1991), Israellachivili (1992), Blanckstein (1986), Puvvada and Blankschtein (1990).

3.4.2 Israelachvili's Method

Israelachvili (1992) developed a thermodynamic framework for micelle formation and then investigated the relationship between intermolecular interaction and different micelle shapes. Different intermolecular interactions determine the formed micelles with varied structures. Molecular geometry has a crucial role in determining the structures of formed micelles. From the molecular geometry, many of the physical properties of surfactant solutions can be quantitatively understood without requiring a detailed knowledge of the complex molecular forces.

Thermodynamic Equations of Micelle Formation

The micelle formation is expressed as a formation of surfactant aggregates with different sizes:

$S + S \rightleftharpoons S_2$ dimers (3.18)

$S + S + S \rightleftharpoons S_3$ trimers

……..

$S + S + S + \ldots \rightleftharpoons S_n$ n-mers

Equilibrium thermodynamics requires that when molecules form aggregated structures in solution, the chemical potentials of all identical molecules in different aggregates are the same. This is expressed as:

$$\mu = \mu_1^0 + k_B T \log x_1 = \mu_2^0 + \frac{1}{2} k_B T \log \frac{1}{2} x_2 = \mu_3^0 + \frac{1}{3} k_B T \log \frac{1}{3} x_3 = \ldots \tag{3.19}$$

monomers dimers trimers

or

$$\mu = \mu_{n_g} = \mu_{n_g}^0 + \frac{k_B T}{n_g} \log\left(\frac{x_{n_g}}{n_g}\right) = \text{constant}, \qquad n_g = 1, 2, 3, \ldots \tag{3.20}$$

where μ_{n_g} is the mean chemical potential of a molecule in a micelle of aggregation number n_g, $\mu_{n_g}^0$ is the standard state of the chemical potential (the mean interaction free energy per molecule) in an micelle of aggregation number n_g, x_{n_g} is the concentration (more strictly the activity) of molecules in aggregates of number n_g (n_g=1, μ_1^0 and x_1 correspond to isolated molecules, or monomers, in solution), and k_B is the Boltzmann constant. Using the law of mass action, equation (3.19) can be derived as follows:

$$\text{Rate of association} = k_1 x_1^{n_g} \tag{3.21}$$

$$\text{Rate of dissociation} = k_{n_g}\left(\frac{x_{n_g}}{n_g}\right) \tag{3.22}$$

where

$$K = \frac{k_1}{k_{n_g}} = \exp\left[\frac{-n_g\left(\mu_{n_g}^0 - \mu_1^0\right)}{k_B T}\right] \tag{3.23}$$

This is the ratio of the two ‘reaction’ rates (equilibrium constants), k_1 and k_{n_g}. Equation (3.23) assumes ideal mixing and is restricted to dilute systems where inter-aggregate interactions can be ignored.

Combining equations (3.19)-(3.23), we obtain:

$$\frac{x_{n_g}}{n_g} = \left[\frac{x_M}{M}\exp\left[\frac{M\left(\mu_M^0 - \mu_{n_g}^0\right)}{k_B T}\right]\right]^{n_g/M} \tag{3.24}$$

If M=1, we have

$$\frac{x_{n_g}}{n_g} = \left[x_1 \exp\left[\frac{\left(\mu_1^0 - \mu_{n_g}^0\right)}{k_B T}\right]\right]^{n_g} \tag{3.25}$$

where M is any arbitrary reference state of aggregates (or monomers) with aggregation number M (or 1). The total solute concentration C is given by

$$C = x_1 + x_2 + x_3 + \ldots = \sum_{n_g=1}^{\infty} x_{n_g} \tag{3.26}$$

Depending on how the standard state chemical potentials μ_1^0 and $\mu_{n_g}^0$ are defined, the dimensionless concentrations C and x_{n_g} can be expressed in volume fraction or mole fraction. The C and x_{n_g} can never exceed unity. Equations (3.24)-(3.26) completely define the system.

Based on the thermodynamic formulation for micelle formation, Israelachvili discussed the relationship between the geometric shapes of micelle and the standard state chemical potentials. For a shape like 'rod' micelles (shown in figure 3.4), the standard state chemical potential is given by

$$\mu_{n_g}^0 = \mu_\infty^0 + \alpha k_B T / n_g \tag{3.27}$$

where $\alpha k_B T$ is the monomer-monomer 'bond' energy in the micelle relative to isolated monomers in solution. As n_g increases the mean free energy $\mu_{n_g}^0$ decreases asymptotically towards μ_∞^0 that is the 'bulk' energy of a molecule in an infinite aggregate.

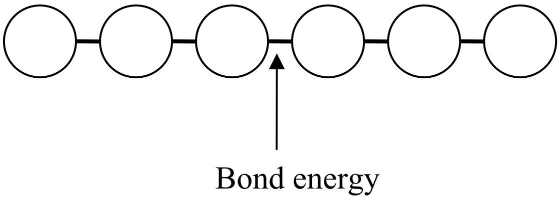


Figure 3.4 One dimensional structure formed by the association of identical monomer units in solution

Similarly, for two-dimensional micelles (disc, sheets)

$$\mu_{n_g}^0 = \mu_\infty^0 + \alpha k_B T / n_g^{1/2} \tag{3.28}$$

For three-dimensional micelles (spheres)

$$\mu_{n_g}^0 = \mu_\infty^0 + \alpha k_B T / n_g^{1/3} \tag{3.29}$$

For the simplest shaped structures-rods, sheets and spheres, the standard state chemical potential of the molecules can be expressed as

$$\mu_{n_g}^0 = \mu_\infty^0 + \frac{\alpha k_B T}{n_g^p} \qquad \text{p=1, 1/2, 1/3} \tag{3.30}$$

where α is a positive constant dependent on the strength of intermolecular interaction. Generally, p is a number that depends on the shape of the micelles.

When n_g is a large number, incorporating equation (3.30) into the equations (3.24)-(3.26) leads to

$$x_{n_g} = n_g \left[x_1 \exp\left[\frac{\left(\mu_1^0 - \mu_{n_g}^0\right)}{k_B T} \right] \right]^{n_g} = n_g \left[x_1 \exp\left[\alpha \left(1 - 1/n_g^p \right) \right] \right]^{n_g} \approx n_g \left[x_1 e^{\alpha} \right]^{n_g} \tag{3.31}$$

In equation (3.31), the limitation of x_1 is $\exp\left[-\frac{\mu_1^0 - \mu_{n_g}^0}{RT} \right]$ or $e^{-\alpha}$. At this condition, the monomer concentration x_1 is the critical micelle concentration (CMC). Thus, in general

$$(x_1)_{\text{crit}} = \text{CMC} \approx \exp\left[-\frac{\left(\mu_1^0 - \mu_{n_g}^0\right)}{RT} \right] \tag{3.32}$$

or

$$(x_1)_{\text{crit}} = \text{CMC} \approx e^{-\alpha} \qquad \text{for all } p \tag{3.33}$$

where p is a number depended on the shape of the micelles. Equations (3.32) and (3.33) define the CMC.

Critical Packing Parameter

Israelachvili (1992) proposed a critical packing parameter (cpp) to describe the surfactant molecule structures as:

$$\text{cpp} = \frac{v}{a_0 l_c} \tag{3.34}$$

where v denotes to the tail chain (or chains) volume, l_c is the critical tail chain length, a_0 is the headgroup area at the head-tail interface, as shown in figure 3.5. The v and l_c can be calculated by empirical equations (Tanford, 1980). a_0 can be measured by experimental method (Lantzsch et al., 1996).

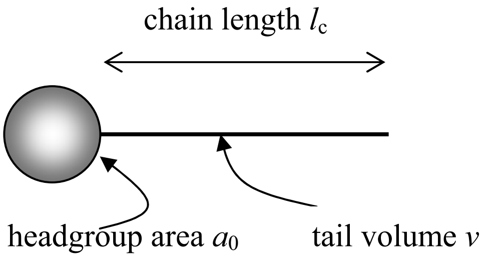


Figure 3.5 The cpp of a surfactant molecule

Table 3.1 shows the relationship of cpp values and micelle structures. Different cpp values correspond to different micelles, as shown in Table 3.1. The cpp value of surfactants can also indicate which phase exists in solution: lamellar, cubic or hexagonal phases.

Table 3.1 Relationship between cpp value and micelle structure

cpp value	Micelle structure	Example*
<1/3	Spherical micelles	SDS in low salt
1/3~1/2	Cylindrical micelles	SDS and CTAB in high salt
1/2~1	Flexible bilayers	Phosphatidyl choline
~1	Planar bilayers	Phosphatidyl ethanolamine
>1	Reversed micelle	Cardiolipin+Ca^{2+}

*SDS: sodium dodecyl sulphate, CTAB: hexadecyl trimethylammonium bromide

Based on the thermodynamic framework, Israelachvili studied the relationships between micelle size distribution, micelle structures and CMC, the aggregation of surfactant molecules into micelles, bilayers, vesicles and biological membranes.

3.4.3 Nagarajan's Method

Nagarajan and co-workers (1991, 1997a) developed a thermodynamic model to calculate CMC, aggregation number and phase separation for non-ionic, anionic, cationic and zwitterionic single and mixed surfactant solutions depending on information of structures and interactions. The method, in details, described the relations between chemical potential (Gibbs free energy) of surfactant solutions and different micelle structures.

Using the condition of ideal mixing in dilute solutions, the chemical potential of micelles with size n_g is given by

$$\mu_g = \mu_g^0 + k_B T \ln x_g \tag{3.35}$$

where μ_g^0 is the standard state of the species g (micelle with aggregation number n_g), x_g is the mole fraction of micelles in solution. The chemical potential of monomer surfactant, μ_1, is given by setting n_g=1 in equation (3.35):

$$\mu_1 = \mu_1^0 + k_B T \ln x_1 \tag{3.36}$$

where μ_1^0 is the standard state of free (monomeric) surfactant in solution and x_1 is the mole fraction of free (monomeric) surfactant in solution.

At equilibrium, the chemical potentials:

$$\frac{\mu_g}{n_g} = \mu_1 \tag{3.37}$$

where n_g is the aggregation number.

The micelles size distribution equation is derived from equation (3.37)

$$x_g = (x_1)^{n_g} \exp\left(-\frac{\mu_g^0 - n_g \mu_1^0}{k_B T}\right) = (x_1)^{n_g} \exp\left(-\frac{n_g \Delta\mu_g^0}{k_B T}\right) \tag{3.38}$$

where $\Delta\mu_g^0$ is the difference in the standard state chemical potentials between a surfactant molecule present in a micelle of size n_g and a monomeric surfactant in solution.

If an expression for $\Delta\mu_g^0$ is available, then the micelle size distribution can be calculated from equation (3.38).

Based on different contributions, Nagarajan developed an equation to calculate $\Delta\mu_g^0$ as:

$$\Delta\mu_g^0 = \left(\Delta\mu_g^0\right)_{tr} + \left(\Delta\mu_g^0\right)_{def} + \left(\Delta\mu_g^0\right)_{\text{int}} + \left(\Delta\mu_g^0\right)_{steric} + \left(\Delta\mu_g^0\right)_{dipole} + \left(\Delta\mu_g^0\right)_{ionic} \tag{3.39}$$

where $\left(\Delta\mu_g^0\right)_{tr}$ is the contribution from surfactant tail, $\left(\Delta\mu_g^0\right)_{def}$ is the contribution of the tail local deformation, $\left(\Delta\mu_g^0\right)_{\text{int}}$ is the contribution of the formation of micelle core–water interface, $\left(\Delta\mu_g^0\right)_{steric}$ describes how polar head groups of surfactant molecules are brought to the surface of the micelle and generate steric repulsion among the head groups, $\left(\Delta\mu_g^0\right)_{dipole}$ is the contribution of the head group dipole interactions and $\left(\Delta\mu_g^0\right)_{ionic}$ is the head group ionic interactions.

The calculation methods for these terms in equation (3.39) can be found in reference of Nagarajan (1997a).

3.4.4 Blankschtein's Method

Puvvada and Blankschtein (1990) proposed an approach that is a blending of a molecular model of micellization with a thermodynamic theory.

Using the principle of multiple chemical equilibria between micelles with different size and monomers, we have

$$\mu_n = n_g \mu_1 \tag{3.40}$$

where μ_n is the chemical potential of micelle with aggregation number n_g and μ_1 is the chemical potential of free monomeric surfactant in solution.

The micelle size distribution is given by

$$x_n = (x_1)^{n_g} \exp\{-\beta n_g g_{mic}(n_g)\} \tag{3.41}$$

where $\beta = \frac{1}{k_B T}$, x_1 is the mole fraction of monomeric surfactant in the solution.

Using the surfactant mass balance relation, equation (3.41) is re-formulated to represent the CMC of the surfactant solution, x_{cmc}, as follows:

$$x_{cmc} \approx \exp\left[\beta\left(g^*_{mic}(sh) - 1\right)\right] \tag{3.42}$$

where g^*_{mic} is the free energy of micellization correlated to different micelle structures (*sh*), *sh* is the shape variable of surfactant solution, such as sphere, cylinder and disk.

The free energy of micellization, g^*_{mic}, represents the free energy change (per monomer) required to form an n-mer, having core radius l_c, and shape *sh*, from *n* individual monomers in water. Its magnitude reflects many complex physical chemical factors such as the hydrophobic effect, hydrogen bonding, conformation free energy changes associated with hydrocarbon chain packing, and steric and electrostatic interactions between the hydrophilic surfactant (head groups).

In the method of Blankschtein, the expression of CMC is similar to that of Nagarajan, but with some variations in the free energy expressions. In this method, the molecular model incorporates the effects of solvent properties and surfactant molecular architecture on physical factors which control micelle formation and growth. The method has been utilized to predict a broad spectrum of micelle solution equilibrium properties as a function of surfactant concentration and temperature. These properties include (1) the critical micelle concentration, (2) the micelle size distribution, (3) the critical surfactant concentration for the onset of phase separation (Puvvada and Blankschtein, 1990, Blankschtein et al., 1997).

3.4.5 Chen's Method

Chen et al. (1996, 2001) proposed a thermodynamic framework for describing the micelle formation of aqueous surfactant solutions. The conventional NRTL activity coefficient model is combined with the framework to correlate and predict the CMC of non-ionic and ionic surfactant solutions. The thermodynamic treatments are slightly different for non-ionic surfactant and ionic surfactant solutions.

Thermodynamic Framework for Non-ionic Surfactant Solutions

As shown in figure 3.6, when the surfactant molecules are dissolved in excess water as free monomeric molecules, both head and tail parts are exposed to or surrounded by water molecules. The physical interactions of the surfactant solution are characterized by the hydrophilic part-water and hydrophobic part-water interactions. The hydrophilic part-water interaction is attractive in nature, and the hydrophobic part-water interaction is repulsive in nature.

When surfactant molecules form micelles, aggregated surfactant molecules can be approximated as effectively removed from the aqueous environment. Only the surfactant molecules stay inside the micelle with a specific orientation. Both head and tail groups are now placed in an "idealized state" where head groups are surrounded by head groups and tail groups are surrounded by tail groups. In such "idealized state" or specific orientation state, the physical interactions of micellar surfactants are characterized by the head group-head group and the tail group-tail group interactions. The "idealized state" is not a pure liquid surfactant state (a random mixing state), but a single surfactant system. In this thermodynamic treatment, the "idealized state" corresponds to the reference state chosen for the aggregated surfactant molecules.

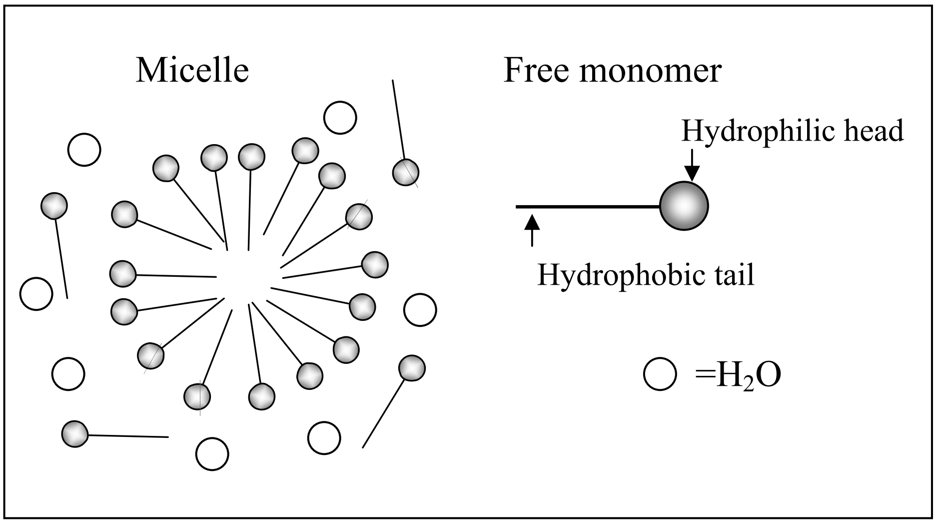


Figure 3.6 Micelle formation and surfactant molecules

At CMC, the monomeric surfactant concentration is at the onset of micelle formation, thus the chemical potential of monomeric surfactants (μ_s) equals that surfactants in micelles (μ_m).

$$\mu_s = \mu_m \quad \text{(at CMC)} \tag{3.43}$$

$$\mu_s = \mu_s^0 + RT \ln a_s \tag{3.44}$$

$$\mu_m = \mu_m^0 + RT \ln a_m \tag{3.45}$$

where μ_s^0 is the reference state of monomeric surfactants, μ_m^0 is the reference state of surfactants in micelles, a_s is the activity of free surfactants (not in micelles) and a_m is the activity of surfactant molecules in the "idealized state". The "idealized state", which is a single surfactant system, is chosen as the reference state for free surfactants and surfactants in micelles. Then we have $\mu_s^0 = \mu_m^0$.

At the micelle formation, the aggregated surfactant molecules (micelles) are considered to be a single surfactant excluding solvent (water) from their interiors. For the single surfactant system, the activities of the two states of surfactants, inside the micelles (a_{m}) and in solvent (a_{s}), should be the same and their activities should be unity:

$$a_{\mathrm{s}}^{\mathrm{cmc}} = a_m = 1.0 \tag{3.46}$$

$$a_{\mathrm{s}}^{\mathrm{cmc}} = x_{\mathrm{s}}^{\mathrm{cmc}} \gamma_{\mathrm{s}}^{\mathrm{cmc}} \tag{3.47}$$

$$x_{\mathrm{s}}^{\mathrm{cmc}} \gamma_{\mathrm{s}}^{\mathrm{cmc}} = 1.0 \tag{3.48}$$

where x_s^{cmc} is the mole fraction of free surfactants at the CMC and $\gamma_{\mathrm{s}}^{\mathrm{cmc}}$ is the activity coefficient of a free surfactant at CMC. Activity coefficient of free surfactant is a function of free surfactant and solvent composition.

For mixed surfactant systems:

$$\sum_s a_s = a_T^{cmc} = 1 \tag{3.49}$$

$$a_T^{cmc} = x_T^{cmc} \gamma_T^{cmc} \tag{3.50}$$

where subscript *T* represents the total surfactant mixture and *s* represents the individual surfactant.

In Chen's work, the polymer NRTL model is applied to calculate the activity coefficients of free surfactants (Chen, 1996).

Li et al. (1998) used the thermodynamic formulation of Chen (1996) with UNIQUAC and SAFT model instead of the NRTL model to correlate the CMC of non-ionic surfactant solutions.

Thermodynamic Framework for Ionic Surfactant Solution

In ionic surfactant solutions, below CMC, the solution consists of free surfactant ions and their counterions. Above the CMC, ions merge into the formed micelles. Three types of charged species may be then considered in the solution: the free surfactant, the counterions not bound to the micellar particles, and the micelles, as shown in figure 3.7.

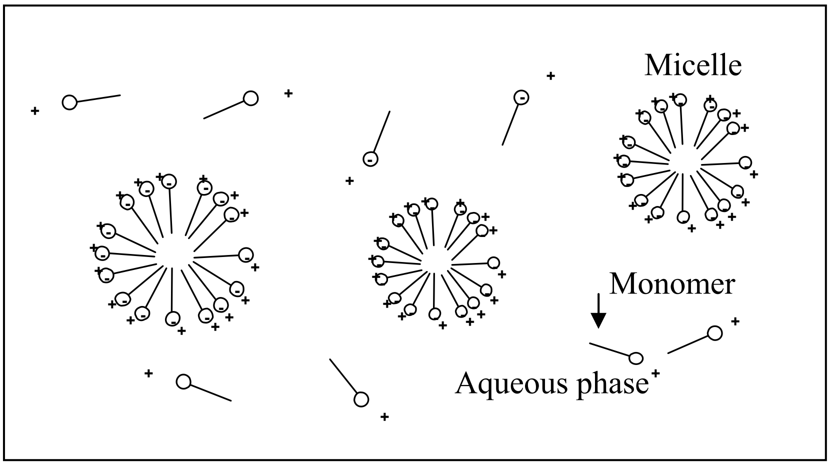


Figure 3.7 Illustration of micelle formation in aqueous ionic surfactant solution

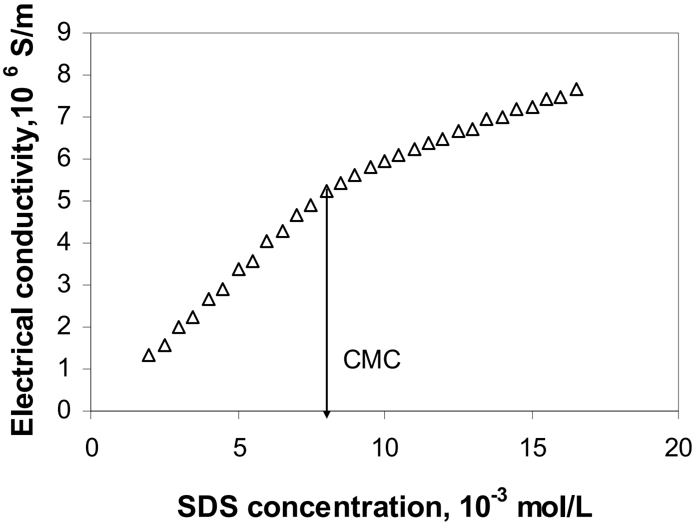


Figure 3.8 Electrical conductivity of a SDS (sodium n-dodecyl sulphate) aqueous solution at 298.15 K. The CMC is 8.21×10^{-3} mol/L. △: Experimental data from Pérez-Rodriguez et al., (1999).

Figure 3.8 shows a conductivity experiment for SDS solution. In figure 3.8, the electrical conductivity of SDS solution continuously increases with surfactant concentration and suddenly changes the slope versus surfactant concentration at CMC. The changed slope (from steep to smooth,) for electrical conductivity indicates that the solution losses ionic charges. However, electrical conductivity of the solution still increases with increasing surfactant concentration after CMC (micelle formation). Because the additional surfactants are considered to form micelles, the increased electrical conductivity suggests that micelles are charged particles (aggregates).

For nonionic surfactants, the activities of two forms of surfactants (monomer and micelle) should be the same at and above the CMC and their activities should be unity, since the micelle form is essentially the reference state, as shown in equation (3.46) –(3.48).

Similarly to non-ionic surfactant solution, for ionic surfactants, the asymmetrical activity coefficients are used at and above CMC as follows:

$$x_{aq}^{cmc}\gamma_{\pm,aq}^{*} = x_{\text{micelle}}\gamma_{\pm,\text{micelle}}^{*} \tag{3.51}$$

where x_{aq}^{cmc} is the CMC of the free monomeric surfactant in the aqueous solution (mole fraction), x_{micelle} is the mole fraction of the surfactants in the micelle state, $\gamma_{\pm,aq}^{*}$ and $\gamma_{\pm,micelle}^{*}$ are the conventional asymmetrical mean activity coefficients of the free monomeric surfactants in the aqueous solution and the aggregated surfactants in the micelle particles, respectively.

The state of aggregated surfactants (micelles) is not the reference state for free surfactant molecules and surfactants in micelles. Essentially, the ionic surfactant solution is an electrolyte solution. The reference state (standard state) for the cation is a hypothetical ideal dilute solution in water when x_C=1, at system temperature and pressure. Similarly, the standard state for the anion is a hypothetical ideal dilute solution when x_A=1. In the hypothetical ideal dilute solution, $\gamma_C=\gamma_A=1$ for all x. For an ionic species (cation and anion), it is a pseudo-pure component.

In the charged micelle particles, the surfactant molecules are self-arranged in a specific orientation, as shown in figure 3.7. The ionic headgroups of surfactant molecules are still dissociated in water solvent at the micelle-aqueous solution interface. At and above the critical micelle concentration, the micelle particles are only composed of surfactant molecules. The mole fraction of surfactant molecules in the micelle is unity.

Therefore, the equilibrium between free monomeric surfactant in the aqueous solution and the aggregated surfactants in the micelle particles can be given as:

$$x_{aq}^{cmc}\gamma_{\pm,aq}^{*} = \gamma_{\pm,\text{micelle}}^{*} \text{ (at } x_{\text{micelle}}=1.0) \tag{3.52}$$

Based on equation (3.52), the CMC (x_{aq}^{cmc}) can be calculated with a suitable activity coefficient model. In the work of Chen et al. (2001), a modified NRTL model containing a Pitzer-Debye-Hückel term for long-range contributions, a NRTL term for short-range contributions and a Flory-Huggins term is used to determine the activity coefficient.

Appendix B gives further explanations for equation (3.52) with emphasizing the basic equations of electrolyte solutions.

Li et al. (2000) proposed a similar thermodynamic treatment for the micelle formation of ionic surfactant solution.

The thermodynamic treatment of Chen et al. (1996, 2001) uses activity coefficient models to describe the non-ideality of surfactant solutions and the micelle formation in the solution. Indeed, the non-ideality of surfactant solution was originally formulated in the work of Tanford (1980) and then neglected due to the assumption of ideal mixing. This ideal mixing assumption is correct for non-electrolytes in the limit of very large dilution.

The method of Chen et al. (1996, 2001) provides a framework for CMC calculation using widely accepted activity coefficient models. Such models have been well developed and used in the chemical industry. However, the method of Chen et al. cannot describe the size or size distribution of micelles in surfactant solution.

3.5 Mixed Surfactant Systems

Mixed surfactant solutions are often used in pharmaceutical and medicinal formulation, oil recovery process, but most commonly in cleaning and detergent products. Surfactants are usually prepared commercially as mixtures rather than pure forms. This is more efficient and economic. The mixed surfactants save on separation costs because the product is generally not required in a pure form for cleaning work. It is thus important to better understand and hence to make better use of such systems.

The regular solution approach proposed by Rubingh has been widely used for mixed surfactant systems due to its simplicity (Hines, 2001). Many binary mixtures have been studied by this method and extended to the general multi-component case (Holland, 1986). In calculating mixed CMC, the regular solution approach requires that the CMC of both pure components (in the binary case) and one measured CMC for the mixed surfactant system. A single adjustable parameter can, then, be obtained and used to calculate CMC of wide composition range. In this method, regular solution assumption is used for micelles other than the surfactant solution. Section 7.4 gives an example for the mixed CMC calculation by this method.

Reviews for the theories of mixed surfactants can be found in the references of Hines (2001) and Ogino et al (1993).

<u>*The Rubingh's approach*</u> (Rubingh, 1979)

In Rubingh's method, the chemical potential of monomeric surfactant 1, μ_1, in a mixed surfactant solution can be written as:

$$\mu_1 = \mu_1^0 + RT \ln x_1^{mon} \tag{3.53}$$

where the activity coefficient of free monomer is assumed to be unity, μ_1^0 is a standard state chemical potential of surfactant 1, x_1^{mon} is the monomer concentration of surfactant 1 (mol fraction).

The chemical potential of surfactant 1 in the mixed micelle, μ_1^M, (two surfactant components in the micelle) is given by

$$\mu_1^M = \mu_1^{M0} + RT \ln \gamma_1 x_1 \tag{3.54}$$

where μ_1^{M0} is the chemical potential of surfactant 1 in pure micelle state, γ_1 and x_1 are the activity coefficient and mole fraction (solvent free) of surfactant 1 in the mixed micelle, respectively.

For surfactant 1 in the pure micelle state, we have

$$\mu_1^{M0} = \mu_1^0 + RT \ln \mathrm{CMC}_1 \tag{3.55}$$

where CMC_1 is the CMC of pure surfactant 1, μ_1^0 is a standard chemical potential of monomeric surfactant 1.

At equilibrium, we have

$$\mu_1 = \mu_1^M \tag{3.56}$$

From equations (3.53)–(3.55), we obtain that

$$x_1^{mon} = x_1 \gamma_1 \mathrm{CMC}_1 \tag{3.57}$$

Similar arguments can be used for surfactant 2 to derive the relation

$$x_2^{mon} = (1 - x_1)\gamma_2 \mathrm{CMC}_2 \tag{3.58}$$

At concentration below the concentration of mixed micelle formation, the concentration of surfactant 1, x_1^{mon}, is simply given by

$$x_1^{mon} = \alpha_1 x_T \tag{3.59}$$

where x_T is the total concentration of surfactant 1 and 2, α_1 is a fraction of surfactant 1 in total mixed solute.

Similarly to component 2,

$$x_2^{mon} = (1 - \alpha_1) x_T \tag{3.60}$$

At the mixed micelle formation, by continuity, equations (3.59)-(3.60) become

$$x_1^{mon} = \alpha_1 \mathrm{CMC}_{\mathrm{mix}} \tag{3.61}$$

$$x_2^{mon} = (1 - \alpha_1)\mathrm{CMC}_{\mathrm{mix}} \tag{3.62}$$

Combining equations (3.57), (3.58), (3.61), (3.62), we obtain

$$\frac{1}{\mathrm{CMC}_{\mathrm{mix}}} = \frac{\alpha_1}{\gamma_1 \mathrm{CMC}_1} + \frac{1 - \alpha_1}{\gamma_2 \mathrm{CMC}_2} \tag{3.63}$$

Using the regular solution approximation, the activity coefficients in the mixed micelle are given as:

$$\gamma_1 = \exp \beta (1 - x_1)^2 \tag{3.64}$$

$$\gamma_2 = \exp \beta x_1^2 \tag{3.65}$$

where β is an adjustable interaction parameter, x_1 is the mole fraction of surfactant 1 in the mixed micelle.

Holland (1986) used this approach to correlate the interaction parameter β for different mixed surfactant solutions. Murphy et al. (2002) reported the interaction parameter β for several cationic surfactant solutions.

3.6 Thermodynamic Functions of Surfactant Solutions

In previous sections of this chapter, some theoretical models of micelle formation have been discussed. However, the thermodynamic functions, ΔG, ΔH and ΔS, of surfactant solutions are also very important for a quantitative understanding of the micelle solution. Although one have acquired considerable knowledge of the surfactant solutions, the thermodynamics of the solution is far from being completely understood. In this section, some general considerations of the thermodynamic functions for surfactant solutions are presented based on the work of Tanford (1980), Hoffmann et al. (1986) and Yaminsky et al. (2001).

The thermodynamic functions, ΔG, ΔH and ΔS, of surfactant solutions are the key to quantitatively understand the behaviour of surfactant solutions. A large amount of reliable experimental work has been carried out to measure these thermodynamic parameters (van Os et al., 1993). Based on phenomenological rules, one may correlate and predict some thermodynamic parameters. Different molecular interpretations of the thermodynamic parameters have been proposed (Yaminsky et al., 2001).

In experimental techniques, ΔG of micelle formation is measured through the determination of the activity of the solute or of the solvent. ΔH is determined by microcalorimeters or precision solution calorimeters (Hoffmann et al., 1986). The ΔS can be obtained from thermodynamic relation: $\Delta G = \Delta H - T\Delta S$.

In practice, ΔH is the most commonly measured property for micelle solution by microcalorimeters. Many commercial microcalorimeters are available. The CMC and enthalpy can be determined directly from the same experiment. Using mass-action model or pseudo-phase model, ΔG can be calculated through measured ΔH (Paula et al., 1995, Garidel et al., 2000).

Using mass-action model, the enthalpy can be related to CMC through van’t Hoff equation (Garidel et al., 2000) as follows:

van’t Hoff equation

$$\frac{d\ln K}{dT} = \frac{\Delta H}{RT^2} \tag{3.66}$$

From thermodynamic relation: $\Delta G^0 = -RT\ln K$, the van’t Hoff equation can be transformed to:

$$\frac{d}{dT}\left(\frac{\Delta G^0}{T}\right) = -\frac{\Delta H^0}{T^2} \tag{3.67}$$

As discussed in section 3.3, assuming a sufficiently high value for aggregation number n_g, the second term of mass-action equation (3.8) becomes very small and can be neglected. Thus, we have

$$\Delta_{mic} G^0 = RT\ln \mathrm{CMC} \tag{3.68}$$

For a single surfactant system, combining equation (3.67) and (3.68), we obtain

$$\frac{d\ln \mathrm{CMC}}{dT} = -\frac{\Delta H_{mic}^0}{RT^2} \tag{3.69}$$

The first derivative of ΔH with respect to temperature yields the change in heat capacity $\triangle C_p$:

$$\Delta C_p = \left(\frac{\partial \Delta H}{\partial T}\right)_p \tag{3.70}$$

The change in entropy ΔS can be obtained by the Gibbs-Helmholtz equation:

$$\Delta S = (\Delta H - \Delta G)/T \tag{3.71}$$

Based on equations (3.68)-(3.71), the relations between CMC and thermodynamic functions can be obtained. In these equations, the Gibbs free energy model is a key factor to give the relation of CMC and thermodynamic functions. As discussed in previous sections, different theories have been proposed to calculate the ΔG, such as pseudo-phase separation model, mass-action model, molecular thermodynamic models, etc. However, in the calorimetric experimental work the pseudo-phase separation model and mass-action model are often used to get Gibbs free energy and entropy of micelle formation (Garidel et al., 2000).

The effect of temperature on the micelle formation is small. For ionic surfactants, the CMC increases with increasing temperature, for non-ionic surfactants, it decreases with increasing temperature. It has been observed that CMC has a minimum value in investigated temperature range for some surfactant systems, such as SDS, octyl glucoside, etc. (Garidel et al., 2000). However, the reason of the CMC minimum in a certain temperature range is not clear at present.

In the micelle formation of surfactant solutions, the enthalpy values are often positive at low temperatures and become negative at higher temperatures, while it is the opposite for entropy. Thus, micelle formation is a entropy-controlled (or entropy-driven) process at low temperatures. For high temperatures, the micelle formation is no longer entropy but enthalpy controlled. Whether enthalpy or entropy dominates the hydrophobic effect, the net is unfavourable dissolution. The aqueous environment remains hostile to hydrocarbons.

The molecular interpretation of thermodynamic functions depends on the understanding of ‘hydrophobic effect’ that controls hydrocarbon solubility in water. The science of hydrophobic effect possible starts with the like-likes-like principle in explanation of solubility that is a traditional part of chemistry. In the early part of 20th century, Langmuir attributed the relatively low solubility of hydrocarbons in water to the strong mutual interaction between hydrocarbon moieties. By contrast, Harkins suggested that the slight solubility of hydrocarbons in water is due to the fact that water is strongly self-associated. In 1960s, Hildebrand, Tanford in 1970s, and van Oss et al. in 1980s essentially reclaimed Harkins’ analysis. Although the energy of water-water cohesion is substantially greater than that of water-hydrocarbon adhesion, hydrocarbon-hydrocarbon interaction energies are about the same as that between water and hydrocarbon (Yaminsky et al., 2001).

3.7 Summary

In this chapter, different thermodynamic treatments for the micelle formation in surfactant solutions are briefly reviewed. Since the concept of micelle or aggregation was first reported by McBain and Swain (1936), it has been widely accepted in research for surfactant solutions. Many experimental results have proved the existence of self-organized aggregates, and many different thermodynamic frameworks have been proposed to explain the micelle formation in surfactant solution. The discussed methods in this chapter are those often used in practice.

In the pseudo-phase theory, the micelles or aggregates are assumed as a macroscopic phase in surfactant solution. The calculation methods of vapour-liquid equilibrium or liquid-liquid equilibrium are used to describe the micelle formation. Because the assumed macroscopic phase (micelles) is corresponded to infinite aggregation number in surfactant solution, this method cannot describe the aggregation number of surfactants.

The mass-action theory treats the micelle formation as the product of a chemical reaction. The chemical equilibrium constants are studied by thermodynamic method. However, this method cannot calculate the phase separation in the surfactant solution.

The molecular thermodynamic framework for micelle formation has two different branches: one relays on detailed molecule descriptions to build up the properties of surfactant solution, the other uses activity coefficient. Figure 3.7 shows the basic characteristics of the two branches.

The thermodynamic frameworks of Tanford, Israelachvili, Blankschtein and Nagarajan are based on molecular structure description (molecular structure method). Two different formulation factors are employed in these methods:

1) The chemical potential of micelle is related to the size of micelle, or aggregation number (the number of surfactant molecules making up a micelle). In the chemical potential expression, the ideal mixing assumption is introduced because micelle formation normally occurs in very dilute solutions.

2) The standard state chemical potential is related to the detailed structural description of surfactant molecules or micelles, such as tail length, headgroup area, tail volume, etc. Different molecular structures give different contributions to the changes of chemical potential. Such changes result in the micelle formation in surfactant solutions. In the approaches of Blankschtein and Nagarajan, the detailed molecule geometry calculation methods have been proposed to estimate the free energy of different surfactants.

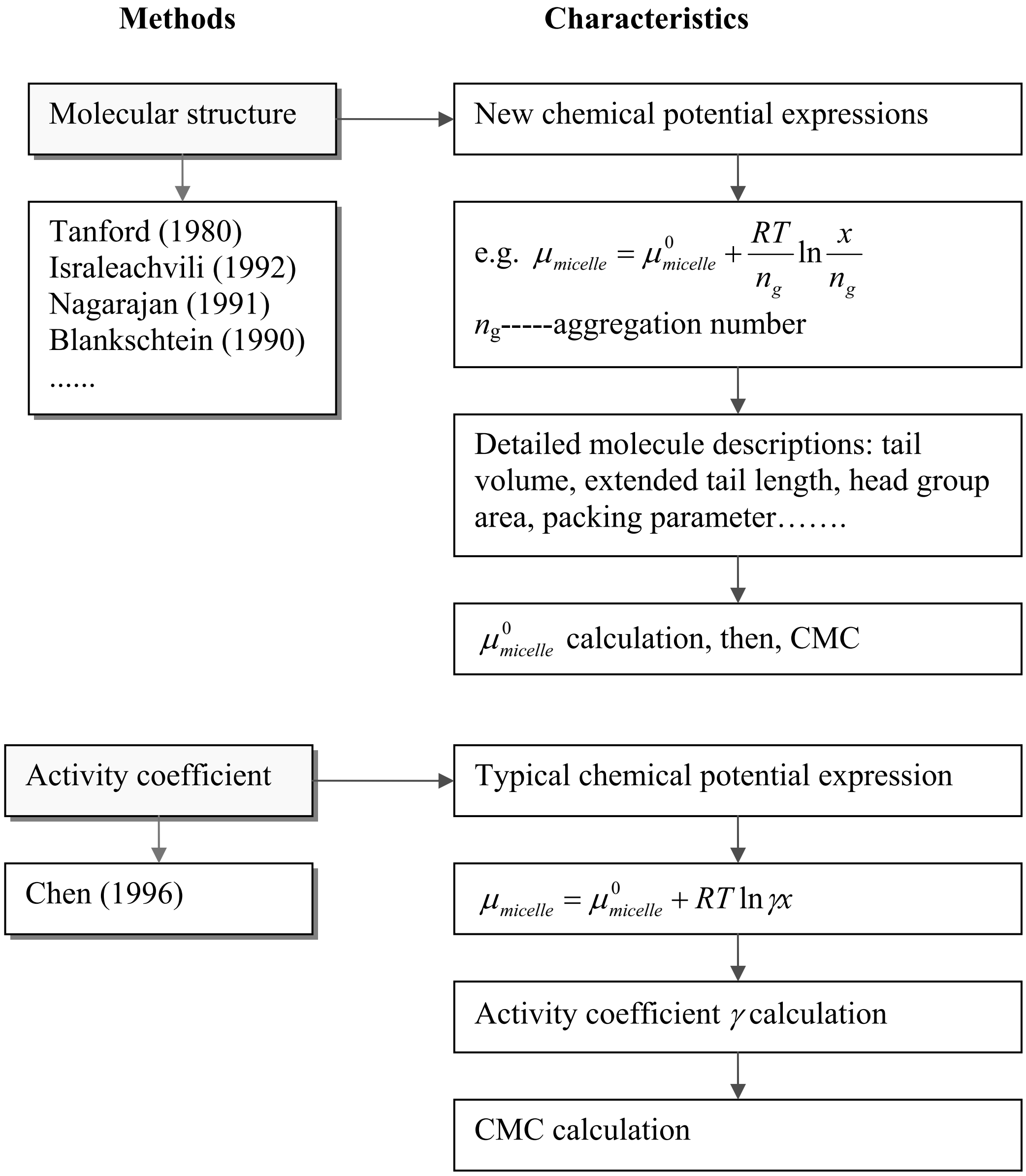


Figure 3.7 Two branches in molecular thermodynamic methods for surfactant solution

As discussed previously, the ideal mixing assumption is correct for nonelectrolytes at a very large dilution, but not for electrolyte solutions. Moreover, the dependence of the chemical potential on the aggregation number, such as equation (3.37), (3.40), gives the possibility of following the aggregation process in detail. But the equations (3.37) and (3.40) cannot be used to calculate phase separation in surfactant system, because the aggregation number tends to infinite in a new surfactant phase formed. Therefore, a complete new set of equations were used to calculate phase separation of surfactant solutions in the molecular structure methods (Puvvada et al., 1990, Nagarajan 1997a).

It can be seen that the molecular structure methods do not take advantage of the extensive work on activity coefficient models carried out in the past decades for solutions of non-electrolytes, electrolytes and polymers in academic and chemical industry, especially for the phase separation calculation.

Chen et al. (1996, 2001) and Li et al. (1998, 2000) proposed slightly different thermodynamic treatments for the micelle formation in surfactant solutions using activity coefficient models, e.g. NRTL and UNIQUAC, to calculate CMC of surfactant solutions. Some typical surfactant solutions, such as alcohol ethoxylates, sodium alkyl sulphates, etc., have been studied by their methods.

Chapter 4 Octanol-water Partition Coefficients for Non-ionic Surfactant Solutions

In this chapter, the octanol-water partition coefficient (*K*ow) for non-ionic surfactant molecules (alcohol ethoxylates) and phthalates are investigated with the UNIFAC method and commercial software. The calculations are compared with a few experimental *K*ow data for these compounds. In Chapter 8, the *K*ow results will be used to establish correlations of toxicity and bio-concentration factor for alcohol ethoxylates.

4.1 Introduction

The *n*-octanol-water partition coefficient (*K*ow) is a widely used property in environmental and biological applications, because it measures the hydrophobic and hydrophilic nature of organic compounds. *K*ow has been used successfully in Quantitative Structure Activity Relationships (QSAR) in various fields (Leo et al., 2003): drug and pesticide design, pharmacokinetics, anaesthesiology, environmental transport and soil binding, toxicology, bioaccumulation, protein folding, enzyme binding, enzymic reactions in non-aqueous solvents, and host-guest complexation.

Many experimental methods have been developed to measure *K*ow for different chemicals (Sangster, 1997). Experimental *K*ow data for more than 20,000 organic compounds have been compiled (Sangster, 2001). However, these measurements are carried out in a very dilute solute concentration region, i.e. in the ranges of part per million (ppm) or parts per billion (ppb). Thus, such measurement can be of considerable uncertainty in some cases and may reach errors up to a few orders of magnitude. At the same time, for many newly released chemicals, *K*ow values have not been measured. Thus, methods for predicting *K*ow are of interest.

Various *K*ow calculation methods have been systematically compiled and compared by several researchers (Sangster, 1997, Buchwald et al., 1998, Derawi et al., 2001). A number of commercial tools are also available for *K*ow prediction, such as ACD/LogP, KowWin and ClogP.

ACD/LogP (ACD/LogP, 2003, *www.acdlabs.com*) is a method developed by Advanced Chemistry Development, Inc. The method used in ACD has not been described in the scientific literature (Sangster, 1997). The calculation in ACD/LogP is based on an algorithm that uses the experimental *K*ow values for over 12,400 structures with more than 1,200 different functional groups. ACD/LogP's internal database contains over 18,400 compounds with experimental *K*ow values collected from different sources.

KowWin (KowWin, 2003, *esc.syrres.com*) is a software developed by Syracuse Research Corporation using the Meylan and Howard approach (Meylan et al., 1995). The program estimates the octanol-water partition coefficient of organic chemicals using an atom/fragment contribution method. Using a training set of 2,410 chemicals with 175 groups and 280 correction factors, a correlation coefficient of 0.98 was found between the experimental and estimated log*K*ow values. The method has been evaluated using a validation set of experimental values for 10,550 chemicals other than those included in the training set with a resulting correlation coefficient of 0.94 and a mean error of 0.35 in log*K*ow. The complete database in KowWin has experimental *K*ow values for 13,058 compounds.

Clog (ClogP, 2003, *www.daylight.com*) is developed by Daylight Chemical Information Systems Inc. with the Hansch and Leo’s fragment approach (Hansch et al., 1995). The method adds together contribution values for structural parts (fragments) of a solute molecule and correction factors dependent upon the particular way the parts are put together. With the use of a large database of reliable experimental *K*ow data, the contribution values of different structural parts (fragments) to the total *K*ow of molecules have been obtained.

Surfactants, such as alcohol ethoxylates (or polyoxyethylene alcohol) $R(CH_2CH_2O)_nOH$, are amphiphilic molecules that include both a hydrophilic and a hydrophobic part. The surfactant molecules are adsorbed at the interface between the two different fluids, e.g. in the water-air, water-octanol interface. Thus, they can significantly change the surface or interfacial tension. This property of surfactant molecules is useful for many different industrial products, e.g. detergents, washing powders, etc. However, exactly because of this surface adsorption, the *K*ow measurements are difficult for surfactants. In the *K*ow measurements, the surfactant molecules accumulate at the octanol-water interface, which results in lower surfactant concentration in the bulk solvent. At the same time, the surfactants may also form emulsions and enhance the mutual solubility of octanol and water by strong interaction with octanol even below their critical micelle concentration (Müller et al., 1999). Thus, it is very useful to develop a predictive method to evaluate the *K*ow of surfactants since the experimental data are often not available. This study is an effort towards this direction.

The UNIFAC method (Fredenslund et al., 1975) is a group contribution method based on the local composition concept. This method has been successfully used to predict many physical properties especially in chemical engineering applications, e.g. vapour-liquid equilibrium (Fredenslund et al., 1975), liquid-liquid equilibrium (Magnussen et al., 1981), etc. *K*ow has also been studied with the UNIFAC model by several researchers. (Chen et al., 1993, Wienke et al., 1998, Derawi et al., 2001). UNIFAC has been proven in some cases to be a good model for predicting *K*ow in the case of lack of experimental data. However there has been no systematic attempt so far to estimate *K*ow for surfactants using UNIFAC.

In this work, the *K*ow of phthalates are first studied as a test because phthalates are often used in different chemical products (plastics, paints, etc.) and are important in many environmental studies (AMI report, 2000). Although phthalates are not surfactant molecules, they have similar functional groups, e.g. –COO, as surfactants. Figure 4.1 illustrates the basic chemical structure of phthalates, where the R_1 and R_2 may be alkyl or aryl groups, etc.

Then, the *K*ow values for alcohol ethoxylates ($R(CH_2CH_2O)_nOH$) are evaluated using UNIFAC model and the 3 commercial tools described previously (ClogP, ACD, KowWin) as well as a recently developed group contribution solvation model (Lin et al., 1999). The prediction results of the various models are compared to the limited experimental *K*ow data for alcohol ethoxylates.

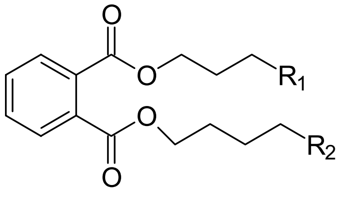


Figure 4.1 Structure of phthalates. R1 and R2 may be alkyl or aryl groups, etc.

4.2 Octanol-water Partition Coefficient and its Calculation

The partition coefficient of a single compound *i* between octanol (O) and water (W) phases can be defined for dilute solutions (Sandler, 1999) at 25°C:

$$K\text{ow} = \frac{C^{O}\gamma_i^{W,\infty}}{C^{W}\gamma_i^{O,\infty}} \tag{4.1}$$

where C^{O} and C^{W} represent the total molar concentrations of the octanol-rich and water-rich phases at 25°C, respectively. Because only a small amount of solute is added to the octanol-water mixture, the solute concentration is very small in both phases. Thus the activity coefficients at infinite dilution, $\gamma_i^{W,\infty}$, $\gamma_i^{O,\infty}$ are used. Using the solubility data of water and octanol in water-rich phase and octanol-rich phase from the Handbook of Chemical Property Estimation Methods (Lyman, 1982), the *K*ow expression in equation (4.1) becomes:

$$K\text{ow} = 0.151\frac{\gamma_i^{W,\infty}}{\gamma_i^{O,\infty}} \tag{4.2}$$

The solubility of water and octanol in the water-rich phase and octanol-rich phase at 25°C is, respectively, 55.3 mol/liter for water, and 4.5×10^{-3} mol/liter for octanol in the water-rich phase; 2.30 mol/liter for water, and 6.07mol/liter for octanol in the octanol-rich phase.

The activity coefficients at infinite dilution can be calculated from different activity coefficient models, e.g. NRTL, UNIQUAC and UNIFAC. In this study the UNIFAC method is chosen to calculate the activity coefficients because it is a predictive tool based on the group contribution principle. Using UNIFAC method, *K*ow can be predicted from the chemical structure information of a compound. The UNIFAC model is presented in Appendix A.

Based on a comprehensive review of these different UNIFAC methods for *K*ow in several chemical families (Derawi et al., 2001, Thomsen et al., 1999), the UNIFAC LLE1 and water-UNIFAC were recommended for predicting the *K*ow. A new UNIFAC model (Micelle) has been also recently developed for predicting the critical micelle concentration for non-ionic surfactants (Cheng et al., 2002). This model is presented in Chapter 5 of this thesis. In “Micelle UNIFAC”, a new functional group (CH_2CH_2O) was introduced into

UNIFAC VLE1; the interaction parameters were obtained from vapor-liquid equilibrium data. These different UNIFAC methods are used to calculate *K*ow in this work.

4.3 Experimental *K*ow Data for Alcohol Ethoxylates and Phthalates

Very few experimental octanol-water partition coefficient data have been reported for alcohol ethoxylates (Morral, et al., 1996) due to the experimental difficulties discussed above. For the same reason, existing *K*ow data for alcohol ethoxylates surfactants may not be very reliable. Thus, *K*ow data for compounds with similar structures are helpful for testing the UNIFAC group interaction parameters.

The alcohol ethoxylates ($R(CH_2CH_2O)_nOH$) are often abbreviated as C_iE_j. Here *i* is the number of alkyl carbon (CH_3-, CH_2-) in the R group and *j* is the number of oxyethylene groups (CH_2CH_2O-) in the molecule. The alcohol ethoxylates also have an alcohol group (-OH). Therefore, the *K*ow data from the same alcohol ethoxylate family, such as 2-methoxyethanol (C_1E_1), 2-ethoxyethanol (C_2E_1), etc., are very useful in this work even though the C_1E_1 and C_2E_1 are not actual surfactant molecules.

In this work, all *K*ow data for surfactants and phthalates are taken from the LOGKOW databank (Sangster, 2001).

4.4 Results and Discussions

The various methods used in this work are summarized in Table 4.1. Using these different methods, the *K*ow prediction results for phthalates are shown in Table 4.2, while the *K*ow results for alcohol ethoxylates are presented in Tables 4.3 and 4.4. Based on these results, the following points summarize our observations:

Table 4.1 Methods used for *K*ow calculations

Method	Abbreviation	Reference
Original UNIFAC VLE 1	VLE1	Hansen et al. 1991
UNIFAC LLE 1	LLE1	Magnussen et al., 1981
UNIFAC VLE 2	VLE2	Hansen et al., 1992
Modified UNIFAC VLE 3	VLE3	Larsen et al., 1987
Water-UNIFAC	H_2O	Chen et al., 1993
UNIFAC for surfactants	Micelle	Cheng et al., 2002
ClogP	ClogP	www.daylight.com
ACD/LogP	ACD	www.acdlabs.com
KowWin	Kwin	esc.syrres.com
Solvation model	GCS	Lin et al., 1999

Table 4.2 log*K*ow prediction results for phthalates with UNIFAC VLE 1, GCS and 3 commercial software methods. All names for phthalates are given as substitute groups.

Phthalate	Exp.*	VLE1	ACD	ClogP	KowWin	GCS
Dimethyl	1.6	1.74	1.62	1.56	1.66	-0.08
Diethyl	2.42	2.64	2.69	2.62	2.65	0.97
Dipropyl	3.64	3.53	3.75	3.68	3.63	2.03
di-iso-propyl	2.83	3.53	3.38	3.24	3.48	1.73
Dibutyl	4.50	4.43	4.81	4.73	4.61	3.09
di-iso-butyl	4.48	4.43	4.44	4.47	4.46	2.79
Dipentyl	5.62	5.32	5.87	5.79	5.59	4.15
Dihexyl	6.82	6.21	6.94	6.85	6.57	5.21
Dioctyl	8.18	8.00	9.06	8.97	8.54	7.34
Didecyl	8.83	9.79	11.19	11.08	10.5	9.46
di-sec-octyl	7.06	8.00	8.69	8.71	8.39	7.03
Ditridecyl	8.4	12.47	14.38	14.26	13.45	12.6
Diallyl	2.98	3.39	3.28	3.11	3.36	0.93
dutylbenzyl	4.73	4.79	4.99	4.98	4.84	2.37
dicyclohexyl	4.9	6.02	5.74	5.62	6.20	5.0
Mean Dev. %		**12**	**14**	**13**	**13**	**37**

* Exp.: Experimental data from Sangster (2001).

Table 4.3 log*K*ow prediction results for alcohol ethoxylates with UNIFAC VLE 1, GCS and 3 commercial software methods

Compound	Exp.*	ClogP	Kwin	ACD	GCS	Micelle	VLE1
2-methoxethanol (C1E1)	-0.77	-0.75	-0.91	-0.80	-1.56	-0.31	-0.83
2-ethoxyethanol (C2E1)	-0.28	-0.22	-0.42	-0.27	-1.02	0.14	-0.38
3,6-dioxa-1-octanol (C2E2)	-0.54	-0.15	-0.69	-0.26	-1.89	0.28	-0.75
iso-propoxyethanol (C3E1)	0.05	0.09	0.00	0.08	-0.65	0.58	0.07
2-butoxyethanol (C4E1)	0.8	0.84	0.57	0.80	0.03	1.03	0.51
3,6-dioxadecanol (C4E2)	0.56	0.91	0.29	0.81	-0.83	1.18	0.15
2-(hexyloxy) ethanol (C6E1)	1.86	1.90	1.55	1.86	1.09	1.92	1.41
3,6-dioxa-1-dodecanol (C6E2)	1.7	1.96	1.28	1.87	0.22	2.07	1.04
Mean Dev. %		**33**	**39**	**22**	**311**	**199**	**36**

* Exp.: Experimental data from Sangster (2001)

Table 4.4 log*K*ow prediction results for alcohol ethoxylates with various UNIFAC methods

Compound	Exp.*	VLE1	LLE1	H_2O	Micelle	VLE2	VLE3
C1E1	-0.77	-0.83	-1.51	-0.96	-0.31	-0.78	-0.60
C2E1	-0.28	-0.38	-1.02	-0.52	0.14	-0.31	-0.06
C2E2	-0.54	-0.75	-1.93	-0.88	0.28	-0.72	-0.30
C3E1	0.05	0.07	-0.53	-0.07	0.58	0.15	0.47
C4E1	0.8	0.51	-0.04	0.38	1.03	0.62	1.01
C4E2	0.56	0.15	-0.95	0.01	1.18	1.55	2.08
C6E1	1.86	1.41	0.94	1.27	1.92	0.21	0.77
C6E2	1.7	1.04	0.03	0.90	2.07	1.14	1.84
Mean Dev.%		**36**	**287**	**80**	**199**	**48**	**135**

* Exp.: Experimental data from Sangster (2001)

In Table 4.2, 4.3 and 4.4,

$$\text{Mean Dev.\%} = \frac{1}{n}\sum_{1}^{n}\frac{\left|\log K\text{ow}^{Exp} - \log K\text{ow}^{\text{Cal}}\right|}{\left|\log K\text{ow}^{\text{Exp}}\right|}\%$$, *n* is the total number of data.

(1) ***K*ow Prediction for Phthalates** From Table 4.2, it can be seen that the VLE1, ACD, ClogP and KowWin methods perform similarly, with VLE1 being slightly more accurate. The GCS method employed here has been originally developed for mono-functional chemicals and yields large deviations for phthalates. Phthalate molecules have structures containing alkyl carbon, aromatic and COO groups, which are multi-functional compounds

(similar to alcohol ethoxylates). It is not surprising that the GCS method cannot satisfactorily predict the *K*ow values for phthalates. Based on these calculations, UNIFAC VLE 1 is recommended for predicting *K*ow for phthalates.

(2) ***K*ow Prediction for Alcohol Ethoxylates**

It is useful to identify the surfactant molecules from the alcohol ethoxylates shown in Table 4.3. D'Arrigo et al. (1991) suggested that the C4E1 molecule is the shortest alcohol ethoxylate surfactant. Following D'Arrigo et al., four compounds of Table 4.3 (C4E1, C4E2, C6E1 and C6E2) can be classified as surfactants. It will be of interest to investigate whether a UNIFAC model can calculate the values of *K*ow for both non-surfactants (C1E1 ~ C3E1) and surfactant molecules (C4E1 ~ C6E1) including both short chain and longer chain surfactants (C4E1, C4E2 to C6E1, C6E2).

The *K*ow value can assist in interpreting the distribution trend of chemicals. Hydrophilic chemicals with low *K*ow values will be largely partitioned into the water-rich phase. Thus, the longer hydrophilic group chain a chemical has, the lower *K*ow value is expected. In Table 4.3, it means that the C4E2 should have lower *K*ow value than C4E1 because the C4E2 has two hydrophilic oxyethylene groups. Similarly, longer hydrophobic chains of a chemical indicate a larger *K*ow value, i.e. *K*ow must increase from C1E1 to C6E1. All *K*ow data shown in Table 4.3 agree with these general considerations.

As shown in Table 4.3, the three commercial tools (ACD, ClogP, KowWin) and UNIFAC VLE 1 perform similarly in the *K*ow prediction for the investigated compounds with ACD showing the lowest deviation. UNIFAC VLE 1 is the best among the various UNIFAC methods for *K*ow calculations, as shown in Table 4.4.

The GCS method for mono-functional chemicals and the UNIFAC micelle method yield larger deviations. The plots of *K*ow prediction results with chain lengths are useful for analysing the general behaviour of the models. Such plots are shown in Figures 4.2-4.4 for three types of alcohol ethoxylate surfactants.

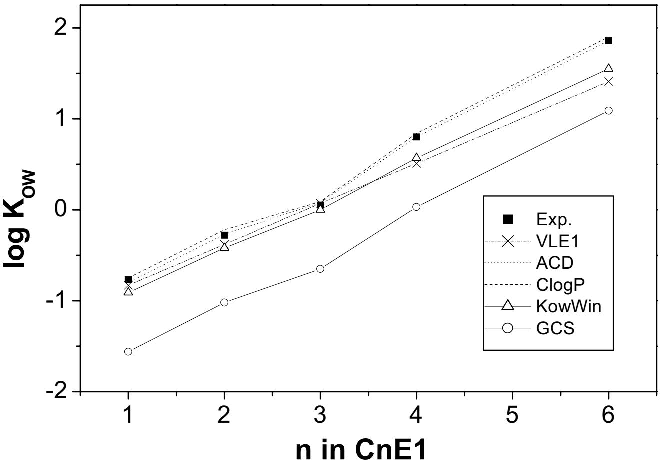


Figure 4.2 Experimental and predicted *K*ow values for CnE1

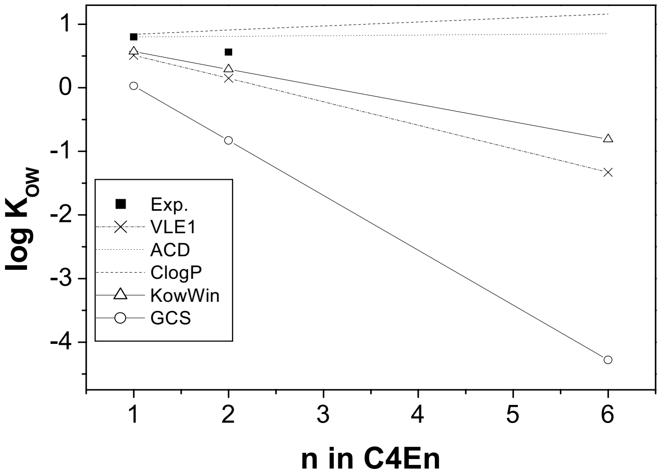


Fig 4.3 Experimental and predicted *K*ow values for C4En

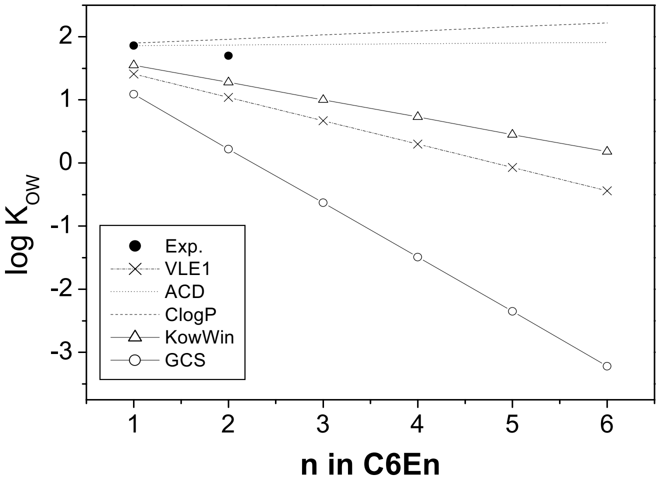


Figure 4.4 Experimental and predicted *K*ow values for C6En.

Figure 4.2 shows that all methods predict the correct trend with increasing alkyl group numbers n in CnE1. However, Figures 4.3 and 4.4 indicate the ACD and ClogP methods exhibit different trends from the VLE1, KowWin and GCS models. It seems that only VLE1, KowWin and GCS follow the experimental trend, i.e. decreasing *K*ow with increasing oxyethylene group number n in C4En and C6En based on the few data available.

Based on these comparisons, it can be concluded that UNIFAC VLE 1 provides, qualitatively, very good *K*ow prediction results for the investigated systems. This method only uses group parameters based on vapour-liquid equilibrium data.

(3) ***K*ow Prediction for alcohol ethoxylates in case no experimental data is available**

The *K*ow values for alcohol ethoxylates, for which no reported experimental *K*ow data is available, are calculated, as shown in Figures 4.5-4.10, using UNIFAC VLE 1, commercial tools and the GCS solvation model. However, the *K*ow calculations of ACD, ClogP and KowWin software produce unreliable results when the alkyl carbon number of alcohol ethoxylates exceeds 12 (indicated by the messages of these three software). The selected surfactants in the *K*ow prediction are currently used in industry.

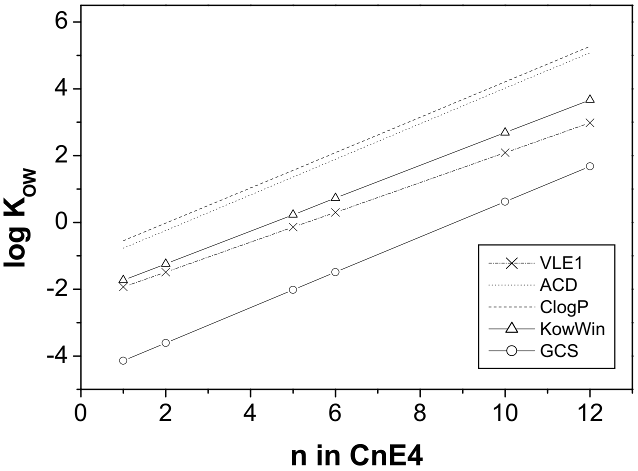


Figure 4.5 Predicted *K*ow values for CnE4

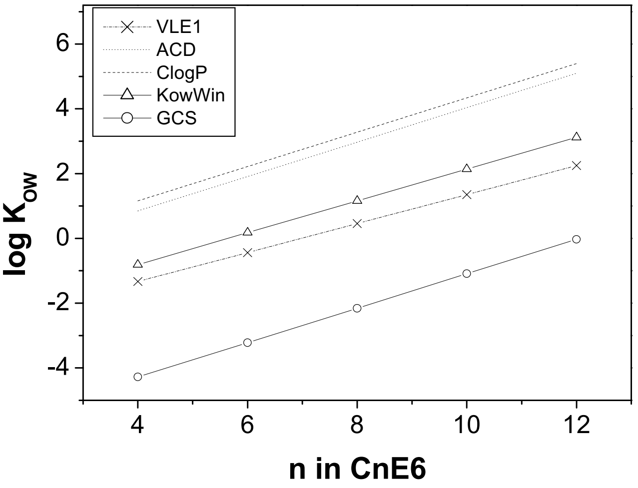


Figure 4.6 Predicted *K*ow values for CnE6

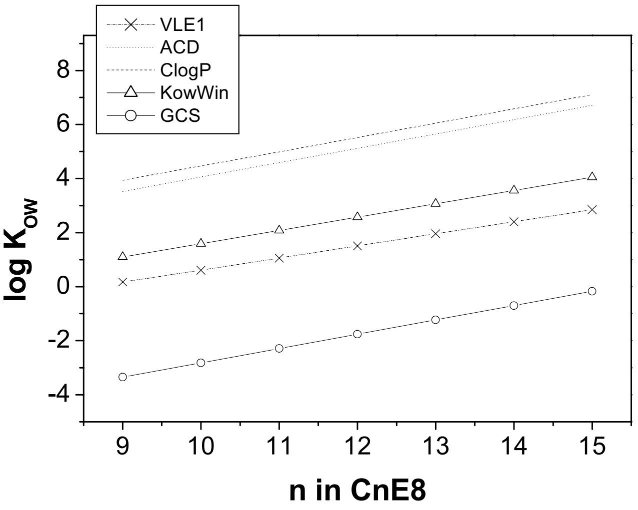


Figure 4.7 Predicted *K*ow values for CnE8

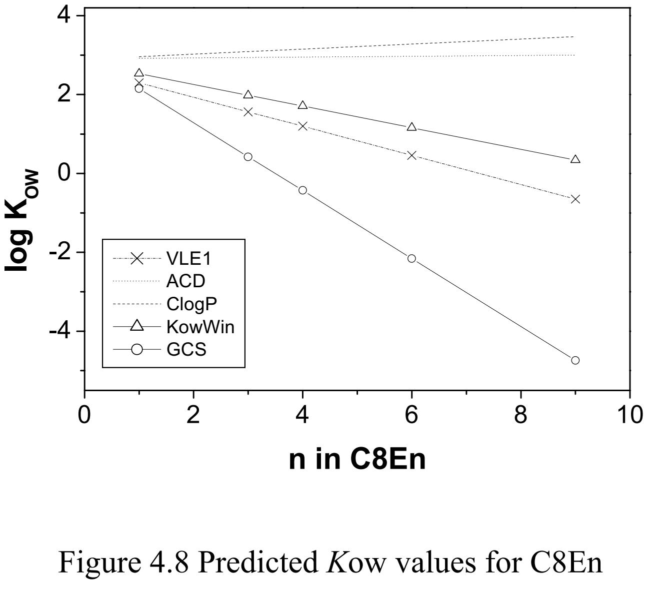


Figure 4.8 Predicted *K*ow values for C8En

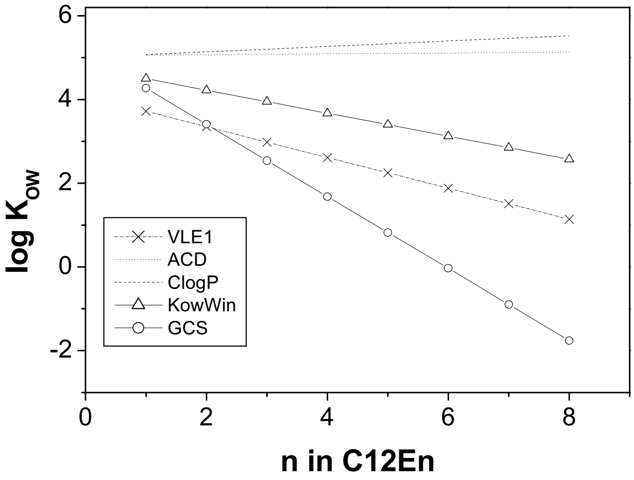


Figure 4.9 Predicted *K*ow values for C12En

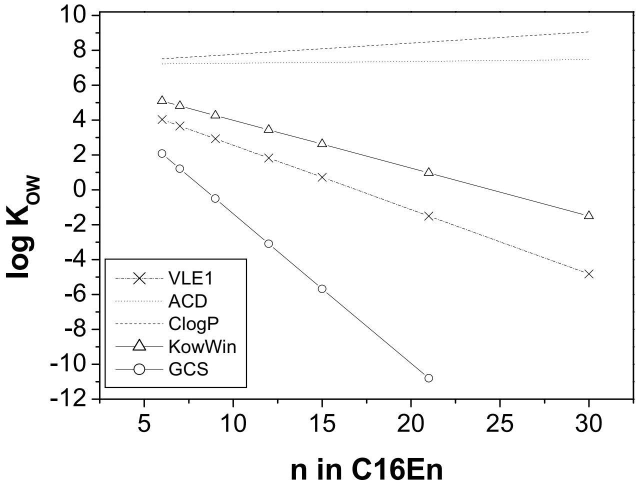


Figure 4.10 Predicted *K*ow values for C16En

4.5 Conclusions

The original UNIFAC VLE 1 model (VLE1) can, at least qualitatively, satisfactorily predict the octanol-water partition coefficients (*K*ow) of phthalates and yields similar results to commercial methods like ACD, ClogP and KowWin that are specifically designed for *K*ow.

Moreover, the VLE1 method can predict reasonably well *K*ow values of alcohol ethoxylates, compared to the limited experimental data available. Again, the performance of VLE1 is similar to the commercial methods. The mono-functional group contribution solvation model (GCS) has the correct tendency with increasing numbers of oxyethylene group (CH_2CH_2O) and alkyl group (CH_2) in alcohol ethoxylates ($R(CH_2CH_2O)nOH$) but it cannot be used for these complex compounds. The ACD and ClogP methods have slightly lower deviations for small alcohol ethoxylates molecules but unlike VLE1, they do not yield the correct trend with increasing oxyethylene group numbers for these compounds. The UNIFAC for surfactant solution method (Micelle) is very similar to ACD and ClogP but has larger deviation in *K*ow prediction for the alcohol ethoxylates. The KowWin can satisfactorily follow the trend with increasing numbers of oxyethylene group and alkyl group in alcohol ethoxylates and has similar deviations as UNIFAC VLE1. Extension of UNIFAC VLE1 method to other classes of non-ionic surfactants is straightforward because the interaction parameters of necessary groups, which may not available, can be estimated from phase equilibrium data for the UNIFAC VLE 1 method. Overall, it can be concluded that the UNIFAC VLE 1 method seems to be the best one among the investigated methods in *K*ow prediction for non-ionic surfactants.

Chapter 5 Critical Micelle Concentration of Nonionic Surfactant Solutions

In this chapter, UNIFAC is combined with a thermodynamic treatment proposed by Chen (1996) to investigate the correlation and prediction of CMC for nonionic surfactant solutions. First, existing UNIFAC models are employed in the prediction of CMC. Second, interaction parameters of UNIFAC groups necessary for modelling alcohol ethoxylate non-ionic surfactants are estimated from experimental CMC data. Alternatively, vapour-liquid equilibrium (VLE) data are used to obtain the interaction parameters for these selected groups. Finally, using these VLE-based parameters, CMC for different aqueous alcohol ethoxylates ($R(CH_2CH_2O)_nOH$) solutions are predicted with the UNIFAC VLE 1 model.

5.1 Recent Progress

Different thermodynamic methods (pseudo-phase, mass action and thermodynamic models) have been proposed to describe the CMC, as discussed in Chapter 3. Among these approaches, the molecular thermodynamic methods are attractive since they can be often used for predictive calculations using limited data.

In chemical engineering, different activity coefficient models are used for describing liquid phase properties, e.g. Wilson, NRTL, UNIQUAC and UNIFAC. These methods have been successfully used for a variety of fluids, e.g. hydrocarbons, polymers, aqueous solutions including aqueous electrolytes. Such activity coefficient models have been widely accepted in chemical industrial applications. Many reliable model parameters are available. However, such models have not been systematically applied to surfactant solutions. Recently, some few applications of such liquid solution models in surfactant solutions have been published, and they are reviewed in this section. These methods can often calculate and/or predict, with reasonable accuracy, the CMC of surfactant solutions.

Chen (1996) proposed a molecular thermodynamic method for the micelle formation using a segment-based NRTL model to correlate the CMC of alcohol ethoxylate + water systems. In his work, the temperature dependent interaction parameters of the NRTL model are obtained from the correlation of binary VLE of water-polyethylene glycol systems and LLE of water + hydrocarbons. CMC of some aqueous alcohol ethoxylate solutions are successfully predicted by this method.

Li et al. (1998) used Chen's thermodynamic treatment and employed the segment-based UNIQUAC model and the statistical associating fluid theory (SAFT) to obtain the activity coefficients of aqueous nonionic surfactant solutions. CMC of single aqueous surfactant system was correlated and predicted for polyoxyethylene surfactant solutions. The interaction parameters of segmented-based UNIQUAC are obtained from experimental CMC data. Temperature dependent interaction parameters are employed in their work. To obtain the SAFT parameters of water, the liquid densities and saturated vapour pressure of pure water between 0-100ºC were correlated in their work. The segment parameters for surfactants in SAFT are regressed by fitting the experimental CMC data at 25ºC.

Flores et al. (2001) and Voutsas, et al. (2001) used a phase separation thermodynamic framework approach to describe the micelle formation of surfactant solutions, in which the micelle phase is approximated as a second liquid phase resulting from the liquid-liquid equilibrium between the solvent and surfactant. The necessary activity coefficients are predicted by UNIFAC. The most promising UNIFAC model in their purpose was found to be the UNIFAC-Lyngby (Larsen, et al. 1987). To improve the results for surfactants containing oxyethylene chains, a new set of parameters was evaluated for a new group (CH_2CH_2O), leading to better CMC prediction for both water and organic solvents, as well as binary solvent systems.

From an application viewpoint, it would be convenient to use structure activity models, possibly based on group contributions, in a thermodynamic treatment for micelle formation, which can correlate and predict the important properties of surfactants, such as the critical micelle concentration and the partition coefficients. The UNIFAC model (Fredenslund et al., 1977) is such a group contribution method for the estimation of activity coefficients. Based on UNIFAC, the CMC data of different surfactant molecules can be used to estimate the interaction parameters of the necessary functional groups.

5.2 Prediction of CMC with Existing UNIFAC Models

Chen (1996) used the original UNIFAC VLE1 (Hansen et al., 1991) to predict the CMC for alcohol ethoxylate surfactant solutions. According to Chen, the predicted CMC values using UNIFAC follow qualitatively the observed trend as the hydrophobic alkyl chain part of surfactants increases. However, UNIFAC cannot (not even qualitatively) yield the observed trend with respect to the hydrophilic chain. In this work, various existing UNIFAC models (see Appendix A) will be evaluated for several aqueous nonionic surfactant systems.

The nonionic surfactants having a polyoxyethylene chain are among the most extensively investigated systems in the literature. The alcohol ethoxylate surfactants are often abbreviated as C_iE_j, where *i* is the number of alkyl carbon and *j* is the number of oxyethylene group (OCH_2CH_2). Due to the fact that existing UNIFAC parameter tables do not contain a separate oxyethylene group, it is necessary to investigate first how well the combination of an ether group (CH_2O) and an alkyl group (CH_2) can represent the oxyethylene group (CH_2CH_2O) for surfactant systems. In such combination, the values of group parameters Q and R for the oxyethylene group (CH_2CH_2O) are estimated as follows:

$$Q_{CH_2CH_2O} = Q_{CH_2O} + Q_{CH_2} = 1.320 \qquad R_{CH_2CH_2O} = R_{CH_2O} + R_{CH_2} = 1.5927$$

Q and R values of group CH_2O and CH_2 are taken from the work of Hansen et al. (1991). The ether main group (CH_2O) interaction parameters are used in these calculations. The values of the interaction parameters for different UNIFAC models are taken from the references given in Appendix A and are listed in Table 5.1.

Table 5.1 UNIFAC interaction parameters for ether-alcohol and ether-water groups (in K)

	$CH_{2(1)}$~$CH_2O_{(2)}$		$CH_2O_{(1)}$~$H_2O_{(2)}$	
	$a_{1\text{-}2}$	$a_{2\text{-}1}$	$a_{1\text{-}2}$	$a_{2\text{-}1}$
UNIFAC VLE 1	251.5	83.36	-314.7	540.5
UNIFAC LLE 1	662.1001	1571.	212.8	64.42
UNIFAC VLE 2	164.2 1.627	251.2 -2.197	82.42 5.0	-90.87 -2.218
UNIFAC VLE 3	230.5 -1.328 -2.476	369.8999 -1.542 -3.228	183.1 -2.507 0.0	19.54 1.293 -8.85
Water-UNIFAC	251.5	83.36	-314.7	540.5

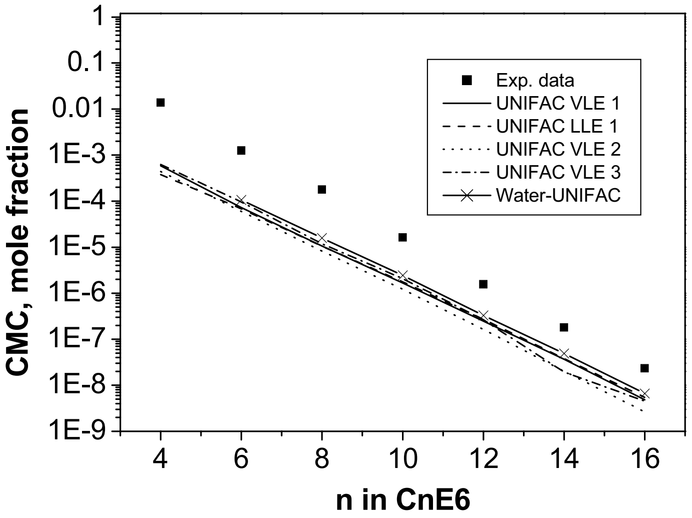


Figure 5.1 CMC prediction results with various UNIFAC models at 25°C for C_nE_6 surfactants with different hydrophobic alkyl chains.

Using equation (3.48) in Chapter 3, the CMC values of different aqueous nonionic surfactant solutions are predicted with the five different versions of UNIFAC (Table 5.1). The prediction results are shown graphically in figures 5.1 to 5.4. It can be seen that all five UNIFAC models have qualitatively similar behaviour in aqueous surfactant solutions. The predicted trends for both the hydrophobic and hydrophilic chains are in agreement with Chen's results (1996). However, these results also show that UNIFAC may be in position to describe properties for surfactant systems and that it may have a potential for describing the micelle formation of aqueous surfactant solutions if appropriate improvements are introduced. In these calculations, experimental CMC data are taken from the following references: Mukerjee and Mysels (1971), Schick (1987), Hinz (1986), van Os et al. (1993).

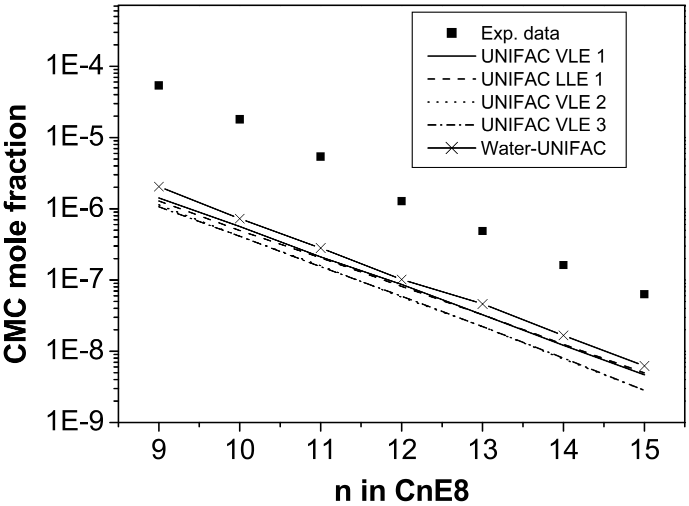


Figure 5.2 CMC prediction results with various UNIFAC models at 25°C for C_nE_8 surfactants with different hydrophobic alkyl chains.

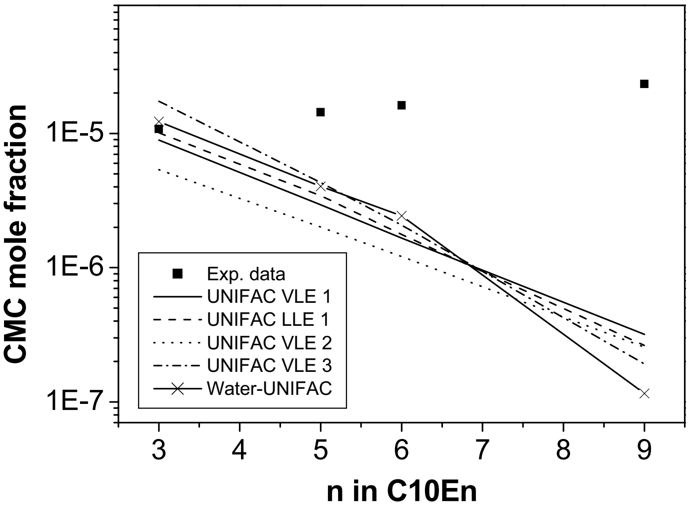


Figure 5.3 CMC prediction results with various UNIFAC models at 25°C for $C_{10}E_n$ surfactants with different hydrophilic groups.

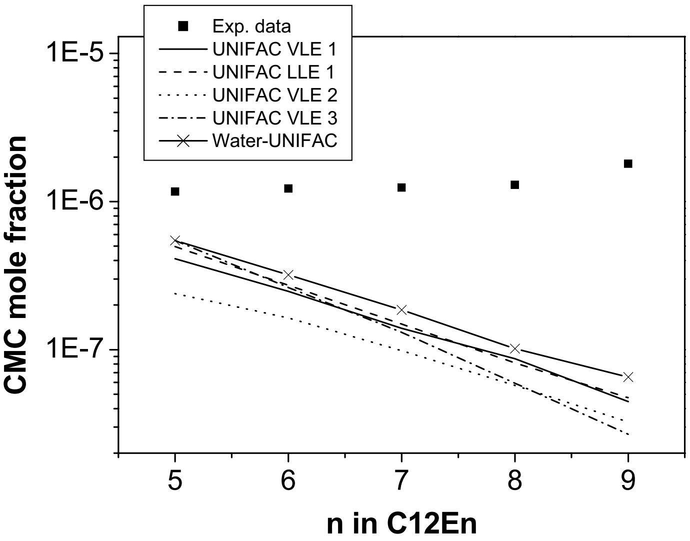


Figure 5.4 CMC prediction results with various UNIFAC models at 25°C for $C_{12}E_n$ surfactants with different hydrophilic groups.

5.3 Towards a UNIFAC Model for Surfactant Solutions

As shown in figures 5.1-5.4, UNIFAC has the correct CMC tendency with varying alkyl number in surfactant molecules, but not with varying oxyethylene number. Therefore it is necessary to further investigate the applicability of UNIFAC to surfactant systems. Since the selection of functional groups plays an important role in UNIFAC, a special new oxyethylene group (CH_2CH_2O) is introduced and evaluated. New interaction parameters for this group are first directly correlated from experimental CMC data. If results from this step are found satisfactory, the CH_2CH_2O interaction parameters would be then estimated solely from vapor-liquid phase equilibrium data. These interaction parameters from the second step will give the possibility for direct CMC prediction through UNIFAC.

5.3.1 The New Oxyethylene Group (OCH_2CH_2) for UNIFAC

Surfactant molecules have a wide range of structural features. For nonionic surfactants alone, several typical structure families are among branched alkyl ethoxylates, linear alkyl ethoxylates, octylphenol ethoxylates, alkanediols, alkyl mono- and disaccharides ethers and esters, ethoxylated alkyl amines and amides, fluorinated linear ethoxylates and amides (Huibers et al. 1996).

Most of these nonionic surfactants contain the oxyethylene group (ethylene oxide oligomers) in the hydrophilic part of the molecule. These surfactants often contain a distribution of polyethylene oxide chain lengths rather than a constant number of units. In this work, two families are studied: the branched alkyl ethoxylates and the linear alkyl ethoxylates, which are widely used in the chemical industry and are among the most extensively investigated nonionic surfactants. They are also considered to be environmental friendly chemicals (AMI report, 2000). These two classes can be represented as the sum of oxyethylene groups, CH_2CH_2O and alkyl groups along with one alcohol group OH. Thus, only one new main UNIFAC group, CH_2CH_2O, needs to be introduced in order to describe these two classes of surfactants.

5.3.2 Existing Interaction Parameters for the Oxyethylene Group

In their study of phase equilibrium of aqueous polymer solutions, Rasmussen et al. (1989) have introduced a special CH_2CH_2O (polyethylene oxide) group in the UNIFAC model and successfully predicted the phase behaviour of aqueous polymer solutions with its group interaction parameters. These group interaction parameters (shown in Table 5.2) have been also used for investigating the applicability of UNIFAC model for predicting CMC values of surfactant solutions. Some prediction results are shown in figure 5.5 (denoted as “Rasmussen”). The calculation is the same as the various UNIFAC methods discussed in section 5.2. As shown in figure 5.5, using the parameters from Rasmussen et al. (1989) , the UNIFAC cannot satisfactorily predict the CMC trends of nonionic surfactants with both increasing hydrophobic and hydrophilic chain-length.

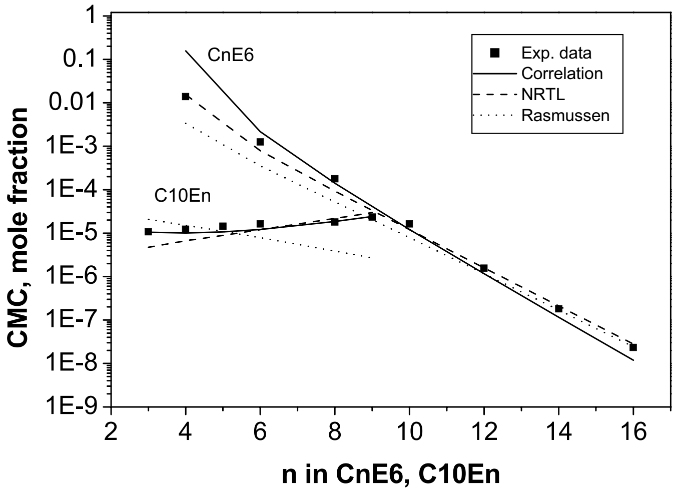


Figure 5.5 Prediction and correlation results of CMC of two C_iE_j surfactants (C_nE_6 and $C_{10}E_n$) at 25°C with different methods.

Another group selection for surfactant molecules could be the special glycolether group, which has been published by Hansen et al. 1991. However, the glycolether-ether interaction parameters are not available in this UNIFAC model. Thus, this special group was not studied further.

5.3.3 Summary

This discussion and the previous calculations in section 5.2 indicate that the possible way for applying UNIFAC to surfactant systems would be to estimate special group interaction parameters. In figure 5.5, the prediction results of the UNIFAC from Rasmussen show that the UNIFAC model with a new oxyethylene group may have the capability for predicting satisfactorily the CMC values for different hydrocarbon chain length in aqueous surfactant solutions. It is thus very valuable to further investigate the potential of the use of a separate oxyethylene group. In order to predict the CMC of surfactant solutions, experimental vapour–liquid equilibrium data for non surfactant solutions will be used to estimate the CH_2CH_2O group interaction parameters with the UNIFAC model. However, it is necessary to verify that the UNIFAC model has indeed the potential of getting 'both trends' for surfactant solutions (i.e. increasing hydrophobic and hydrophilic chains). One of the ways to do so is an estimation of CH_2CH_2O parameter values directly from CMC data.

5.4 Correlation of CMC Using UNIFAC

The interaction parameters of CH_2CH_2O group are obtained by directly regressing CMC data. In order to obtain the UNIFAC interaction parameter values of the oxyethylene group, the thermodynamic condition, equation (3.48), is used for converting the experimental CMC values to activity coefficients. The logarithm of activity coefficients is used as the objective function (F) in the interaction parameter estimation with CMC data:

$$F = \sum_j \left(\ln \gamma_{i,Exp} - \ln \gamma_{i,\mathrm{UNIFAC}} \right)_j^2 \tag{5.1}$$

where j is the jth data point of a data set.

The UNIFAC interaction parameters between the oxyethylene group CH_2CH_2O and CH_2 and H_2O groups are regressed using the CMC data by minimizing this objective function, equation (5.1). The existing interaction parameters for CH_2O-OH pair (Hansen, et al., 1991) are used. The interaction parameters of the remaining groups are also taken from Hansen, et al. (1991). The details of the regression method can be found in the reference (Fredenslund et al., 1977). Typical regression results are shown in figure 5.5, denoted as "Correlation". The obtained parameter values are shown in Table 5.2, denoted as "Correlation". For comparison the prediction results from NRTL model (Chen, 1996) are also presented in figure 5.5.

These results indicate that UNIFAC with the new group has the potential of representing the CMC values of different types of aqueous surfactant solutions. Other local composition model, e.g. NRTL and UNIQUAC, may behave in a similar way.

5.5 Prediction of CMC Using UNIFAC

As a second step, the interaction parameters of CH_2CH_2O group will be obtained from VLE data. The UNIFAC interaction parameter pairs are the same as in the correlation procedure described in the previous section (5.4). Two interaction parameter pairs, CH_2CH_2O-CH_2 and CH_2CH_2O-H_2O are estimated from VLE data. Due to the fact that CH_2CH_2O group can be treated as the combination of group CH_2O and CH_2, the CH_2CH_2O main group should include several subgroups, such as CH_3CH_2O, CH_3CHO, CH_2CH_2O, CH_2CHO, CHCHO, CH_2CO, CH_3CO. Moreover, proximity effects cannot be neglected for this group. Considering the proximity effects, the agreement between UNIFAC and phase equilibrium data is not very satisfactory for mixtures containing glycol ethers, 1,4-dioxane, 1,3 -dioxolane, etc. (Kehiaian et al., 1989, Wu et al., 1989). For non-ionic surfactants, only the linear oxyethylene group is involved in branched alkyl ethoxylates and linear alkyl ethoxylates. Thus, only those systems including linear ether components are selected for the parameter estimation to avoid further complexity in the parameter estimation.

The existing VLE phase equilibrium data of important ethers with non-polar solvents have been reviewed and published by IUPAC (Marsh et al., 1999). However, VLE data for ether + water systems are scarce. Considering previous investigations for ether-water interaction parameters (Skjold-Jørgensen, 1980, Larsen, 1986), we have only selected the water +1,4-dioxane system (Kortuem et al., 1977) for regressing the CH_2CH_2O-H_2O interaction parameters. The following experimental VLE data have been used for the parameter estimation of CH_2CH_2O-CH_2: n-hexane+dibutyl ether (Marsh et al., 1980) and butylmethyl ether + heptane (Treszczanowicz, 1986). No LLE data have been used. The estimation is based on the same objective function as before (equation 5.1). The interaction parameters regressed from VLE data are listed in Table 5.2.

Table 5.2 UNIFAC interaction parameters (in K)

	$CH_{2(1)}$-$CH_2CH_2O_{(2)}$		$CH_2CH_2O_{(1)}$-$H_2O_{(2)}$	
	a_{1-2}	a_{2-1}	a_{1-2}	a_{2-1}
Rasmussen et al. (1989)	106.60	63.55	546.0	-120.4
Correlation from CMC (this work)	22.24	-66.99	25.14	-18.24
Estimation from VLE (this work)	-31.87	84.75	134.95	-67.77

Using the UNIFAC interaction parameters from vapour-liquid equilibrium data (Table 5.2), CMC has been predicted using equation (3.48). The predicted results are shown in the figures 5.6-5.10, and are also compared with the correlation results (section 5.4).

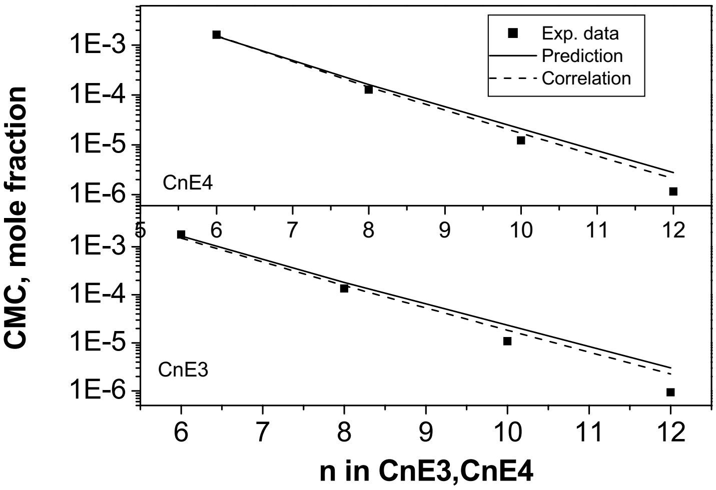


Figure 5.6 Predicted and correlated CMC values with UNIFAC VLE 1 model at 25°C for two C_iE_j surfactants (C_nE_3 and C_nE_4) with different hydrophobic alkyl chains.

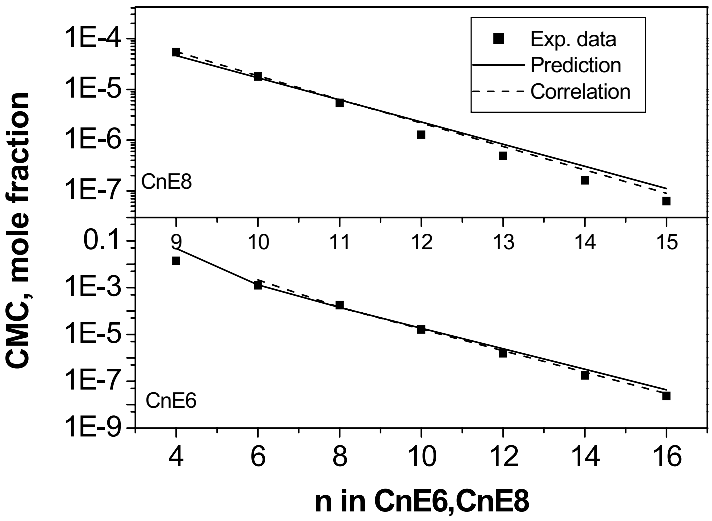


Figure 5.7 Predicted and correlated CMC values with UNIFAC VLE 1 model at 25°C for two C_iE_j surfactants (C_nE_6 and C_nE_8) with different hydrophobic alkyl chains.

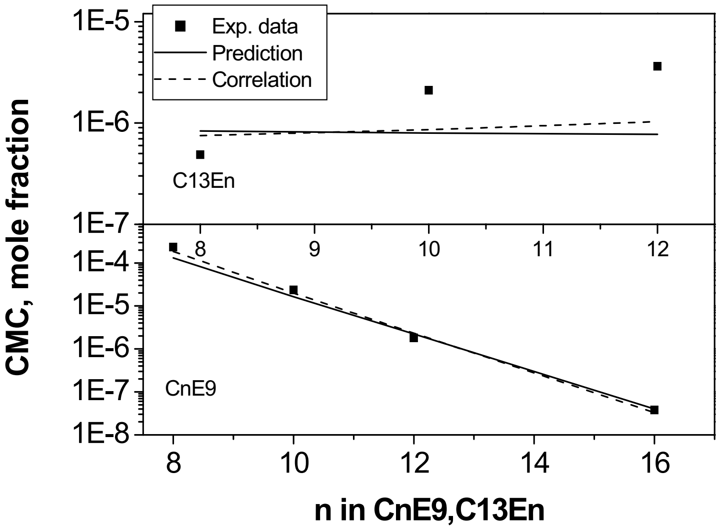


Figure 5.8 Predicted and calculated CMC values with UNIFAC VLE 1 model at 25°C for two C_iE_j surfactants (C_nE_9 and $C_{13}E_n$) with different hydrophobic or hydrophilic groups.

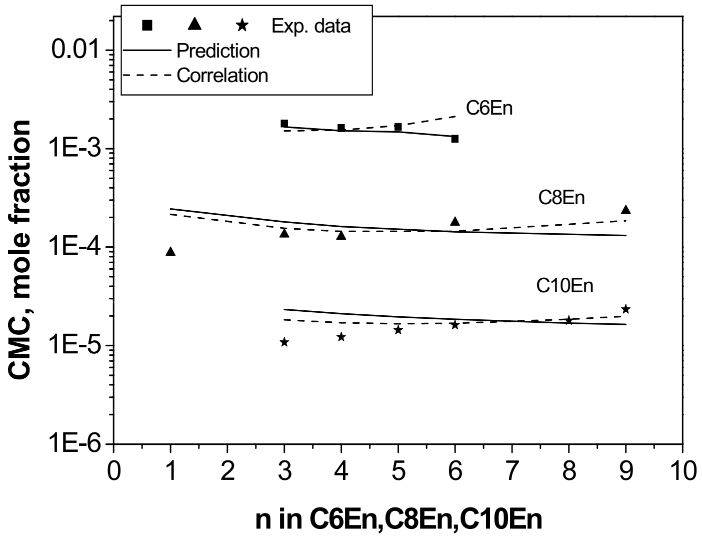


Figure 5.9 Predicted and correlated CMC values with UNIFAC VLE 1 model at 25°C for three C_iE_j surfactants (C_6E_n, C_8E_n and $C_{10}E_n$) with different hydrophilic groups.

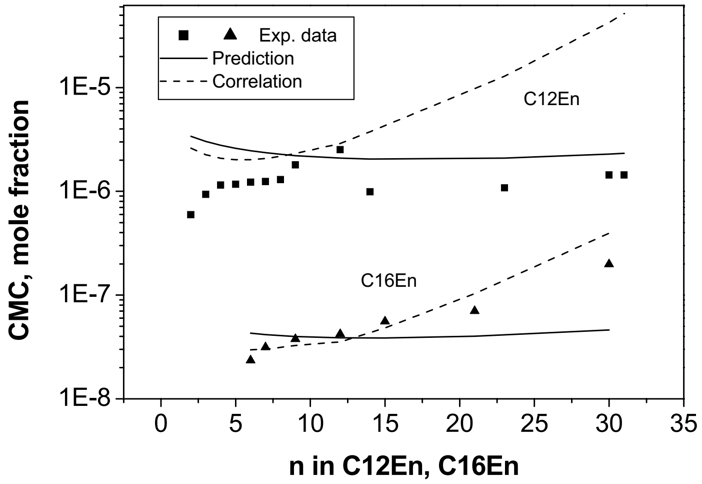


Figure 5.10 Predicted and correlated CMC values with UNIFAC VLE 1 model at 25°C for two C_iE_j surfactants ($C_{12}E_n$ and $C_{16}E_n$) with different hydrophilic groups.

From these results, it can be seen that the UNIFAC model, with the interaction parameter from VLE data, can quantitatively represent CMC for different aqueous non-ionic surfactant solutions. Specifically, the UNIFAC model predicts well the observed trends of hydrophobic alkyl and hydrophilic chain for these nonionic surfactant solutions. Slight deviations in the hydrophilic tendencies could be attributed to the fact that interaction parameters are estimated only from water+1,4-dioxane VLE data. The values of oxyethylene group interaction parameters could be different in the linear and cyclical states. On the other hand, the obtained CMC data are from different data sources; only part of them being from the collection of Mukerjee et al. (1971) in which CMC data have been carefully reviewed. Experimental CMC data may be subject to errors, which can be difficult to assess due to lack of a method for testing the consistency of CMC data.

5.6 Discussion and Conclusions

Different UNIFAC methods have been systematically investigated for water + alcohol ethoxylate systems. The results show that the original UNIFAC VLE 1, modified UNIFAC

VLE 3, UNIFAC LLE 1, the linear temperature dependent UNIFAC VLE 2 and water UNIFAC methods predict qualitatively correct the observed trend of the CMC with hydrophobic chain for aqueous nonionic surfactant solutions, but fail to predict the CMC trend with the hydrophilic chain. By introducing a new group, the oxyethylene group (CH_2CH_2O), and estimating its interaction parameters from vapour-liquid equilibrium data, the original UNIFAC VLE 1 method can provide good prediction for micelle formation in water + alcohol ethoxylate systems with both the hydrophobic and hydrophilic trends. Because the UNIFAC model has a large amount of interaction parameters readily available in reference (Hansen et al., 1991), it should be in principle applicable to other nonionic surfactant solutions, e.g. alkyl phenol-oxyethylene, if (when required) new functional group parameters are introduced and estimated from available phase equilibrium data.

Besides the phase equilibrium data, osmotic coefficient and enthalpy data can also be applied to estimate the interaction parameters of the CH_2CH_2O group in the UNIFAC model. Dearden et al. (1996), Sato et al. (1988), van Os et al. (1993), McGinnis et al. (1997) have published these types of data. Because the osmotic coefficients are directly obtained from vapour pressure measurement of aqueous surfactant solutions, the osmotic coefficient data could be used to get the group interaction parameters in surfactant molecules, e.g. CH_2CH_2O group. In this way, UNIFAC may give better prediction results. However, interaction parameter estimation using osmotic coefficient data cannot completely overcome certain limitations of UNIFAC, such as the proximity effects.

Modelling of micelle formation in mixed surfactant systems is at the beginning. However, mixed surfactant systems are very important in industrial applications. In the mixed aqueous surfactant solutions, more than one nonionic surfactant may exist in micelles. In many cases, these solutions also contain salts and ionic surfactants as additives. Chen (1996) has proposed a thermodynamic framework for mixed surfactant systems, but this has not been applied to a specific mixed surfactant solution.

Chapter 6 The UNIFAC Model for Aqueous Electrolyte Solutions

The purpose of this chapter is to select and evaluate a model to describe the mean activity coefficients of electrolyte solutions, which will be applied to ionic surfactant solution.

The ionic (cationic or anionic) surfactant molecules dissociate into cations and anions in aqueous solutions. Such solutions exhibit typical electrolytic properties. The electrical conductivity of the solution can be measured, and can be used experimentally to determine the critical micelle concentrations (CMC) of ionic surfactant solutions (Mukerjee et al., 1971); as shown in figure 2.5 (Chapter 2) and figure 3.8 (Chapter 3). Thus, a model for organic electrolyte solutions is required to calculate the properties of ionic surfactant solutions, such as mean activity coefficients.

In this chapter, the modelling of aqueous electrolyte solutions is first briefly reviewed, emphasizing the efforts of extending the UNIQUAC or UNIFAC model to aqueous electrolyte solutions. Achard's electrolyte UNIFAC method (Achard et al. 1994a, b) is then described and modified. It has been found that the structural parameter (Q, R) of ions used in this model and other UNIQUAC based models did not follow Flory-Huggins assumption ($Q/R \leq 1$). Thus, structural parameters (Q, R) of ions for the UNIFAC model are estimated from ionic radii based on the condition $Q/R<1$. Mean activity coefficients of some aqueous and organic electrolyte solutions are studied with the modified Achard electrolyte UNIFAC model using the new set of structural parameters.

6.1 Modelling of Aqueous Electrolyte Solutions

6.1.1 Definitions of Electrolyte Solutions

When dissolved in a high-dielectric-constant solvent like water, an electrically neutral electrolyte $M_{\nu+}X_{\nu-}$ is dissociated into ν_+ positive ions (cations) each with a charge z_+, and ν_-

negative ions (anion) of charge z_-. Charges are given in normalized units where z_+=1 for a proton. Electrolyte dissociation is represented by

$$\mathrm{M}_{v+}\mathrm{X}_{v-} \rightleftharpoons v_+\mathrm{M}^{z+} + v_-\mathrm{X}^{z-} \tag{6.1}$$

Electroneutrality requires that

$$v_+z_+ + v_-z_-=0 \tag{6.2}$$

Equation (6.2) expresses a chemical equilibrium. The criterion for chemical equilibrium is that the chemical potentials follow the equation:

$$\mu_{\mathrm{M_{v+}X_{v-}}} = v_+\mu_{\mathrm{M^{z+}}} + v_-\mu_{\mathrm{X^{z-}}} \tag{6.3}$$

Using the molality scale for activity coefficients, the chemical potential of the electrolyte is:

$$\mu_{\mathrm{M_{v+}X_{v-}}} = \mu^*_{\mathrm{M_{v+}X_{v-}}} + v_+RT\ln(m_+\gamma_{+m}) + v_-RT\ln(m_-\gamma_{-m}) \tag{6.4}$$

where

$$\mu^*_{\mathrm{M_{v+}X_{v-}}} = v_+\mu^*_{\mathrm{M^{z+}}} + v_-\mu^*_{\mathrm{X^{z-}}} \tag{6.5}$$

In equation (6.5), $\mu^*_{\mathrm{M^{z+}}}$ is the chemical potential of ion M (with charge z_+) in a hypothetical ideal solution. A similar definition is used for $\mu^*_{\mathrm{X^{z-}}}$.

Equation (6.4) can also be written in another form:

$$\mu_{\mathrm{MX}} = \mu^*_{\mathrm{MX}} + RT\ln(m_+^{v+}m_-^{v-}) + RT\ln(\gamma_{+m}^{v+}\gamma_{-m}^{v-}) = \mu^*_{\mathrm{MX}} + RT\ln(a_+^{v+}a_-^{v-}) \tag{6.6}$$

where the subscripts on MX have been dropped for convenience.

The mean (ionic) molality ($m_\pm$) and the mean (ionic) activity coefficient ($\gamma_{\pm\mathrm{m}}$) are defined by

$$m_\pm = \left(m_+^{v+}m_-^{v-}\right)^{1/v} \tag{6.7}$$

$$\gamma_{\pm m} = \left(\gamma_{+m}^{v+}\gamma_{m-}^{v-}\right)^{1/v} \tag{6.8}$$

where $v=v_+ + v_-$. With equation (6.6), we have

$$a_\pm = \left[(a_+)^{v+}(a_-)^{v-}\right]^{1/v} = m_\pm\gamma_{\pm m} \tag{6.9}$$

where $a_\pm$ is the mean (ionic) activity.

A thermodynamic model is needed for the mean activity coefficient $\gamma_{\pm\mathrm{m}}$.

6.1.2 Activity Coefficient Models

The work of Debye and Hückel in 1923 is one of the first theoretical attempts in modelling electrolytes (Laidler, 1999). In Debye-Hückel theory, the water or solvent is regarded as a dielectric continuum, the solvent molecules are not explicitly taken into account. The ions are regarded as individual spheres. This is a simplified representation of a very dilute solution. The Debye-Hückel theory only considers the energy of charging-up a system. That implies the existence of an uncharged system of molecules that needs to be charged. If the Debye-Hückel theory is used without any additional terms, it only represents the behaviour of very dilute solutions. Starting with the Debye-Hückel theory, many researchers have proposed their methods to represent concentrated electrolyte solutions.

Loehe and Donohue (1997) have reviewed modelling approaches for thermodynamic properties of aqueous electrolyte solutions. Theoretical and engineering models for the thermodynamic properties of strong electrolyte solutions have advanced significantly since the 80's. Significant progress has been made in the ability to calculate various properties of single and mixed strong electrolyte solutions over a wide range of temperature and composition, including effects of various non-electrolytes, solvents and supercritical components. Engineering models for thermodynamic properties of electrolyte solutions may be divided into three catalogues: (1) local composition and hydration models; (2) empirical and semi-empirical equations of state for strong electrolytes; and (3) equations for mixed solvents, mixed electrolytes, and mixtures of supercritical gases and electrolytes. In this work, we focus on local composition models.

Many such semi-empirical local composition models have been proposed using a Debye-Hückel type term for the long-range contribution, but different expressions for the short-range contribution, e.g. UNIQUAC, NRTL, Wilson, van Laar and Margules equations (Prausnitz et al., 1999). The models of Cruz and Renon (1978) and Chen et al. (1982, 1986), use NRTL; the model of Zerres and Prausnitz (1994) uses an extended van Laar equation. In Pitzer's model (1973, 1980), a virial series is used for the short-range contribution.

The electrolyte NRTL model of Chen et al. is based on two important assumptions: (1) the local composition of cations around cations is zero, and similarly for anions, which is equivalent to assuming that repulsive forces between ions of like charge are extremely large (like-ion repulsion assumption); (2) the distribution of cations and anions around a central solvent molecule is such that the net local ionic charge is zero (local electroneutrality assumption). Based on these assumptions, Chen derived an expression for the short-range contribution to the excess Gibbs energy that includes two adjustable parameters. Chen's model reproduces well the mean ionic activity coefficients of aqueous single electrolytes up to a molality of six. For multi-salt systems, this model requires binary parameters obtained from data of the corresponding binary systems. Recently, Chen et al. (2001) modified their electrolyte NRTL model and extended it to aqueous organic electrolytes. The proposed extension has three terms: the Pitzer-Debye-Hückel term, the local composition term from an NRTL-type expression, and the Flory-Huggins term. This NRTL version for aqueous organic electrolytes was then applied to micelle formation of aqueous sodium carboxylate solutions.

6.2 Efforts in Extending the UNIQUAC/UNIFAC Methods to Electrolyte Solutions

Many efforts have been reported for extending the UNIQUAC or UNIFAC models (as short-range term) for electrolyte solutions. Only some of the efforts are discussed here.

Christensen et al. (1983 a, b)

Christensen et al. investigated aqueous electrolyte solutions with the UNIQUAC model. In their work, the excess Gibbs energy of solution includes three terms: (1) a Debye-Hückel term from Robinson and Stokes (1965); (2) a term of the Brøndsted-Guggenheim type, which is an empirical expression given by Guggenheim referring to the interaction between cations and anions; (3) a UNIQUAC term. It is assumed that the local composition of cations around cations and anions around anions is very small, due to the strong repulsive electrostatic interaction between charges of the same sign. This corresponds to a high positive value for the interaction parameter between two cations or two anions. This assumption is equivalent to the "like-ion repulsion assumption" of Chen et al. (1982). Another assumption is to arbitrarily set the value of interaction parameters of water-water and cation-anion to zero. For ions, the structural parameters are calculated using the ionic radii in crystals. The ionic radii in crystals can be found in CRC handbook (Lide, 2002). For a single electrolyte system, three estimated parameters, i.e. $u_{\text{cation-H2O}}$, $u_{\text{anion-H2O}}$ in the UNIQUAC term and one $\beta_{\text{cation-anion}}$ in the Brøndsted-Guggenheim term, are used to correlate the activity coefficients of electrolyte solutions.

Sander et al. (1984, 1986)

To correlate and predict salt effects in vapour-liquid equilibria for water and cosolvent mixtures, Sander et al. (1984, 1986) combined the Debye-Hückel term and a modified UNIQUAC equation with concentration-dependent interaction parameters. The model parameters are ion-specific, and no ternary parameters are required. In Sander's model, some of the interaction parameters between cations and anions are set to be zero. Instead of using the "like-ion repulsion assumption" of Chen et al. (1982), the interaction parameters between like ions are also set to zero. The volume (R) and surface area (Q) parameters of cations were modified. This is because the very small values of the ionic radii of the cations lead to Q-values of the order of 0.1 to 0.5. Q–values of this magnitude reduce the fitting capabilities of the UNIQUAC equation. For the anions, the R and Q are calculated from ionic radii in crystals. However, a large number of parameters are needed: 7 for a salt/solvent system and 14 for a salt/co-solvent system. Sander's model suffers from improper combination of Lewis-Randall and McMillan-Mayer formalisms. This deficiency was later corrected by Macedo et al. (1990).

Kikic et al. (1991)

Kikic et al. developed a UNIFAC model for correlation of vapour liquid equilibria in mixed solvent-salt systems. The model of Kikic et al. used the same thermodynamic framework as Sander's. UNIFAC is used for the short-range contribution term instead of UNIQUAC. The Debye-Hückel expression is used for long-range interactions. The assumptions for interaction parameters are the same as in Sander's method. The volume and surface area parameters of ions are taken from Sander's work.

Thomsen et al. (1996, 1997, 1999)

Thomsen et al. modified Sander's model (1986) with a linear temperature dependence of the binary interaction parameters and extended the UNIQUAC model to correlate and predict the thermal properties and phase behaviours of aqueous electrolyte systems. The interaction parameters are estimated from Gibbs energy of formation, enthalpy of formation and heat capacities for electrolytes. Thomsen's model sets the water-water and the like cation interaction parameters to zero. The volume and surface area parameters of ions are regressed from experimental data.

Li et al. (1994)

Li et al. proposed an excess Gibbs energy (G^E) model for electrolyte systems based on the results from statistical thermodynamics and took into account the interactions between all species present in the electrolyte solution. In this model, the electrolyte solution is treated as a non-electrolyte solution plus charge interactions. It is assumed that the charge interactions are both direct and indirect: direct interactions between charges, indirect effects under the influence of the electric field created by the charges. Both direct and indirect effects depend on the ionic strength of the solution. The expression of excess Gibbs energy for electrolyte solutions is:

$$G^{\mathrm{E}} = G^{\mathrm{E}}_{\mathrm{LR}} + G^{\mathrm{E}}_{\mathrm{MR}} + G^{\mathrm{E}}_{\mathrm{SR}} \tag{6.10}$$

where the $G^{\mathrm{E}}_{\mathrm{LR}}$ represents the long-range (LR) interaction due to the electrostatic forces, and mainly describes the direct effects of charge interactions. $G^{\mathrm{E}}_{\mathrm{LR}}$ is calculated with the Debye-Hückel theory modified by Fowler and Guggenheim. $G^{\mathrm{E}}_{\mathrm{MR}}$ represents the indirect effects from the noncharge short-range interactions of the non-electrolyte solutions, and is called the middle-range (MR) interaction contribution. $G^{\mathrm{E}}_{\mathrm{MR}}$ is computed by an expression proposed by Li et al. (1994), $G^{\mathrm{E}}_{\mathrm{SR}}$ expresses the short-range interaction, and is calculated by the UNIQUAC model. The volume and surface area parameters are fixed to 1.0 for ions. For a single electrolyte solution, four parameters are required to describe the cation-anion interactions; eight parameters are needed for ion-solvent interactions. Based on the thermodynamic framework of Li et al. (1994), Yan et al. (1999) used the UNIFAC model, instead of UNIQUAC, to describe the short-range interaction contribution and introduced group interaction parameters to the middle-range term. The volume and surface area parameters of ions in the UNIFAC model are treated as adjustable parameters.

Lu and Maurer (1993)

Lu and Maurer combined ionic solvation equilibria and physical interaction forces for mixed electrolyte solutions. In this model, the Debye-Hückel model is used for the long-range term, and the UNIQUAC model is used for the short-range term to represent the excess Gibbs energy. The UNIQUAC structural parameters of charged species are approximated by the ionic radii of ions. Furthermore, for all ionic species the UNIQUAC size R and surface Q parameters are set equal to each other. For the interaction parameters, it is assumed that: (1) the interaction parameters are equal to 2000 K for ions carrying same sign charges, (2) the interaction parameters between cation-anion are equal to that of anion-cation, (3) the interaction parameters between any ion and a water molecule are zero since these interactions are taken into account by the solvation reaction, and (4) the interaction parameter between water molecules is set to zero. For the ions of a strong electrolyte, there remain only 3 “pure component” parameters, which are, the unsolvated ionic radius, solvation number and solvation equilibrium constant. There are two binary parameters for interactions between a cation and an anion, that is, one size correction parameter and one energy parameter. Lu et al. (1996) further extended this method to various temperatures.

Achard et al. (1994a, b)

Achard et al. (1994a, b) proposed a modified UNIFAC method to correlate and predict salt effects on vapour-liquid equilibria of mixed solvent systems and extend the method for weak electrolytes in aqueous solutions. The model of Achard et al. combined a term of the Debye-Hückel type with a modified UNIFAC equation based on solvation phenomena. In Achard’s method, the volume and surface area parameters of ions are computed by combining the ionic radii in crystals with hydration numbers. The method has been used to represent salt effects on vapour-liquid equilibrium of mixed solvent systems, the pH in complex aqueous solutions, especially the water activity and osmotic pressure of organic electrolyte solutions, i.e. amino acids, carboxylic acids, phosphates and carbonates (Achard et al. 1993, 1994a, b). This model was chosen for further study in this work.

6.3 Achard's Electrolyte UNIFAC Model and its Modifications

6.3.1 Achard's Electrolyte UNIFAC Model

In the electrolyte UNIFAC method proposed by Achard et al. (1994a, b), the excess Gibbs energy (g^E) is divided into two terms, one resulting from short-range (SR) interactions (physical forces, solvation phenomena between water and ionic species), and the other from long-range (LR) electrostatic interactions:

$$\frac{g^E}{RT} = \frac{g^{E,SR}}{RT} + \frac{g^{E,LR}}{RT} \tag{6.11}$$

or similarly for activity coefficients:

$$\ln\gamma_i = \ln\gamma_i^{SR} + \ln\gamma_i^{LR} \tag{6.12}$$

The activity coefficient models used in equation (6.12) are the modified UNIFAC method (Larsen et al., 1987) for the short-range interaction term and the extended form of the Debye-Hückel expression given by Pitzer (1973, 1980) for the long-range interaction term. In addition a set of solvation equations is also proposed to account for the hydration of ions by water molecules (formation of clusters) in the activity coefficient calculations.

In UNIFAC, the interaction parameter is expressed as $a_{ij} = u_{ij} - u_{jj}$ with $u_{ij} = u_{ji}$ following the work of Christensen et al. (1983). The u_{ij} interaction energies are used instead of a_{ij}, as they are proportional to the interaction forces between species *i* and *j*. The assumptions for the interaction parameters (energies) are:

(i) The repulsion forces between ions of like charge are very large and the resulting interaction energies (u_{cc} and u_{aa}) are set equal to 2500K. The subscripts *c*, *a* represent cations and anions, respectively.

(ii) The attractive forces between a cation and an anion (u_{ca}) are set to zero to preserve the predictive capabilities of the model, so that it is not necessary to have experimental data for every water-electrolyte system.

(iii) The interaction energy between two water molecules is equal to −700K. This value is calculated from the enthalpy of vaporization of water at 25ºC.

The alkyl group energy parameter u_{kk} is calculated as follows:

$$u_{kk} = a_{kw} - a_{wk} + u_{ww} \tag{6.13}$$

where w represents the water and k represents the hydrocarbon solvent group.

These assumptions for the interaction parameters are summarized in Table 6.1.

Table 6.1 Interaction parameters for a solution of a single electrolyte in Achard's method (in K)*

	Cation(c)	Anion(a)	H_2O(w)
Cation(c)	u_{cc}-u_{cc}=0	u_{ca}-u_{aa}=-2500	u_{cw}-u_{ww}= u_{cw} +700
Anion(a)	u_{ac}-u_{cc}=-2500	u_{aa}-u_{aa}=0	u_{aw}-u_{ww}= u_{aw} +700
H_2O(w)	u_{wc}-u_{cc}= u_{wc} –2500	u_{wa}-u_{aa}= u_{wa}-2500	u_{ww}-u_{ww}=0

* u_{wc}=u_{cw}, u_{aw}=u_{wa}, u_{ca}=u_{ac}

The unknown interaction parameters for a single electrolyte solution are u_{cw}, u_{aw} . In some cases, the cation-anion interaction parameter, u_{ca}, is also used as an adjustable parameter to improve model behaviours.

The solvation phenomena are considered in the model as chemical association between water and ionic species. It is this behaviour that causes the non-ideality of electrolyte solutions. To account for the solvation phenomena of aqueous electrolyte solutions, two different standard states are proposed: one is the non-hydrated standard state, which corresponds to the classical standard state; the other is the hydrated standard state.

In the hydrated standard state, water molecules are chemically bound to ionic species and to form clusters. This is taken into account in the calculation of ionic structural parameters and mole fractions of water and cluster with a set of solvation equations to get structural parameters for hydrated species and mole fraction as follows.

Structural Parameters for Hydrated Species

$$R_k^{'} = R_k + Nh_k R_1 \tag{6.14}$$

$$Q_k^{'} = Q_k + Nh_k Q_1 \tag{6.15}$$

where $R_k^{'}$ and $Q_k^{'}$ are the structural parameters of hydrated species *k*, R_k and Q_k are the structure parameter calculated by ionic radii in crystals, Nh_k is the hydration number, and is fitted simultaneously with interaction parameters, R_1 and Q_1 are the volume and surface area parameters of water. For a single electrolyte system, there are two Nh_k parameters: one for cations, the other for anions. There are four unknown parameters for a single aqueous electrolyte solution: two parameters for the interaction energy and two parameters for the hydration number.

Mole Fractions Corresponding to the Hydrated Standard State (*H*)

The mole fraction of water, x_1^H, is given by:

$$x_1^H = \frac{x_1 - \sum_{j=2}^{N} Nh_j x_j}{1 - \sum_{j=2}^{N} Nh_j x_j} \tag{6.16}$$

The mole fraction of ionic species, x_i^H, is given by

$$x_i^H = \frac{x_i}{1 - \sum_{j=2}^{N} Nh_j x_j} \tag{6.17}$$

The structural parameters and mole fraction in the hydrated state are used in the UNIFAC model. The activity coefficients in the hydrated standard state, $\gamma_i^{SR,H}$, and classical standard state, γ_i^{SR}, are related as follows:

$$\gamma_1^{SR} = \gamma_1^{SR,H} \frac{x_1^H}{x_1} \tag{6.18}$$

$$\gamma_i^{SR} = \gamma_i^{SR,H} \frac{x_i^H}{x_i} \left[\gamma_1^{SR} x_1^H\right]^{-Nh_i} \quad (i \neq 1) \tag{6.19}$$

where subscript 1 is the water, the notation '*H*' refers to the hydrated reference state, $\gamma_1^{SR,H}$ and $\gamma_i^{SR,H}$ are calculated with Larsen's UNIFAC model (Larsen et al., 1987) using the mole fractions and structural parameters of hydrated species. The γ_1^{SR} and γ_i^{SR} are used as the short-range term activity coefficients. A complete activity coefficient expression can now be obtained by combining the short-range and long-range terms.

6.3.2 Modifications of Achard's Method

In aqueous electrolyte solutions, solvation phenomena have been studied experimentally by mobility investigations (Robinson and Stokes, 1959). When an electrolyte, $M_{v+}X_{v-}$, is dissolved into water, it completely (or partially) dissociates and attains ionic solvation equilibria in the solution:

$$M^{z+} + h_+H_2O \rightleftharpoons M^{Z+}\cdot h_+H_2O \tag{6.20}$$

$$X^{z-} + h_-H_2O \rightleftharpoons X^{z-}\cdot h_-H_2O \tag{6.21}$$

Where h_+ and h_- are the number of water molecules in a solvation complex with cation and anion, respectively. In the aqueous electrolyte solution, the polar solvent (water) can shield the electric field originating from the point charge of an ion by forming a shell around it. In solution, these ions permanently carry water molecules with them that are regarded as part of the ion. The ions and water molecules are chemically associated. The solvation phenomena determine the effective size of ions. As can be seen from the above equations, the solvation equilibria depend on the concentration and temperature of the system. In Achard's method, the solvation phenomena are considered to be independent to concentration and temperature. The hydration numbers are obtained by a regression of mean activity coefficient data for electrolyte solutions.

To account for the hydration phenomena, different methods have been proposed by Robinson and Stokes (1959), Lu and Maurer (1993), Chen et al. (1999) and the Achard's work. These methods can partly capture the complex hydration phenomena for electrolyte solutions. However, in this research work, we focus on the micelle formation in ionic surfactant solutions. Hydration equations may lead to additional complexity, thus they are not used. Instead, we use ionic radii to calculate the structural parameters R and Q. All other assumptions for group interaction parameters in the Achard's model remain unchanged.

Activity Coefficient for the Modified Achard Model

The asymmetrical convention activity coefficient (γ_i^*) is expressed:

$$\ln\gamma_i^* = \ln\gamma_i^{*,\mathrm{PDH}} + \ln\gamma_i^{*,\mathrm{UNIFAC}} \tag{6.22}$$

where the asymmetrical Pitzer-Debye-Hückel (PDH) (1973, 1980) expression is used to account for the long-range ion-ion interaction term, UNIFAC is used for the short-range interaction term for the completely dissociated electrolyte in aqueous solutions. Without using the hydration number, the solvation equations for structural parameters and mole fractions are not valid. The interaction parameters reported in Achard's work cannot be used in equation (6.22) because the hydration number variable is not used. In equation (6.22), the reference state is the pure liquid for the solvent at the temperature and pressure of the mixture. For a solute species, the reference sate is at infinite dilution in water at the system temperature and pressure. Appendix B gives detailed descriptions for the reference state. Because original UNIFAC is a symmetric expression, it is normalized using terms with "infinite-dilution activity coefficient in water" for each ion, in order to obtain an expression based on the asymmetric convention.

Long-range Interaction Term

The Pitzer-Debye-Hückel equation for any species is

$$\ln\gamma_i^{*,PDH} = -\left(\frac{1000}{M_s}\right)^{1/2} A_\phi \left\{\left(\frac{2Z_i^2}{\rho}\right)\ln\left(1+\rho I_x^{1/2}\right) + \frac{Z_i^2 I_x^{1/2} - 2I_x^{3/2}}{1+\rho I_x^{1/2}}\right\} \tag{6.23}$$

$$I_x = \frac{1}{2}\sum Z_i^2 x_i \tag{6.24}$$

where I_x is the ionic strength on a mole fraction basis, M_s is the molecular weight of the solvent, A_ϕ is the usual Debye-Hückel parameter and ρ is the 'closest approach' parameter. The value of ρ depends on the electrolyte as well as the expression used to represent the short-range interactions. The value of 14.9 from Pitzer's work (1980) is used for ρ. The Debye-Hückel parameter A_ϕ is from Chen's correlation (1982):

$$A_\phi = A\exp(\Delta T/T_0) + B(\exp(\Delta T/T_0))^2 + C\ln(T/T_0) + D\Delta T + E\left(T^2 - T_0^2\right) + F(T_0/T) \tag{6.25}$$

where $\Delta T = T - T_0$, T_0=273.15 K, A=–61.4453, B=2.864468, C=183.5379, D=–0.6820223, E=7.875695×10^{-4}, F=58.95788.

Short-range Interaction Term

For the UNIFAC model, the linear temperature-dependent UNIFAC method (Hansen et al., 1992) is used instead of the UNIFAC model of Larsen et al. (1987) in Achard's work. The assumptions for the interaction parameters of UNIFAC are taken from Achard's work (Table 6.1). The interaction parameters of Hansen et al., (1992) are given by the temperature dependent equation:

$$a_{ij} = a_{ij,1} + a_{ij,2}\left(T - T_0\right),\ (T_0\text{=298.15 K}) \tag{6.26}$$

By using $a_{ij,1} = u_{ij,1} - u_{jj,1}$, $a_{ij,2} = u_{ij,2} - u_{jj,2}$, the linear temperature dependent parameter is reformulated to:

$$a_{ij} = u_{ij,1} + u_{ij,2}\left(T - T_0\right) - \left(u_{jj,1} + u_{jj,2}\left(T - T_0\right)\right) \tag{6.27}$$

If the u_{jj} can be treated as temperature independent, we have

$$a_{ij} = u_{ij,1} + u_{ij,2}\left(T - T_0\right) - u_{jj} \tag{6.28}$$

For a solution of single electrolyte, the interaction parameters between ions (i) and water (w) (or other groups) are

$$a_{iw} = u_{iw} - u_{ww} = u_{iw,1} + u_{iw,2}\left(T - T_0\right) - u_{ww} \tag{6.29}$$

where $u_{ww} = -700\,\text{K}$ at 298.15 K from Achard's work, $u_{\text{iw},1}$ and $u_{\text{iw},2}$ are two unknown interaction parameters.

The interaction parameters between cation (c) and anion (a) are

$$a_{ca} = u_{ca} - u_{aa} = -2500\,\text{K},\ a_{ac} = u_{ac} - u_{cc} = -2500\,\text{K} \tag{6.30}$$

The interaction parameters are summarized in Table 6.2. The unknown interaction parameters for a single electrolyte aqueous solution are $u_{\text{cw},1}$, $u_{\text{cw},2}$, $u_{\text{aw},1}$ and $u_{\text{aw},2}$.

The modified Achard model can be used to organic electrolyte. For organic electrolytes, the cation or anion may contain alkyl groups, e.g. sodium butanoate. By using the UNIFAC method, the anion $C_4H_7O_2^-$ of sodium butanoate ($C_4H_7O_2^-Na^+$) can be divided as one CH_3, two CH_2, and one COO^- group. The interaction parameters between the alkyl group and water can be taken from Hansen's results (1992), as shown in Table 6.2. The interaction parameters between alkyl group (CH_2) and ionic group or ions can be calculated as:

$$a_{ij} = u_{ij} - u_{jj} = u_{ij,1} + u_{ij,2}\left(T - T_0\right) - u_{jj} \tag{6.31}$$

For an alkyl group, u_{jj} is calculated as:

$$u_{jj} = a_{jw} - a_{wj} + u_{ww} \tag{6.32}$$

where w refers to the water, u_{ww}=–700 K, a_{jw} and a_{wj} are the interaction parameters of Hansen (1992) at 25ºC because the value of u_{ww} is taken at 25ºC, without using the temperature dependent relation.

Table 6.2 Linear temperature dependent parameters $a_{ij}= u_{ij,1}+ u_{ij,2}(T–T_0) – u_{jj}$ for single electrolyte solutions for the modified Achard model in this work (in K)*

	Cation(c)	Anion(a)	H_2O(w)	CH_2
Cation(c)	0	u_{ca}=0 u_{aa}=2500	$u_{cw,1}$ $u_{cw,2}$ u_{ww}=–700	$u_{cCH2,1}$ $u_{cCH2,2}$ u_{CH2CH2}
Anion(a)	u_{ac}=0 u_{cc}=2500	0	$u_{aw,1}$ $u_{aw,2}$ u_{ww}=–700	$u_{aCH2,1}$ $u_{aCH2,2}$ u_{CH2CH2}
H_2O(w)	$u_{wc,1}$ $u_{wc,2}$ u_{cc}=2500	$u_{wa,1}$ $u_{wa,2}$ u_{aa}=2500	0	335.00** 0.0106
CH_2	$u_{CH2c,1}$ $u_{CH2c,2}$ u_{cc}=2500	$u_{CH2a,1}$ $u_{CH2a,2}$ u_{cc}=2500	905.60** 0.8618	0

* $u_{wc,1}=u_{cw,1}$, $u_{wc,2}=u_{cw,2}$, $u_{aw,1}=u_{wa,1}$, $u_{aw,2}=u_{wa,2}$, $u_{aCH2,1}=u_{CH2a,1}$, $u_{aCH2,2}=u_{CH2a,2}$, $u_{CH2c,1}=u_{cCH2,1}$, $u_{CH2c,2}=u_{cCH2,2}$

** using the equation of Hansen et al. (1992) to calculate $a_{CH2,H2O}$.

For alkyl groups, the structural parameters R and Q are taken from existing UNIFAC parameter table. The R and Q parameters for ionic species will be approximated by a new method other than fitting (together with interaction parameters of ions) to experimental data of aqueous electrolyte solutions. This new approximation method and results are presented in the next section.

6.4 Structural Parameter Calculation for Ions

6.4.1 Structural Parameter Calculation

Abrams and Prausnitz's Approach

Abrams and Prausnitz (1975) proposed the structural parameter calculation method for the UNIQUAC model. The effects of molecular size and shape are evaluated by structural parameters obtained from pure-component data. The structural parameters are, respectively, the van der Waals volume and surface area of the molecule relative to those of a standard segment:

$$R_k = \frac{V_{wk}}{V_{ws}} \tag{6.33}$$

$$Q_k = \frac{A_{wk}}{A_{ws}} \tag{6.34}$$

where V_{wk} and A_{wk} are the van der Waals volume and area of the molecule given by Bondi (1968), V_{ws} and A_{ws} are the van der Waals volume and area of a standard segment. The methylene segment (-CH_2-) was arbitrarily chosen as the standard segment. The volume of the standard sphere in terms of its radius r_{ws} is given by

$$V_{ws} = \frac{4}{3}\pi\, r_{ws}^3 \tag{6.35}$$

and the area by

$$A_{ws} = 4\pi\, r_{ws}^2 \tag{6.36}$$

Based on these equations, Abrams and Prausnitz (1975) derived the following equations:

$$R_k = V_{wk} / 15.17 \tag{6.37}$$

$$Q_k = A_{wk} / (2.5\times 10^9) \tag{6.38}$$

where R_k and Q_k are, respectively, the dimensionless volume and surface area parameters for the UNIQUAC model, and 15.17 and 2.5×10^9 are normalization factors derived from CH_2 group. The derivation of these equations is reproduced in Appendix C based on the work of Abrams and Prausnitz (1975). In UNIFAC, the same method is used for the structural parameters.

Structural Parameter of Ions

Christensen et al. (1983b) employed the ionic radii in crystal data to calculate the R and Q parameters of charged ions in their work of UNIQUAC for electrolyte solutions. Based on the work of Christensen et al., Sander (1984) found that the Q parameters for cations are too small for practical applications. The small Q values are of the order of 0.1 to 0.5 and reduce the fitting capabilities of the UNIQUAC model. Sander then used arbitrary fixed larger values for the Q parameters of cations. Macedo et al. (1990) and Kikic et al. (1991) used the same values as Sander's in their work for UNIQUAC and UNIFAC models. Thomsen et al. (1999) further treated the R and Q as adjustable parameters in their extended UNIQUAC model. Achard et al. (1994) considered hydration effects for ions and used the hydration number with ionic radii in crystal to obtain the R and Q parameters. Li et al. (1994) used fixed R and Q parameters for all different ions. R and Q values from different researchers are listed in Table 6.3.

Table 6.3 R and Q values of ions from different researchers

User Ion	Christensen (1983b)		Sander (1984)		Achard et al. (1994a,b)		Thomsen et al. (1999)	
	R	Q	R	Q	R*	Q*	R	Q
Na^+	0.1426	0.2732	3.0	3.0	2.54922	3.9331	1.4034	1.1990
K^+	0.3912	0.5354	3.0	3.0	3.11144	4.6748	2.2304	2.4306
Ca^{2+}	0.1614	0.2967	1.0	1.0	2.99214	4.6045	4.4440	1.444
Cl^-	0.9861	0.9917	0.9861	0.9917	0.9860	0.9917	10.386	10.197
Br^-	1.2331	1.1510	1.2331	1.1510	NA	NA	NA	NA
H_2O	0.92	1.4	0.92	1.4	0.92	1.4	0.92	1.4

*Results of hydrated R and Q
NA: no values available

6.4.2 Effects of Structural Parameters on UNIQUAC/UNIFAC

For UNIQUAC equation, structural parameters R and Q were introduced to account for the effects of molecular size and shape through use of Staverman's combinatorial entropy as a boundary condition for athermal mixtures (Abrams and Prausnitz, 1975). In UNIQUAC (or UNIFAC) model, the combinatorial term measures the athermal mixing; the residual term is determined by differences in intermolecular forces and in free volume. The combinatorial term is often the dominant term in solution of non-electrolytes (Prausnitz, 1999, p422).

As discussed above, Sander (1984) suggested that the Q values for cations are too small for practical applications, larger Q values are needed. Oppositely, Anderson and Prausnitz (1978) found that using smaller Q values for some molecules, such as alcohols etc., can improve fitting results in some strong non-ideal systems, such as hydrogen-bonding alcohol systems.

In order to study the influence of the R and Q parameters on Achard's electrolyte UNIFAC model, the experimental mean activity coefficient data of $NaCl+H_2O$ system (at 25°C) are correlated with the modified Achard model proposed in this work (without using the hydration number). In this correlation, the R and Q parameters are taken from Table 6.3 based on the work of Christensen et al. (1983b), and Sander (1984), respectively. The correlation results are presented in figure 6.1. The obtained interaction parameters are given in Table 6.4. For this single electrolyte solution, UNIFAC is identical to UNIQUAC.

Table 6.4 Interaction parameters of the modified Achard model for the $NaCl+H_2O$ solution at 25°C with R and Q parameters from Table 6.3 (in K)

	Using R and Q of Christensen et al. (1983b)			Using R and Q of Sander (1984)		
Ion	Na^+	Cl^-	H_2O	Na^+	Cl^-	H_2O
Na^+	0.0	0 2500	-1279.0 -700	0	0 2500	-727.6 -700
Cl^-	0.0 2500	0.0	-1088.0 -700	0 2500	0	-889.1 -700
H_2O	-1279.0 2500	-1088.0 2500	0.0	-727.6 2500	-889.1 2500	0

In figure 6.1, "Comb." and "Resid." represent, respectively, the combinatorial term and the residual term contributions of UNIFAC (short-range interaction part) to mean activity coefficient, using the R and Q values of Christensen et al. (1983b) in Table 6.3, and "Fit" is the correlation results. Similarly, "Comb., Sander" and "Resid., Sander" are, respectively, the contributions of the combinatorial and residual term of UNIFAC (short-range interaction part) using R and Q values from Sander (1984) in Table 6.3, and "Fit, Sander" is the correlation results. In the figure 6.1, "PDH" is the contribution of Pitzer-Debye-Hückel term to mean activity coefficient. Figure 6.1 shows that the correlation results of "Fit, Sander" are better than that of "Fit".

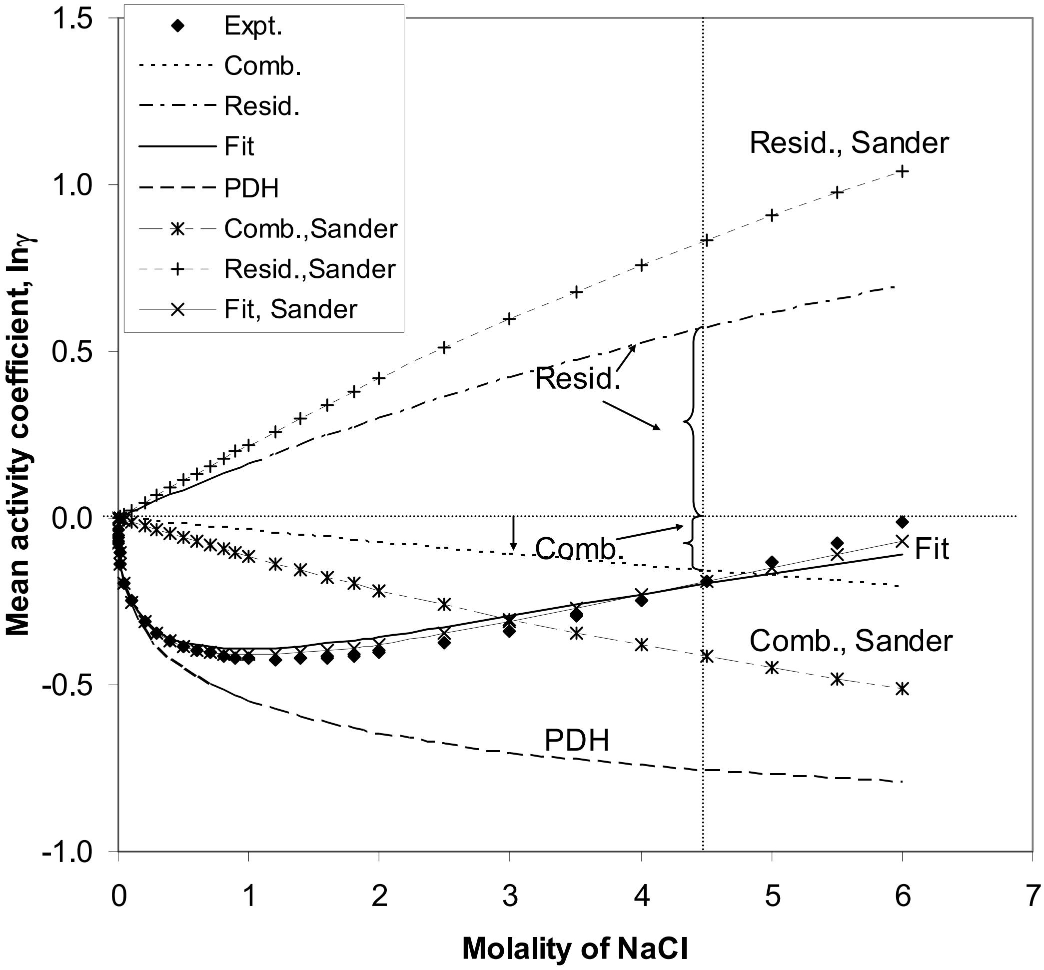


Figure 6.1 Comparison of the combinatorial (Comb.) and residual (Resid.) term contributions using the modified Achard's model for the NaCl+H_2O system at 25ºC with different R and Q values. "Comb." and "Resid.": R and Q values from Christensen (1983b) (Table 6.3). "Comb., Sander" and "Resid., Sander": R and Q values from Sander (1984) (Table 6.3). PDH is the contribution of Pitzer-Debye-Hückel term to mean activity coefficient.

As can be seen in figure 6.1, the combinatorial term contribution decreases linearly as salt concentration increases, while the residual term contribution increases rapidly as salt concentration increases. The combinatorial term does not contribute significantly to the activity coefficient of the UNIFAC while the residual term dominates the UNIFAC.

However, the combinatorial term of UNIFAC (or UNIQUAC) equation is often the dominant term in non-electrolytes solutions (Prausnitz, 1999, p422). The PDH term dominates the mean activity coefficient at dilute concentration range and has an almost constant contribution at high concentrations.

Compare to the experimental curve in figure 6.1, the PDH term has a large negative contribution to the mean activity coefficient, and cannot capture the mean activity coefficient behaviour at high concentrations in which the short-range interaction has to be account for. The UNIFAC is used to account for the short-range interaction and correct the large negative contribution of PDH term to mean activity coefficient. At high concentration, the residual term of UNIFAC corrects the negative contribution of PDH, but the combinatorial term of UNIFAC increases the negative contribution of PDH. If the combinatorial term has lager contribution than that of PDH term at high concentrations, the residual term will compete with combinatorial term other than PDH term with increasing concentration. Because the PDH term contribution is almost a constant, it does not reflect the changing of molecular forces with increasing concentration of electrolytes. At high concentrations, the short-range term should dominate the behaviour of activity coefficient model. Figure 6.1 shows that using larger Q values in UNIFAC (Sander's method) modifies the combinatorial term contribution, then, improves the correlation results in this system. The Q parameter has a key role in the model.

In UNIQUAC and UNIFAC models, the Q and R parameters are calculated from pure component property and are used to describe molecule size and shape. Based on Sander's work, the Q parameter is very important to UNIQUAC fro electrolytes. However, the ratio Q/R is the measure of the shape of molecules, not Q or R. Thus, it is necessary to further investigate the limitations of these parameters from the physical derivation of UNIQUAC (Abrams and Prausnitz, 1975, Maurer and Prausnitz, 1978).

Physical Interpretation of the Q/R ratio of ions

As can be seen from Table 6.3, the ratio Q/R as reported by several researchers (Christensen, 1983b, Achard et al., 1994a, b) is greater than 1 for most R and Q values. The work of Thomsen et al. (1999) represented an exception. However, based on the physical derivation of UNIQUAC model (Abrams and Prausnitz, 1975, Maurer and Prausnitz, 1978), the Q/R>1.0 cannot be valid for UNIQUAC, because it does not follow the 'physical' upper limit of Q/R=1 for the combinatorial entropy of mixing (and therefore Gibbs energy) in UNQUAC.

The ratio Q/R is a measure of the shape of long-chain molecules, and was originally applied to flexible chain molecules that differ significantly in size by Flory and Huggins. Several researchers have investigated the effects of the ratio Q/R (Prausnitz et al., 1999, p423, Donohue and Prausnitz, 1975). For a monomer, Q/R= 1. As R becomes very large for a linear chain, Q/R→2/3 and for a sphere (or cube), Q/R→0. For globular molecules, the ratio Q/R lies between zero and unity. Flory-Huggins assumed that Q/R=1.0, it gives an upper limit for the combinatorial entropy of mixing, the Q/R=1 is the highest value of Q/R. The combinatorial term (Staverman's formula) of UNIQUAC (UNIFAC) is not exact but similar to that of Flory-Huggins (Kikic et al., 1990). When Q/R>1 is used in UNQUAC (or UNIFAC), the combinatorial term of the model is not physically correct.

Current R and Q parameters of UNIFAC and UNIQUAC follow Q/R<1 except for the groups H_2O, OH, HCOOH and FCH_2O which are adjusted empirically to obtain better agreement. In aqueous solutions, simple ions with hydrated water molecules can be approximated as globular particles, and thus we would expect Q/R<1.

As mentioned above, Anderson et al. (1978) modified the Q parameter in UNIQUAC to get better fitting results for systems containing hydrogen-bonding components, such as water or lower alcohols. However, in this work, the Q/R is less than 1.0 for alcohols. Strong molecular interactions do not change the Q/R ratio.

In order to keep the 'physical' upper limit, Q/R=1, for the combinatorial term in UNIQUAC (UNIFAC), a new method is proposed to calculate the R and Q parameters for ions.

6.4.3 A New Estimation Method for the Structural Parameters of Ions

Following the R and Q parameter calculation method for UNIQUAC model (Abrams and Prausnitz, 1975, reproduced in Appendix C), the volume (V_i) and surface area (A_i) of an ion i can be approximated by its radius (r_i) as follows:

$$V_i = \frac{4}{3}\pi r_i^3 \tag{6.39}$$

$$A_i = 4\pi r_i^2 \tag{6.40}$$

The R_i and Q_i of the ion are calculated as following:

$$R_i = \frac{V_i}{V_s} \tag{6.41}$$

$$Q_i = \frac{A_i}{A_s} \tag{6.42}$$

where V_s and A_s are, respectively, the volume and surface area of a standard segment, which are computed based on the radius (r_s) of the standard segment. Applying the condition Q/R< 1.0, we have

$$\frac{Q_i}{R_i} = \frac{A_i / A_s}{V_i / V_s} = \frac{r_s}{r_i} < 1.0 \tag{6.43}$$

This equation suggests that the radius of a standard segment should be smaller than that of a charged ion, $r_s < r_i$. For hydrocarbon fluids, the standard segment methylene group ($-CH_2-$) is indeed the smallest of all hydrocarbon groups, and has a radius of 1.818Å (Abrams and Prausnitz, 1975).

However, if we compare the radius of this standard segment, 1.818Å, with the radii of charged ions in crystals, as shown in Table 6.5, we see that the radius of the standard segment ($-CH_2-$) is larger than those of most ions, especially of the cations. In the work of Christensen (1983b) and Sander (1984), the R and Q parameters are based on the value 1.818Å as the radius of a standard segment. Therefore, in the work of Christensen (1983b) and etc., the obtained R and Q yield a Q/R ratio greater than 1, as shown in Table 6.3.

Table 6.5 Comparison of the ionic radii in crystal with the radius of $-CH_2-$*

Ion/group	$-CH_2-$	Na^+	K^+	Ca^{2+}	Cl^-	Br^-
Radius, Å	1.818	1.02	1.38	1.00	1.81	1.96

*Ionic radii are from CRC Handbook (Lide, 2002)

If we follow the 'physical' limit for the R and Q parameters, a smaller radius for the standard segment should be used in the R and Q calculation for ions, assuming that the R and Q parameters of ions in aqueous solution could be approximated by the ionic radii in crystal.

Using the same method as Abrams and Prausnitz (1975), the radius of a standard segment can be derived using a specific reference fluid.

The standard segment is defined as a sphere such that for a linear poly-segment molecule of infinite length the identity

$$\frac{Z}{2}(R-Q)=R-1 \tag{6.44}$$

is satisfied. The coordination number Z is set equal to 10. The volume of the standard sphere in terms of its radius r_s is given by

$$V_s=\frac{4}{3}\pi\, r_s^3 \tag{6.45}$$

and the area by

$$A_s=4\pi\, r_s^2 \tag{6.46}$$

The volume and area of an n-mer poly-segment molecule are n times the volume and area of a reference molecule (ref);

$$V_i=nV_{ref} \tag{6.47}$$

$$A_i=nA_{ref} \tag{6.48}$$

Substitution of equations (6.41)-(6.42), (6.45)-(6.48) into (6.44) as n tends to infinity yields the following equations:

$$\frac{10}{2}\left(\frac{nV_{ref}}{V_s}-\frac{nA_{ref}}{A_s}\right)=\frac{nV_{ref}}{V_s}-1 \tag{6.49}$$

or

$$5\left(\frac{V_{ref}}{V_s}-\frac{A_{ref}}{A_s}\right)=\frac{V_{ref}}{V_s}-\frac{1}{n} \tag{6.50}$$

As $n\to\infty$, $\frac{1}{n}\to 0$ and we obtain

$$4\frac{V_{ref}}{V_s}=5\frac{A_{ref}}{A_s} \tag{6.51}$$

The volume and surface area of a reference molecule are calculated from the sphere equation. Thus we obtain:

$$4\frac{\frac{4}{3}\pi r_{ref}^3}{\frac{4}{3}\pi r_s^3}=5\frac{4\pi r_{ref}^2}{4\pi r_s^2} \tag{6.52}$$

$$r_s=\frac{4}{5}r_{ref} \tag{6.53}$$

where r_s is the radius of the standard segment and r_{ref} is the radius of the reference molecule.

Arbitrarily choosing the r_{ref} value to be 1.25 Å/molecule, the radius of the standard segment can be obtained as r_s=1.0Å /molecule. Substituting r_s into equation (6.45)-(6.46) yields a standard segment volume and a standard segment area, V_s and A_s per mole.

$$V_s=2.5229\ \mathrm{cm^3/mol} \tag{6.54}$$

$$A_s=7.5687\times10^8\ \mathrm{cm^2/mol} \tag{6.55}$$

With the new normalization factors, the *R* and *Q* are calculated as:

$$R_k=V_k/2.5229 \tag{6.56}$$

$$Q_k=A_k/(7.5687\times10^8) \tag{6.57}$$

where V_k and A_k are the molar volume and molar surface area of ion *k*, respectively.

There is no universally accepted method for obtaining the ionic radii in aqueous solutions. Recently, Marcus (1988, 1997) collected approximate values of ionic radii in aqueous solutions. In Marcus' work, the ionic radius is the mean ion-water distance, i.e. the mean inter-nuclear distances between the mono-atomic ions or the central atoms of polyatomic ions and the oxygen atoms of the water molecules in their first hydration shells. These ionic radii values are in good agreement with the Pauling-type crystal ionic radii for the mono-atomic ions for coordination number 6 (Marcus, 1988), as shown in Table 6.6. In the CRC handbook (Lide, 2002), ionic radii values are reported for only 9 anions: F^-, Cl^-, I^-, OH^-, O^{2-}, S^{2-}, Se^{2-} and Te^{2-}. These anions do not include typical anions in ionic surfactant molecules, e.g. COO^-, OSO_3^-, etc. However, from the work of Marcus, the ionic radii of

COO^-, OSO_3^- can be estimated through the data of ions HSO_4^-, HCO_3^-. Thus, in this work, the Marcus' ionic radii are used to estimate the volume and surface area of cations and anions using the equations (6.56)-(6.57).

Table 6.6 Ionic radii and R and Q parameters for some ions. R and Q are calculated from equations (6.56) and (6.57) using Marcus radii (1997)

Ion	Radius, Å (Marcus)*	Radius, Å (CRC)**	R	Q
Na^+	1.02	1.02	1.0612	1.0404
K^+	1.38	1.38	2.6281	1.9044
Ca^{2+}	1.00	1.00	1.000	1.000
Cs^+	1.70	1.67	4.9130	2.8900
Ag^+	1.15	1.15	1.5209	1.3225
NH_4^+	1.48	n.a.	3.2418	2.1904
Al^{3+}	0.53	0.54	0.1489	0.2809
Cl^-	1.81	1.81	5.9298	3.2761
Br^-	1.96	1.96	7.5296	3.8416
NO_3^-	1.79	n.a.	4.2623	2.6291
SO_4^{2-}	2.30	n.a.	7.1817	3.7227
$COO^{-(1)}$	1.56	n.a.	3.7964	2.4336
$OSO_3^{-(2)}$	1.90	n.a.	6.8590	3.6100
$SO_3^{-(3)}$	1.70	n.a.	4.9130	2.8900
H_2O	1.38	n.a.	0.92	1.4

(1), (2), (3) ionic radii are the values of ions HCO_3^-, HSO_4^-, and HSO_3^-, respectively
* Ionic radii from Marcus (1997)
**Ionic radii from the CRC Handbook (Lide, 2002) with coordination number 6
n.a.: values not available

Table 6.6 provides values of R and Q for some ions, while more values are listed in Appendix D. In most cases, the Q<R in Table 6.6, but the R and Q parameters of Al^{3+} do not follow this requirement. This is because the radius of Al^{3+} is smaller than that of the standard segment (r_s=1.0 Å/molecule), the same cases for Ca^{2+} and some other cations, as shown in Appendix D.

These R and Q values in Table 6.6 are used in the modified Achard method for aqueous electrolyte solutions. In the modified Achard model, the R and Q parameter for the hydrocarbon and water (H_2O) groups are directly taken from the existing UNFAC parameter table. However, the R and Q parameters of ions are based on the new normalization factors.

These new normalization factors are not the same as that for the hydrocarbon groups. Since two sets of normalization factors, one for ions and one for hydrocarbon groups, are used, the R and Q parameters of ions should be considered as semi-empirical values.

6.4.4 Effects of New Structural Parameters

Using the modified Achard model, the effects of new structural parameters on the contributions of combinatorial and residual term are investigated. The mean activity coefficient data of NaCl+H_2O system at 25ºC is correlated in this investigation.

As was shown in Figure 6.1, the residual term dominates the UNIFAC model using structural parameters from Christensen, et al. (1983b). Using larger Q values from Sander (1984), the distribution of combinatorial and residual term contributions has been modified, correlation results are improved

Using the new structural parameters from Table 6.6, the mean activity coefficient data of NaCl+H_2O system at 25ºC are correlated to compare the combinatorial and residual term contributions. The correlation results using two different sets of R and Q parameters, 'Old', 'New', are presented in figures 6.2-6.3. The 'Old' R and Q parameters are calculated using the original method of Abrams and Prausnitz (1975), and the 'New' one is calculated with equations (6.56)-(6.57). With the new set of R and Q parameters, the modified Achard model gives better correlation results for the NaCl+H_2O system, as shown in Table 6.7 and figure 6.3. For comparison, the correlation results using the Q and R parameters of Sander (1984) (see also Table 6.3) are also given in Table 6.7 and figure 6.3. As can be seen, the correlation results with 'New' Q and R parameters are very similar to that of using Q and R of Sander's.

Comparing the term contributions in figure 6.2, using "new" R and Q values, the combinatorial term together with PDH term dominate the mean activity coefficient in this system. The combinatorial term has a larger negative contribution than that of PDH. The residual term has a large positive contribution for this system as the electrolyte solution is characterised by large heats of mixing. The short-range term, which corresponds to short-range forces, dominates the model behaviour in the region of high electrolyte concentrations.

In Table 6.7, %AAD γ_m is the average absolute deviation for mean activity coefficient (molality scale) and is calculated by equation (6.58).

$$\%\mathrm{AAD}\gamma_{\mathrm{m}} = \frac{1}{n}\sum_{i=1}^{n}\frac{\left|\gamma_i^{cal} - \gamma_i^{\exp t}\right|}{\gamma_i^{\exp t}} \times 100 \tag{6.58}$$

where *n* is the number of data points.

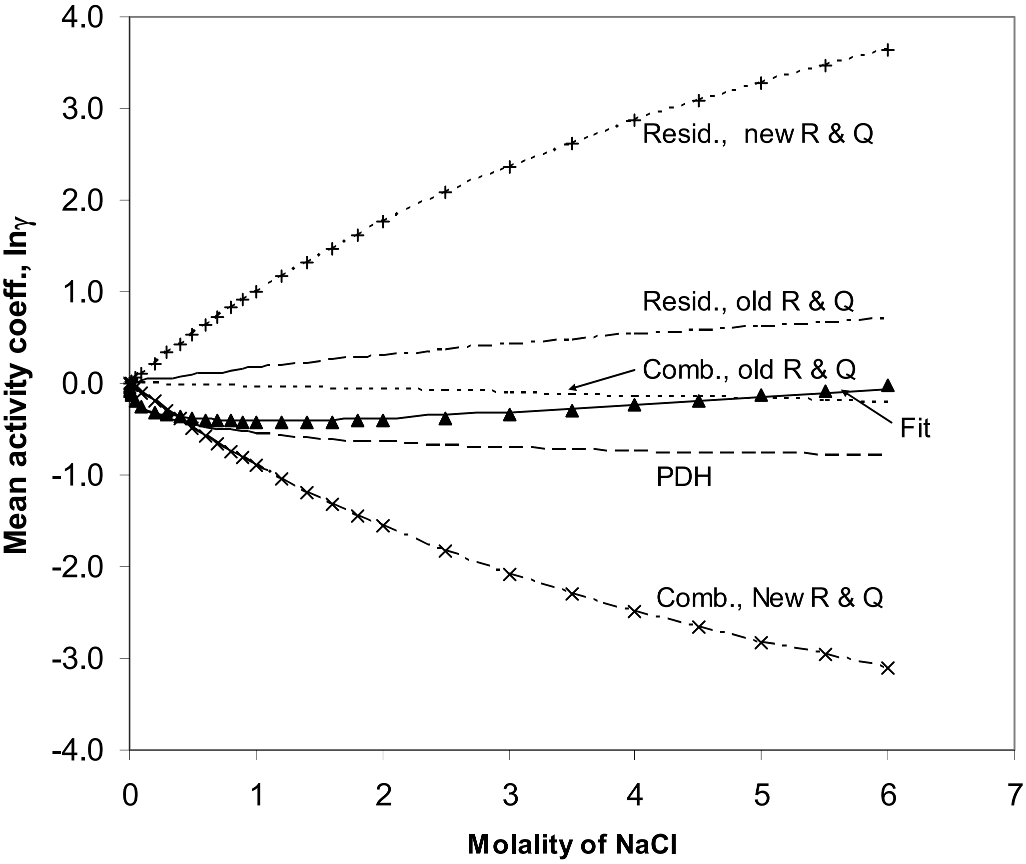


Figure 6.2 Comparison of combinatorial (Comb.) and residual (Resid.) term contributions of UNIFAC using the modified Achard's model for NaCl+H_2O system at 25°C. "New R & Q" and "Old R & Q": see Table 6.7. ▲: Experimental data. "Fit": fitting results. PDH is the contribution of Pitzer-Debye-Hückel term to mean activity coefficient.

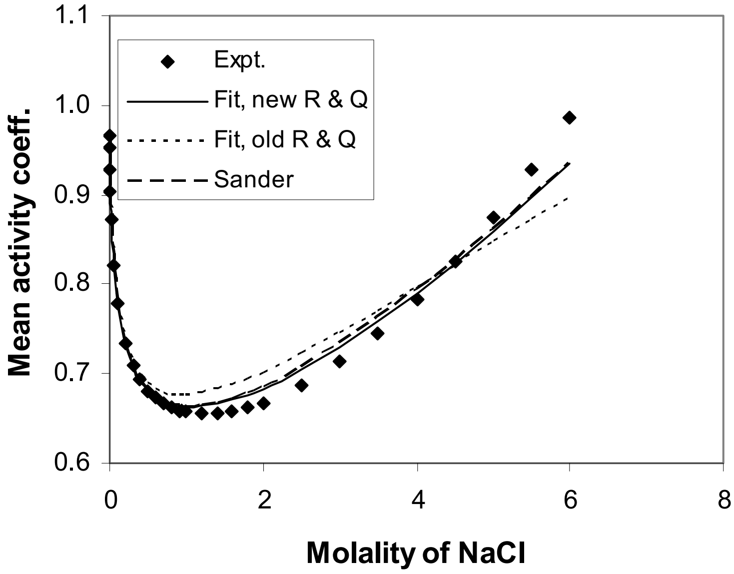


Figure 6.3 Mean activity coefficient correlation results with different structural parameters using the modified Achard's model for NaCl+H_2O at 25°C. "New R & Q" and "Old R & Q": see Table 6.7. Sander: using Q and R parameter from Sander (1984) in Table 6.3.

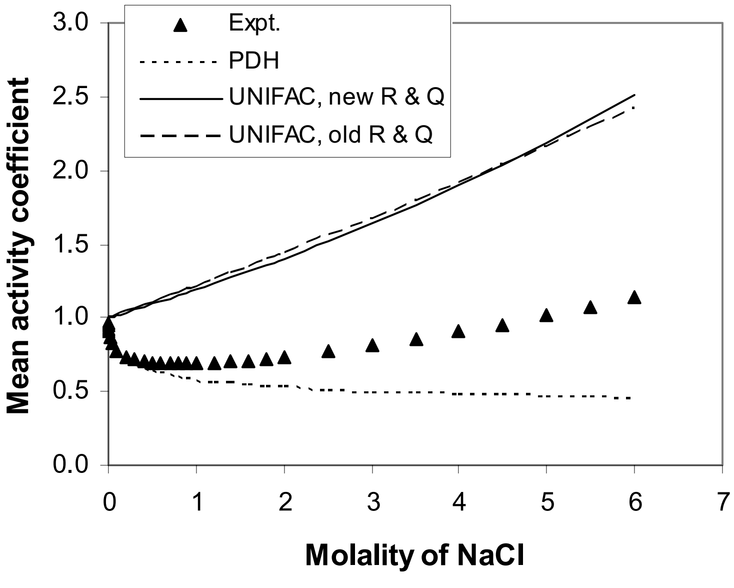


Figure 6.4 Comparison of short-range (UNIFAC) and long-range (PDH) term contributions using the modified Achard model for NaCl+H_2O system at 25°C. "New R & Q" and "Old R & Q": see Table 6.7.

Table 6.7 Regression results for the NaCl+H_2O solution at 25°C using different R and Q parameters

	New R & Q from Table 6.6		Old R & Q from Christensen in Table 6.3		R & Q from Sander in Table 6.3	
Ion	R	Q	R	Q	R	Q
Na^+	1.0612	1.0404	0.1426	0.2732	3.0	3.0
Cl^-	5.9298	3.2761	0.9861	0.9917	0.9861	0.9917
Interaction parameter	$u_{Na+,H2O} = -1145.8$ $u_{Cl-,H2O} = -975.9$		$u_{Na+,H2O} = -1279$ $u_{Cl-,H2O} = -1088$		$u_{Na+,H2O} = -727.6$ $u_{Cl-,H2O} = -889.1$	
%AAD γ_m	1.08		3.22		1.65	

Short-range and Long-range Contributions

The excess Gibbs energy of electrolyte solutions consists of both short-range and long-range contributions. The long-range contribution dominates in the dilute concentration region. The short-range contribution becomes important at high concentrations. In figure 6.4, a comparison of the short-range (UNIFAC) contribution and long-range (PDH) contribution is shown using the modified Achard's model for the NaCl+H_2O system at 25ºC. The short-range contribution increases almost linearly as ionic strength increases, while the long-range contribution decreases rapidly in the very dilute region and then tends to a constant value at high ionic strength.

In the short-range (UNIFAC) contribution calculation, the "new" and "old" R and Q parameters are, respectively, used. As can be seen in figure 6.4, different R and Q parameters do not significant change the short-range contribution, but the distribution of the combinatorial and residual term contributions (shown in figure 6.2).

6.5 Application of the Modified Achard Method to Solutions of Single Electrolytes

6.5.1 Correlation of Mean Activity Coefficient Data

The modified Achard method as described previously is used to correlate the mean activity coefficient data of single electrolyte systems. The objective function used is:

$$F = \sum_i \left(\ln \gamma_{\pm m,i}^{*,\mathrm{cal}} - \ln \gamma_{\pm m,i}^{*,\mathrm{exp}} \right)^2 \tag{6.59}$$

Mean activity coefficients in molality scale are used, as typically they are reported in molality basis. The mean activity coefficient ($\gamma_{\pm m}^*$) in molality scale is obtained from the mole-fraction based activity coefficient ($\gamma_\pm^*$) as follows:

$$\ln \gamma_{\pm m}^* = \ln \gamma_\pm^* - \ln\left(1 + M_s \left(v_c + v_a\right) m / 1000\right) \tag{6.60}$$

$$\ln \gamma_\pm^* = \frac{1}{v_c + v_a} \left(v_c \ln \gamma_c^* + v_a \ln \gamma_a^* \right) \tag{6.61}$$

where the subscripts *c* and *a* denote to the cations and anions, respectively, *m* is the molality of electrolyte, M_s is the molecule weight of solvent, and v_c and v_a are the stoichiometric coefficients of cation and anion, respectively. The asymmetrical convention activity coefficient of the short-range contribution (UNIFAC) is transferred by (Prausnitz et al., 1999, p225):

$$\ln \gamma_i^{*,\mathrm{UNIFAC}} = \ln \gamma_i^{\mathrm{UNIFAC}} - \ln \gamma_i^{\infty,\mathrm{UNIFAC}} \tag{6.62}$$

The experimental mean activity coefficient data at 25°C are taken from the work of Robinson and Stokes (1959) and Hamer and Wu (1972). At first, the interaction parameter estimation is based only on the mean activity coefficient data for the systems investigated. Then, osmotic coefficients are calculated using the interaction parameters obtained.

In order to investigate the model's capability and compare the correlation results to those of the electrolyte NRTL model by Chen et al. (1982), salt-dependent interaction parameters are estimated. Mean activity coefficients at 25ºC for different types of electrolyte solutions are correlated with the modified Achard model. The correlation results are given in Table 6.8 and compared with those of the electrolyte NRTL and extended UNIQUAC (Thomsen et al., 1999) models. Like the proposed electrolyte UNIFAC model, the electrolyte NRTL model also applies a local composition expression to account for the short-range contribution term with two adjustable interaction parameters. The extended UNIQUAC model uses UNIQUAC equation as the short-range contribution term. Except two interaction parameters, the extended UNIQUAC used also R and Q of ions as adjustable parameters.

In Table 6.8, %AAD γ_m is the average absolute deviation for mean activity coefficient (molality scale), and is calculated by equation (6.58), %AAD $\o_i$ is the average absolute deviation for osmotic coefficients and is calculated as follow:

$$\%\text{AAD}\,\phi_i = \frac{1}{n}\sum_{i=1}^{n}\frac{\left|\o_i^{cal} - \o_i^{\exp t}\right|}{\o_i^{\exp t}} \times 100 \qquad (6.64)$$

where n is the number of data points.

In Table 6.8, Max. m represents the maximum molality used in the parameter estimation. The results (mean activity coefficient and osmotic coefficient) of modified Achard's method for the NaCl+H_2O system at 25ºC are shown in figures 6.5-6.6 and compared with extended UNIQUAC method. The mean activity coefficient and osmotic coefficient of extended UNIQUAC for the NaCl+H_2O system at 25ºC are obtained from SPECS software (SPECS, 2003). As can be seen from figures 6.5-6.6, the maximum deviations appeared around the highest concentration that is very close to the saturation point of the NaCl+H_2O system. The %AAD γ_m values of the electrolyte NRTL model presented in Table 6.8 are taken directly from Chen et al. (1999).

Table 6.8 Correlation results with salt-dependent interaction parameters*

Salt	$u_{c,w}$, K	$u_{a,w}$, K	%AAD γ_m	%AAD $\o_i$	%AAD γ_m NRTL	%AAD γ_m UNIQUAC	Max. m
NaCl	-1145.8	-975.9	1.08	1.17	1.37	2.21	6.0
KCl	335.67	-1173.4	0.13	0.11	0.23	1.55	4.5
CsBr	-1327.0	279.7	1.38	1.25	0.52	n.a.	5.0
$AgNO_3$	-1391.9	692.1	1.13	1.77	0.77	n.a.	6.0
NH_4NO_3	-1329.7	629.6	1.83	2.09	0.93	n.a.	6.0
$NaNO_3$	-1437.1	436.7	0.24	0.25	0.12	1.0	6.0
$CaCl_2$	-1817.8	11.25	10.01	5.22	14.0	14.4	6.0
Na_2SO_4	-1298.5	430.2	0.63	0.76	1.43	1.25	4.0

*subscript c, a and w represent the cation, anion and water, respectively.
n.a.: no interaction parameters available for cations or anions.

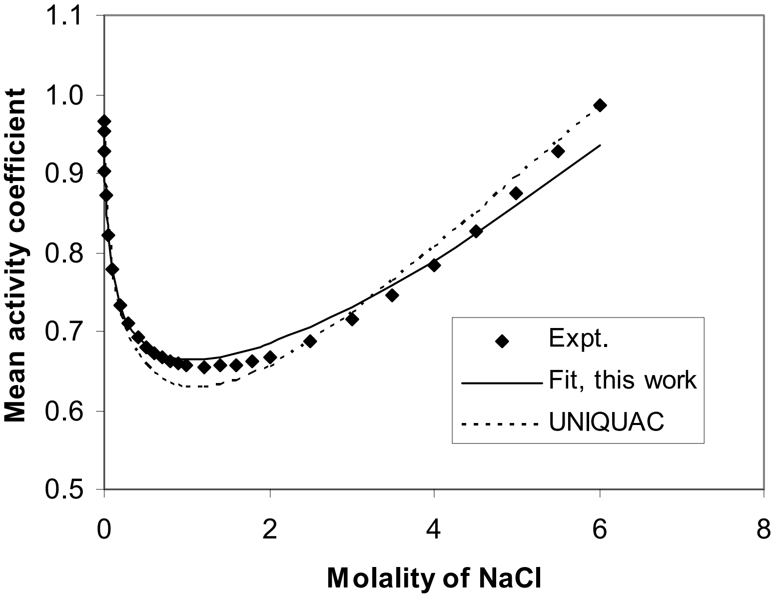


Figure 6.5 Mean activity coefficient for NaCl+H_2O at 25ºC. Expt.: experimental data. Fit, this work: correlation results of modified Achard's model. UNIQUAC: calculation results with extended UNIQUAC using the SEPCS software (SPECS, 2003).

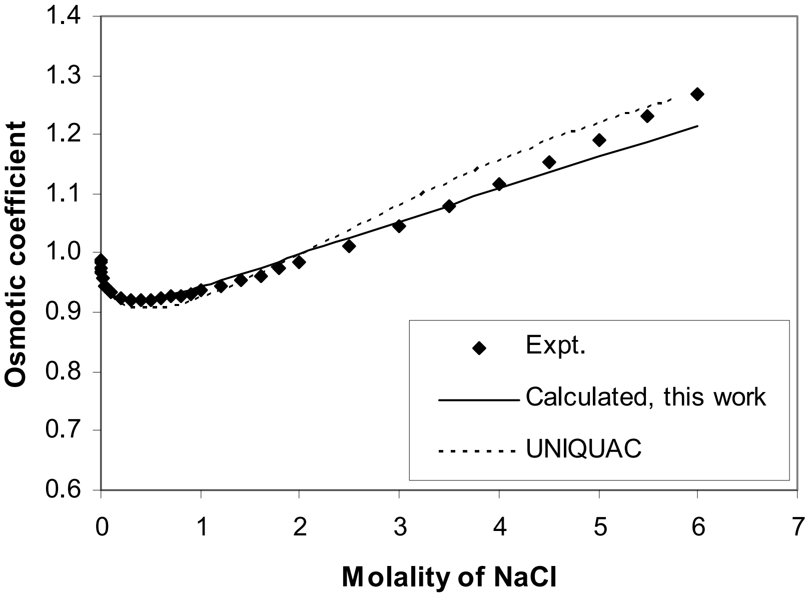


Figure 6.6 Osmotic coefficient for NaCl+H_2O at 25ºC. Expt.: experimental data. Calculated, this work: Calculation results using parameters obtained from NaCl+H_2O at 25ºC by modified Achard's model. UNIQUAC: calculation results with extended UNIQUAC using the SEPCS software (SPECS, 2003).

The correlation results of Table 6.8 show that the mean activity coefficients of single aqueous electrolyte solutions are successfully correlated with the modified Achard model using two salt-dependent interaction parameters. The deviations of the correlation have the same order as electrolyte NRTL model and smaller than that of extended UNIQUAC. However, the extended UNIQUAC gives better results around saturation points, as shown in figures 6.5 and 6.6. It was the purpose of the extended UNIQUAC to simulate electrolyte solutions around saturation points (Thomsen et al., 1996, 1997, 1999).

The salt-dependent interaction parameters have some patterns, as shown in Table 6.8 the highlight parts. The interaction parameters between Na^+ and H_2O (u_{NaH2O}) have similar values in different electrolyte solutions, i.e. $NaCl+H_2O$, $NaNO_3+H_2O$ and $Na_2SO_4+H_2O$ where these values are -1145.82, -1437.08 and -1298.46 K, respectively. The interaction parameters between NO_3^- and H_2O are also close each other in the solutions $AgNO_3+H_2O$, $NH_4NO_3+H_2O$ and $NaNO_3+H_2O$. However, the interaction parameter between Cl^- and H_2O in $CaCl_2+H_2O$ system is very different from other systems containing H_2O and Cl^- ($NaCl+H_2O$, $KCl+H_2O$). In fact, the model cannot successfully correlate the mean activity coefficient of the $CaCl_2+H_2O$ system in which a particularly large non-ideality appears at the high concentration range. Electrolyte NRTL and extended UNIQUAC exhibit the same as the modified Achard model for $CaCl_2+H_2O$ system. From these parameter similarities, it seems that it is possible to use the assumption of group independence (group contribution concept) for the ions interaction. Following the group contribution concept of the UNIFAC method, it can be assumed that the interaction parameters between the ionic groups and the water group do not depend on the electrolyte solutions. This means the interaction parameter between Na^+ and H_2O does not depend on the system $NaCl+H_2O$ or $NaNO_3+H_2O$ system, but is merely ion-dependent. The ions can be treated as separate UNIFAC functional groups. Based on the group contribution concept, the Na^+–H_2O, Cl^-–H_2O group interaction parameters obtained from the $NaCl+H_2O$ solution are employed to the other electrolyte solutions.

Starting from the $NaCl+H_2O$ solution, the interaction parameters of different ions-water are estimated. The mean activity coefficient data (25°C) of single electrolyte solutions are used in the interaction parameter estimation with the modified Achard model. The results are presented in Table 6.9.

Table 6.9 shows that when the functional group interaction parameter between Cl^- and H_2O is used, good correlation is obtained for the KCl + H_2O system, but not for the CsCl and $CaCl_2$ aqueous solutions. When using the functional group interaction parameter between Na^+ and H_2O, the model can successfully correlate the mean activity coefficients of $NaNO_3$ and NaBr solutions, but not of the Na_2SO_4 solution. Similarly, the model cannot successfully correlate the mean activity coefficients of $AgNO_3$ and NH_4NO_3 solutions with the functional group interaction parameter between NO_3^- and H_2O.

Table 6.9 Correlation results using the proposed modified Achard model and salt-independent parameters (group contribution concept)*

Salt	$u_{cw,1}$, K	$u_{aw,1}$, K	u_{ca}, K	%AAD, γ_m	Max. m	Notes
NaCl	-1145.82	-975.9	0.0	1.08	6.0	
KCl	-1041.74	-975.9	0.0	3.37	4.5	
	-1099.57	-975.9	-1002.68	0.09	4.5	use u_{ca}
CsCl	-1053.2	-975.9	0.0	11.0	6.0	
$CaCl_2$	-1375.35	-975.9	0.0	14.7	6.0	
	-1433.31	-975.9	-1187.81	5.93	6.0	use u_{ca}
$NaNO_3$	-1145.82	-872.81	0.0	5.68	6.0	
NaBr	-1145.82	-1038.85	0.0	0.96	4.0	
Na_2SO_4	-1145.82	-785.80	0.0	13.4	4.0	
	-1145.82	-975.9	-2100.13	1.34	4.0	use u_{ca}
$AgNO_3$	-922.15	-872.81	0.0	7.7	6.0	
NH_4NO_3	-1059.51	-872.81	0.0	12.0	6.0	
CsBr	-1053.2	-1038.85	0.0	12.3	5.0	Prediction

*subscript c, a, and w represent cation, anion and water, respectively.

With the functional group interaction parameter obtained from different systems, the mean activity coefficients of CsBr solution are predicted with the modified Achard's model, and as shown in Table 6.9, the prediction result is rather poor.

As shown in Table 6.9, interaction parameters between cations and anions are used in some cases for improving the correlation for KCl, $CaCl_2$ and Na_2SO_2 systems. Better correlation results for the systems are obtained. However, using the cation-anion interaction parameter, the model is not as predictive one.

6.5.2 Temperature Effects

It is important for a model to represent the mean activity coefficients at different temperatures. The modified Achard model is used to correlate the mean activity coefficients at different temperatures for aqueous NaCl and KCl solutions. In this investigation, linear temperature-dependent interaction parameters are used in the modified Achard method, as discussed above (see Table 6.2). The mean activity coefficient data at different temperatures are fitted simultaneously. The experimental data at different temperatures are obtained from the IVC-SEP databank for electrolyte solutions (IVC-SEP, 2003). For the NaCl solution, the mean activity coefficient data in the temperature range from 273.15 to 373.15 K are used in the regression. For the KCl solution, the temperature range of the experimental data is from 273.15 to 343.15K.

The correlation results are shown in Table 6.10 and in figures 6.7-6.8 for some temperatures. Figures 6.9-6.10 show the calculations for the osmotic coefficients using the interaction parameters obtained from regression of the mean activity coefficient data.

For comparison, the mean activity coefficient data of the KCl+H_2O system at different temperatures are first correlated with four interaction parameters, as shown in Table 6.10 (labelled 'Set2'). Then, we employ the interaction parameters from the NaCl+H_2O system, and estimate only the K^+-H_2O parameter (group contribution). The interaction parameter results using the group contribution concept are also given in Table 6.10 (labelled 'Set 1'). The correlations results with the two different cases are similar, as shown in Figure 6.8. For these solutions, the modified Achard method can successfully correlate the mean activity coefficient behaviours at different temperatures.

Table 6.10 Correlation results with the temperature dependent parameters for the modified Achard model*

Salt	$u_{cw,1}$, K	$u_{cw,2}$, K	$u_{aw,1}$, K	$u_{aw,2}$, K	%AADγ_m	Notes
NaCl	-1154.39	-1.439	-974.422	-0.834	1.8	
KCl	-1040.23	-1.423	-974.422	-0.834	1.6	Set 1
	654.555	7.831	-1209.17	-2.499	0.47	Set 2

*subscript c, a, and w represent the cation, anion and water, respectively.

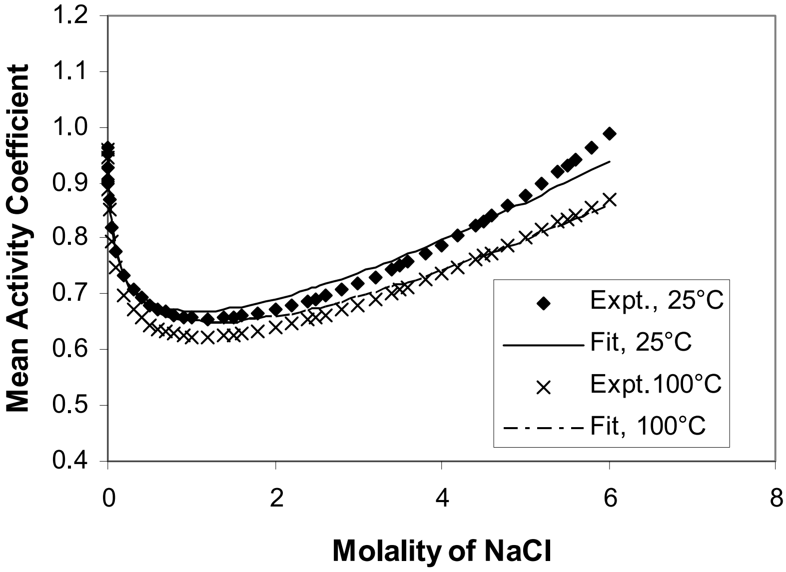


Figure 6.7 Mean activity coefficient (experimental and modified Achard model) for $NaCl+H_2O$ at 25 and 100ºC.

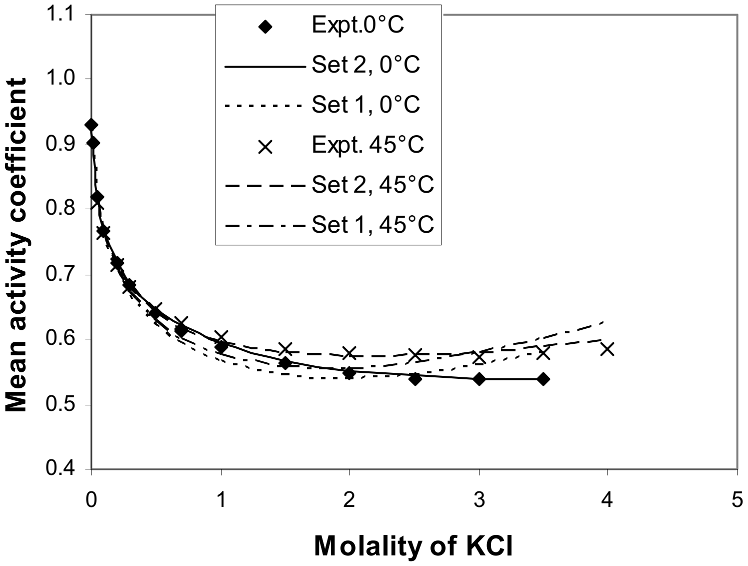


Figure 6.8 Mean activity coefficient (experimental and modified Achard model) for $KCl+H_2O$ at 0 and 45ºC. 'Set 2' represents the four parameter estimation results. 'Set 1' represents the two parameter estimation results.

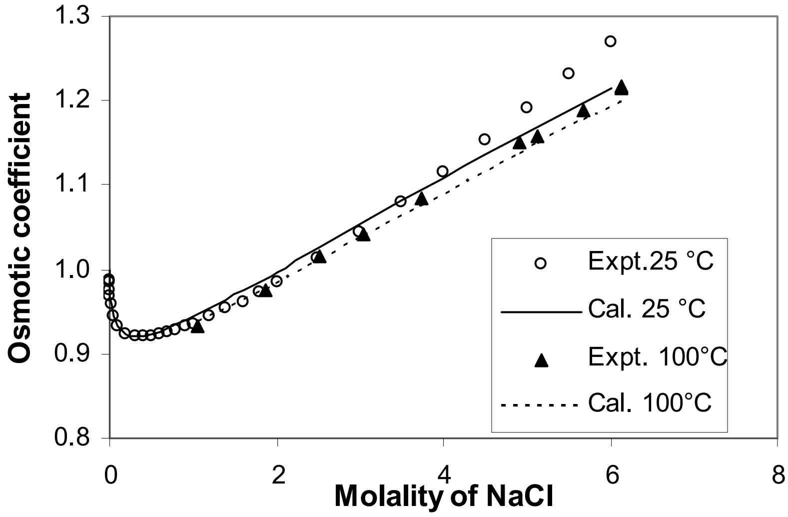


Figure 6.9 Osmotic coefficient (experimental and modified Achard model) using parameters obtained from mean activity coefficient data correlation for NaCl+H_2O at different temperatures.

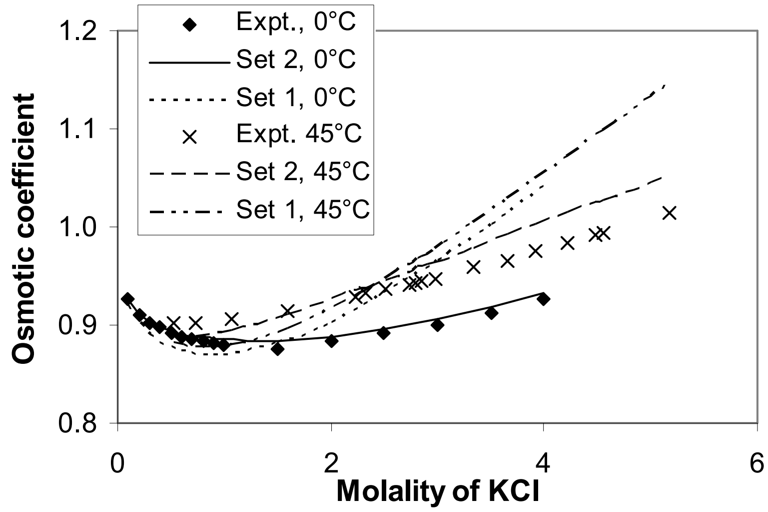


Figure 6.10 Osmotic coefficient (experimental and modified Achard model) using parameters obtained from mean activity coefficient correlation for KCl+H_2O at different temperatures.

6.5.3 Correlation for Organic Electrolytes

As discussed before, ionic surfactant solutions are considered as organic electrolyte solutions. In order to investigate the capability of the proposed modified Achard model, sodium carboxylate aqueous solutions are studied with this model.

Mean activity coefficient of sodium carboxylate aqueous solutions are correlated with modified Achard model using the new structural parameters in Table 6.6. The investigated sodium carboxylates are aqueous solutions of CHO_2Na (C1), $C_2H_3O_2Na$ (C2), $C_3H_5O_2Na$ (C3), $C_4H_7O_2Na$ (C4), and $C_5H_9O_2Na$ (C5). The UNIFAC functional groups are CH_2, COO^- and Na^+. The mean activity coefficient data of the five sodium carboxylate solutions at 25ºC (Robinson and Stokes, 1959) are simultaneously correlated with the model.

Table 6.11 shows the correlation results by two different cases. In case B, interaction parameters between CH_2 and H_2O are taken from UNIFAC (Hansen et al. 1992), u_{NaH2O} is from the results of NaCl+H_2O solution in Table 6.10. Three interaction parameters are estimated simultaneously in case B. However, u_{CH2Na} was given a fixed value in the parameter estimation because it reaches a large value in the estimation process. The absolute average deviation of mean activity coefficient (%AAD γ_m) is 15.6 in this case.

To improve the correlation, one of the interaction parameters between CH_2 and H_2O is re-estimated. Thus, four interaction parameters are estimated simultaneously in case A. The %AAD γ_m is 1.09 in this case. The correlation results of case A are shown in figure 6.11. With the interaction parameters obtained in case A, osmotic coefficients of the five sodium carboxylate solutions at 25ºC (Robinson and Stokes, 1959) are calculated and shown in figure 6.12.

Figures 6.11-6.12 show that the model captures the mean activity coefficients and osmotic coefficients behaviour with a regression of 4 interaction parameters. The Pitzer's electrolyte solution model needs 2 or 3 parameters for a single sodium carboxylate solution (Pitzer, 1991). In the work of Chen et al. (2001), modified NRTL model needs 6 interaction parameters to correlate mean activity coefficients of the five sodium carboxylate solutions.

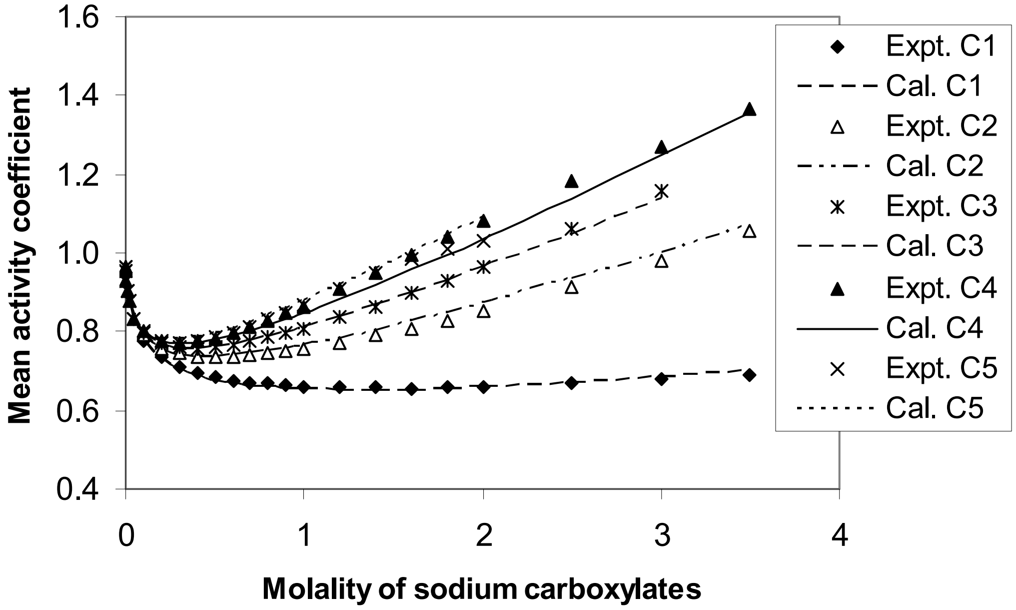


Figure 6.11 Mean activity coefficient (experimental and modified Achard model) for five sodium carboxylate solutions at 25ºC. Correlation results of case A of Table 6.11.

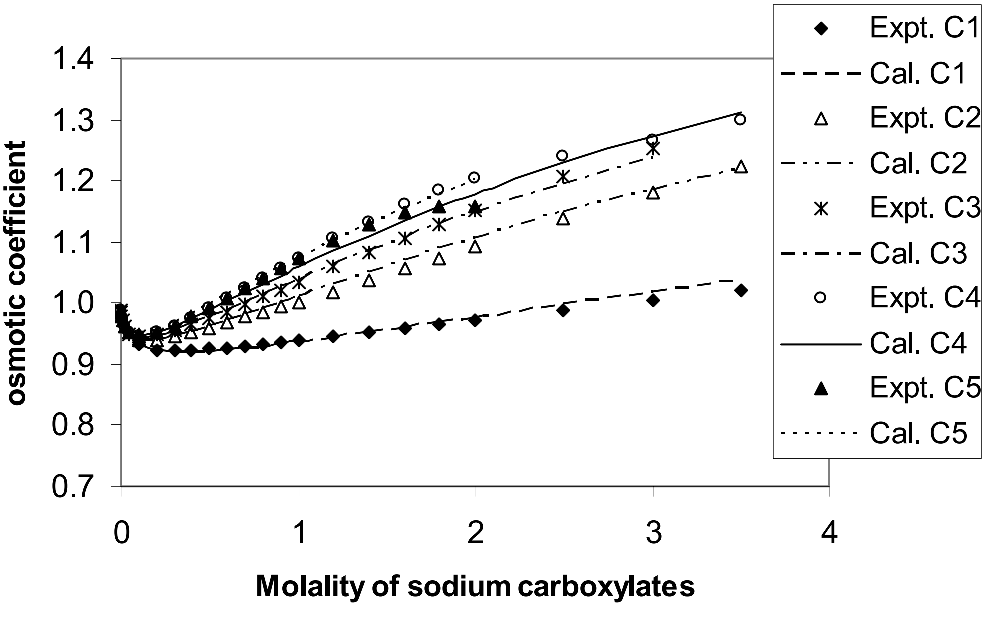


Figure 6.12 Osmotic coefficient (experimental and modified Achard model) for five sodium carboxylate solutions at 25ºC. Calculation results of case A of Table 6.11

Table 6.11 Interaction parameter results of modified Achard model for sodium carboxylate aqueous solutions (in K)

u_{ij}*	Case A	Comments	Case B	Comments
CH_2/COO^-	4632.1	Fit	5000.0	Fit
COO^-/H_2O	–845.77	Fit	–996.73	Fit
CH_2/Na^+	4500.0	Fit	4500.0	Fit
CH_2/H_2O	-227.86	Fit	905.6	Hansen et al. 1992
H_2O/CH_2	335.0	Hansen et al. 1992	335.0	Hansen et al. 1992
Na^+/H_2O	–1154.82	Table 6.10	–1154.82	Table 6.10
%AAD γ_m	1.09		15.6	

*$u_{H2O,H2O}$= –700 K, $u_{CH2,CH2}$=–129.4 K

6.6 Summary

In this chapter, Achard's electrolyte UNIFAC method (Achard et al. 1994a, b) is used to investigate the mean activity coefficient of aqueous solutions of single electrolytes. Previously reported R and Q values of ions, including these by Achard et al. (1994a, b), do not follow the condition Q/R<1 suggested by the Flory-Huggins theory. According to the Flory-Huggins theory, Q/R=1 is the upper 'physical' limit for the ratio Q/R in the combinatorial entropy of mixing for non-electrolyte fluids. The physical derivation of UNIQUAC and UNIFAC cannot be valid with Q/R>1.

Three modifications in Achard's method were made.

1) First, the hydration numbers and solvation equations are not used.

2) Second, the R and Q parameters are re-estimated based on ionic radii. Following the structural parameter calculation method of Abrams and Prausnitz (1975), it is found that the radius of a standard segment should be smaller than that of ionic radii of ions in order to maintain the Q/R<1 condition. Thus, a new, smaller standard segment radius than that of –CH_2- is selected to calculate the volume and surface area of ions based on ionic radii from Marcus (1997). Then, new structural parameters R and Q for ions are obtained and used in the modified Achard model. The new R and Q parameters change the distribution of the contributions to mean activity coefficient from combinatorial and residual terms of UNIFAC.

3) The third modification concerns the interaction parameters. Instead of using the modified UNIFAC method of Larsen et al. (1987), the linear T-dependent UNIFAC method of Hansen et al. (1992) is adopted in this work. All other assumptions on interaction parameters from Achard's model remain unchanged.

Using the proposed modified Achard model, mean activity coefficients of single electrolyte solutions are calculated for several systems. Using two salt-dependent interaction parameters, the model shows similar deviation to those of the electrolyte NRTL model, and give better results than that of extended UNIQUAC model for the mean activity coefficients.

Using the UNIFAC group contribution concept, ions are treated as functional groups. With the ionic functional groups, the mean activity coefficient data for some single electrolyte solutions are correlated with the modified Achard model. For some systems, the model can successfully correlate the mean activity coefficient data with the ions treated as functional groups. Problems occur for other systems.

In addition, the model can capture the mean activity coefficient of some aqueous solutions of single electrolytes at different temperatures.

The modified Achard model can simultaneously and successfully correlate the mean activity coefficient data of five sodium carboxylate solutions at 25ºC using four interaction parameters.

Chapter 7 Critical Micelle Concentration of Ionic Surfactant Solutions

In this chapter, recent progress in modelling the micelle formation of ionic surfactant solutions is first outlined. The modified Achard model is applied to study the CMC of ionic surfactant solutions based on the thermodynamic framework of Chen et al. (2001) for micelle formation. The CMC of four surfactant families, i.e. sodium alkyl sulphates, sodium alkyl sulfonates, sodium carboxylates and potassium carboxylates, is investigated. CMC values of sodium alkyl sulphates (AS) and alkyl trimethylammonium bromides (TAB) ternary surfactant mixtures are calculated by regular solution method.

7.1 Recent Progress for Modelling Ionic Surfactant Solutions

Recently, Hines (2001) reviewed the progress for modelling surfactant solutions. The understanding for such solution at a theoretical level is still poor. Douheret and Viallard (1982) proposed a mass action law model with a two-parameter expression for the activity coefficients of ionic species to represent the micelle formation in ionic surfactant solutions. Based on a mass-action model with a single micellar aggregate species, Burchfield and Woolley (1984) suggested an activity coefficient model for aqueous ionic surfactant solutions. The micellar solution is treated as mixed electrolytes by using the Guggenheim equation. Huibers et al. (1997) investigated the relationship between the molecular structure and the CMC of anionic surfactants using a quantitative structure-property relationship approach. A linear regression model is constructed for 119 anionic surfactants. Amos et al. (1998) proposed a model incorporating the distribution of micellar size. The model of Amos et al. is based on a mass-action equilibrium approach that includes micelle-micelle interactions as a function of size for multi-component surfactant solutions consisting of micellar aggregates, monomer, counterions, and electrolytes.

Li et al. (2000) use SAFT (statistical associating fluid theory), together with the mean spherical approximation (MSA), to calculate the activity coefficients of aqueous ionic surfactant solutions. In Li's method, the monomeric surfactant ions are assumed to be in a state of physical equilibrium with the surfactant ions in the micelle at CMC. Their chemical potentials are equal at CMC. The method of Li et al. describes molecules as chains of hard sphere segments and includes the contributions from hard sphere-hard sphere and dipole-dipole interactions, the chain formation, the Lennard-Jones and charge-charge interactions.

Recently, as discussed in chapter 3, Chen et al. (2001) proposed a thermodynamic framework to represent CMC of ionic surfactants in aqueous solutions using activity coefficient model. In their framework, the activity coefficients of surfactant are correlated by an extended NRTL model for organic electrolyte solutions.

In this study, the thermodynamic framework of Chen et al. (2001) is used to represent the micelle formation of ionic surfactant solutions. Instead of using the extended electrolyte NRTL model, the modified Achard model as developed in the previous Chapter will be used to calculate the activity coefficients in ionic surfactant solutions.

7.2 Equations for the CMC Correlation

7.2.1 Activity Coefficient Calculations

Based on Chen's framework, experimental CMC data from different surfactant solutions are correlated using the modified Achard model. The activity coefficient is the product of a long-range asymmetrical Pitzer-Debye-Hückel (PDH) term and a short-range UNIFAC model as follow:

$$\ln \gamma_{\pm,aq}^{*} = \ln \gamma_{\pm,aq}^{*,\mathrm{PDH}} + \ln \gamma_{\pm,aq}^{*,\mathrm{UNIFAC}} \tag{7.1}$$

The expressions of the Pitzer-Debye-Hückel (PDH) term and the UNIFAC model term were presented in Chapter 6.

The activity coefficients of cations and anions in the aqueous solution (*aq*) and the micelle aggregates (micelle) are calculated as follows:

$$\ln \gamma_{i,aq}^{*} = \ln \gamma_{i,aq}^{*,\mathrm{PDH}} + \ln \gamma_{i,aq}^{*,\mathrm{UNIFAC}} \tag{7.2}$$

$$\ln \gamma_{i,\mathrm{micelle}}^{*} = \ln \gamma_{i,\mathrm{micelle}}^{*,\mathrm{PDH}} + \ln \gamma_{i,\mathrm{micelle}}^{*,\mathrm{UNIFAC}} \tag{7.3}$$

$$\ln \gamma_{i,\mathrm{micelle}}^{*,\mathrm{PDH}} = -0.9571 \tag{7.4}$$

$$\ln\gamma_{i,\mathrm{micelle}}^{*,\mathrm{UNIFAC}} = -\ln\gamma_i^{\infty,\mathrm{UNIFAC}} \tag{7.5}$$

where $\ln\gamma_{i,\mathrm{micelle}}^{*,\mathrm{PDH}}$ is set to –0.9571, which is the limiting value of the PDH term for univalent ions as the electrolyte concentration approaches unity and $\ln\gamma_i^{\infty,\mathrm{UNIFAC}}$ is the infinite dilute activity coefficient calculated by the UNIFAC model. The molality scale mean activity coefficient ($\gamma_{\pm m}^*$) is obtained from the mole fraction mean activity coefficient ($\gamma_{\pm}^*$) by equations (6.60)-(6.61) in Chapter 6. The asymmetrical activity coefficient of UNIFAC model is calculated by equation (6.62) in Chapter 6.

7.2.2 Interaction Parameters

As discussed in Chapter 6, the interaction parameters (a_{ij}) between ions and other groups of the modified Achard model depend on temperature as follows (Hansen et al., 1992):

$$a_{ij} = u_{ij,1} + u_{ij,2}\left(T - T_0\right) - u_{jj} \tag{7.6}$$

For non-ionic groups, the interaction parameters are calculated by the original equation of Hansen et al. (1992), i.e. equation (6.26) in Chapter 6.

For alkyl groups (CH_3, CH_2), u_{jj} in equation (7.6) is calculated as:

$$u_{jj} = a_{jw} - a_{wj} + u_{ww},\ T_0\text{=298.15 K} \tag{7.7}$$

where w refers to the water, u_{ww}=–700 K, a_{jw} and a_{wj} are the interaction parameters between water and hydrocarbon groups from Hansen et al. (1992). u_{ww} is computed only at 25ºC by Achard et al. (1994b). The $u_{\mathrm{CH2,CH2}}$ interaction parameter at 25ºC is calculated from equation (7.7) as follow:

$$u_{\mathrm{CH2,CH2}} = a_{\mathrm{CH2,H2O}} - a_{\mathrm{H2O,CH2}} + u_{\mathrm{H2O,H2O}} = 905.6 - 335.0 + (-700) = -129.4\ \mathrm{K} \tag{7.8}$$

In the aqueous solution of sodium alkyl sulphates ($C_nH_{2n+1}OSO_3^-Na^+$), for example, there are groups H_2O, CH_3, CH_2, and ions OSO_3^-, Na^+. The interaction parameters between these groups are summarized in Table 7.1. The groups CH_3 and CH_2 belong to the same UNIFAC main functional group “CH_2”.

In Table 7.1, the interaction parameters between CH_2 and H_2O are taken from Hansen et al. (1992). The interaction parameters estimated results from aqueous NaCl solutions can be used for the parameters between Na^+ and H_2O, i.e. $u_{cw,1}$, $u_{cw,2}$ in Table 6.10 (Chapter 6). Hence, there are 6 unknown interaction parameters for the sodium alkyl sulphate solution, i.e. $u_{CH2a,1}$, $u_{CH2a,2}$, $u_{CH2c,1}$, $u_{CH2c,2}$, $u_{aw,1}$, $u_{aw,2}$.

The structural parameters of cation and anion used in the modified Achard model are taken from Table 6.6 (Chapter 6). Those of CH_3, CH_2 and H_2O are from the UNIFAC structural parameter table (Fredenslund et al. 1977).

Table 7.1 Summary of interaction parameters for sodium alkyl sulphate solutions (in K) *

Group	CH_2	OSO_3^-(a)	Na^+(c)	H_2O(w)
CH_2	0	$u_{CH2a,1}$ $u_{CH2a,2}$ $u_{aa}=2500$	$u_{CH2c,1}$ $u_{CH2c,2}$ $u_{cc}=2500$	905.6** 0.8618
OSO_3^-(a)	$u_{aCH2,1}$ $u_{aCH2,2}$ $u_{CH2CH2}=129.4$	0	$u_{ac,1}=0$ $u_{ac,2}=0$ $u_{cc}=2500$	$u_{aw,1}$ $u_{aw,2}$ $u_{ww}=-700$
Na^+(c)	$u_{cCH2,1}$ $u_{cCH2,2}$ $u_{CH2CH2}=-129.4$	$u_{ca,1}=0$ $u_{ca,2}=0$ $u_{aa}=2500$	0	$u_{cw,1}=-1154.39$ $u_{cw,2}=-1.439$ $u_{ww}=-700$
H_2O(w)	335.0** 0.0106	$u_{wa,1}$ $u_{wa,2}$ $u_{aa}=2500$	$u_{wc,1}=-1154.39$ $u_{wc,2}=-1.439$ $u_{cc}=2500$	0

* $u_{wc,1}=u_{cw,1}$, $u_{wc,2}=u_{cw,2}$, $u_{aw,1}=u_{wa,1}$, $u_{aw,2}=u_{wa,2}$, $u_{aCH2,1}=u_{CH2a,1}$, $u_{aCH2,1}=u_{CH2a,1}$, $u_{CH2c,1}=u_{cCH2,1}$, $u_{CH2c,2}=u_{cCH2,2}$

** from Hansen et al. (1992)

7.2.3 Objective Function

The objective function (F) is used as:

$$F = \sum_i \left(\ln x_{aq}^{cmc,cal} - \ln x_{aq}^{cmc,\exp} \right)_i^2 \tag{7.9}$$

where $x_{aq}^{cmc,\exp}$ represents the experimental value of CMC in mole fraction scale and $x_{aq}^{cmc,cal}$ represents the calculated value of CMC also in mole fraction scale. A least-square method, Levenberg-Marquard algorithm (Fletcher, 1980), is used to minimize the objective function.

The reported molality scale CMC values are converted to mole fractions. The critical micelle concentration (CMC) data of Mukerjee et al. (1971) and Brandrup et al. (1975) are used in the interaction parameter estimation.

7.3 CMC Correlation

7.3.1 CMC Correlation with the Modified Achard Model

The CMC of three surfactant families, sodium alkyl sulphates, sodium alkyl sulfonates and potassium carboxylates, are studied with the modified Acahrd model. The sodium alkyl sulphates, sodium alkyl sulfonates and potassium (sodium) carboxylates are, respectively, abbreviated as $CnOSO_3Na$, $CnSO_3Na$ and CnCOOK(Na), where Cn refers to the carbon number of the alkyl chain. These surfactant solutions are widely used in practice and extensively investigated in various applications. The group assignments for these surfactant molecules are presented in Table 7.2. The structural parameters of the groups are given in Table 7.3.

Table 7.2 Group assignments for surfactant molecules

Surfactant family	Abbreviation	Group Assignment*
Sodium alkyl sulphates	$CnOSO_3Na$	CH_3, CH_2, Na^+(c), OSO_3^-(a)
Sodium alkyl sulfonates	$CnSO_3Na$	CH_3, CH_2, Na^+(c), SO_3^-(a)
Potassium carboxylates	CnCOOK	CH_3, CH_2, K^+(c), COO^-(a)
Sodium carboxylates	CnCOONa	CH_3, CH_2, Na^+(c), COO^-(a)

* c: cation, a: anion

Table 7.3 Structural parameter values

Group	R	Q	Comments
CH_3	0.9011	0.848	
CH_2	0.6744	0.540	
Na^+	1.0612	1.0404	
K^+	2.6281	1.9044	
OSO_3^-	6.8590	3.6100	From HSO_4^- data
SO_3^-	4.9130	2.8900	From HSO_3^- data
COO^-	3.7964	2.4336	From HCO_3^- data
H_2O	0.92	1.40	

(i) Sodium Alkyl Sulphates ($C_nH_{2n+1}OSO_3^-Na^+$)

In order to evaluate the thermodynamic framework for micelle formation by Chen et al. (2001), and the capability of the modified Achard model, the CMC data of sodium alkyl sulphates in aqueous solution are correlated in two approaches using this model. In the first approach, all CMC data of different surfactants within the same family are put into the same data set and simultaneously fitted with the model. In the second approach, the CMC data of two or three surfactant components are simultaneously fitted. With the interaction parameters obtained by these CMC data, the CMC of other surfactants in the same chemical family is calculated.

First Approach

The CMC data of surfactants with various alkyl chain lengths at different temperatures are simultaneously fitted with the model. The interaction parameters between CH_2 and H_2O are taken from Hansen et al. (1992). The interaction parameters between Na^+ and H_2O are taken from parameter estimation results of NaCl + H_2O system (Tables 6.9 in Chapter 6). The unknown interaction parameters are: $u_{\mathrm{CH2OSO3,1}}$, $u_{\mathrm{CH2OSO3,2}}$, $u_{\mathrm{CH2Na,1}}$, $u_{\mathrm{CH2Na,2}}$, $u_{\mathrm{OSO3H2O,1}}$, $u_{\mathrm{OSO3H2O,2}}$.

In correlating the CMC data, it was noted that $u_{\mathrm{CH2Na,1}}$ reaches a very large value. In order to reduce the number of simultaneously estimated parameters, this and another two parameters were set as follows:

$$u_{\mathrm{CH2Na,1}}=4500,\ u_{\mathrm{CH2Na,2}}=0.0,\ u_{\mathrm{OSO3H2O,2}}=0.0 \tag{7.10}$$

With this large value for interaction parameter $u_{\mathrm{CH2Na,1}}$, the relevant term (τ_{CH2Na}) in residual part of UNIFAC equation (see Appendix A) is small and can be neglected, because

$$\tau_{\mathrm{CH2Na}} = \exp\left(-\frac{a_{\mathrm{CH2Na}}}{T}\right) \tag{7.11}$$

where a_{CH2Na} is calculated by equation (7.6). The reason for setting $u_{\mathrm{OSO3H2O,2}}=0.0$ is that the CMC values do not change significantly with temperature for sodium alkyl sulphate solutions in the experimental temperature range (280-350K), as shown in figure 7.1. Using these assumptions, the number of unknown interaction parameters is reduced to 3 for sodium alkyl sulphate systems.

All reported CMC data for sodium alkyl sulphates are simultaneously fitted. The solid lines in Figure 7.1 and 7.2 show the fitting results. The parameter estimation results are given Table 7.4. The results show that the thermodynamic expression of micelle formation combined with the modified Achard method can describe satisfactorily both temperature and chain length effects of CMC.

Table 7.4 Parameter estimation results (bold numbers) of two approaches for sodium alkyl sulphates (in K). All other parameters can be found in Table 7.1

	CH_2~OSO_3^-(a)	H_2O~OSO_3^-(a)	CH_2~Na^+(c)	Na^+~H_2O(w)
First approach	$u_{\mathrm{aCH2,1}}=\mathbf{-46.29}$ $u_{\mathrm{aCH2,2}}=\mathbf{1.449}$	$u_{\mathrm{wa,1}}=\mathbf{556.19}$ $u_{\mathrm{wa,2}}=0$	$u_{\mathrm{CH2c,1}}=4500^*$ $u_{\mathrm{CH2c,2}}=0$	$u_{\mathrm{cw,1}}=-1145.8$ $u_{\mathrm{cw,2}}=0$
Second approach	$u_{\mathrm{aCH2,1}}=\mathbf{-7.162}$ $u_{\mathrm{aCH2,2}}=\mathbf{0.718}$	$u_{\mathrm{wa,1}}=\mathbf{668.13}$ $u_{\mathrm{wa,2}}=0$	$u_{\mathrm{CH2c,1}}=4500^*$ $u_{\mathrm{CH2c,2}}=0$	$u_{\mathrm{cw,1}}=-1154.39$ $u_{\mathrm{cw,2}}=-1.439$

* fixed value

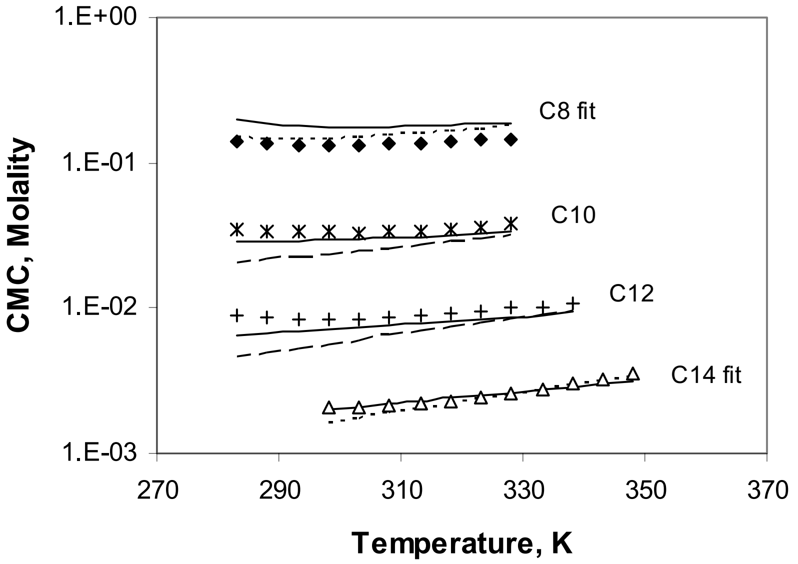


Figure 7.1 Results for C_8OSO_3Na (C8 fit), $C_{10}OSO_3Na$ (C10), $C_{12}OSO_3Na$ (C12), and $C_{14}OSO_3Na$(C14 fit) at different temperatures. Points: experimental CMC values. Solid lines: fitting results of first approach, dotted lines: fitting results of second approach, dashed lines: calculation results.

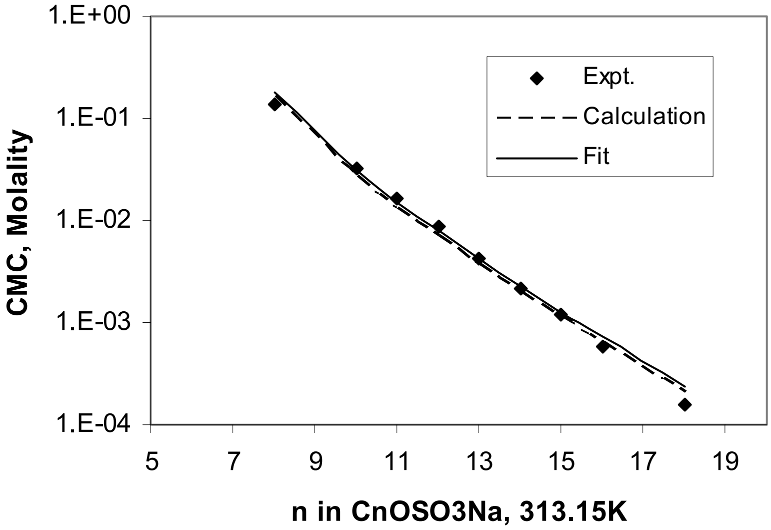


Figure 7.2 Results for $CnOSO_3Na$ (n=8-18) with different carbon numbers in alkyl chain at 313.15K. Points: experimental CMC values. Solid line: fitting results of first approach, dashed line: calculation results.

Second Approach

In order to investigate the predictive capability of the modified Achard model, two binary systems: $C_8OSO_3Na+H_2O$ and $C_{14}OSO_3Na+H_2O$ are selected to obtain the group interaction parameters. That means that the interaction parameters $u_{CH2OSO3,1}$, $u_{CH2OSO3,2}$ and $u_{OSO3H2O,1}$ are re-estimated using the CMC data of only these two systems. The obtained interaction parameters can be then applied to other surfactant systems in same surfactant family. The correlation results are shown in figures 7.1 with dotted lines labelled ‘C8 fit’ and ‘C14 fit’. The obtained interaction parameters in the second approach are given in Table 7.4.

Using the interaction parameters obtained, the CMC values of $C_{10}OSO_3Na$, $C_{12}OSO_3Na$, and $CnOSO_3Na$ (n=8-18) are calculated with the modified Achard model. The calculation results are shown in figures 7.1-7.2 with dashed lines.

Figures 7.1-7.2 show that the modified Achard model can successfully calculate the CMC values of sodium alkyl sulphates. Both temperature and chain length effects can be captured. However, the model underestimates the CMC values at lower temperatures for the surfactants $C_{10}OSO_3Na$ and $C_{12}OSO_3Na$. The model gives good estimates for the CMC values of $CnOSO_3Na$ (n=8-18) with different carbon numbers in the alkyl chain at 313.15 K.

The surfactant+H_2O binary systems used in these two approaches are summarized in Table 7.5.

Table 7.5 Surfactant+H_2O binary systems used for interaction parameter estimation in two approaches

Surfactant family	Second approach		First approach	
	Component	Data	Component	Data
Sodium alkyl sulphates	C_8OSO_3Na	CMC vs. T	C_8OSO_3Na	CMC vs. T
	$C_{14}OSO_3Na$	CMC vs. T	$C_{10}OSO_3Na$	CMC vs. T
			$C_{12}OSO_3Na$	CMC vs. T
			$C_{14}OSO_3Na$	CMC vs. T
			$CnOSO_3Na$ (n=8-18)	CMC vs. n
Sodium alkyl sulfonates	C_8SO_3Na	CMC vs. T	C_8SO_3Na	CMC vs. T
	$C_{10}SO_3Na$	CMC vs. T	$C_{10}SO_3Na$	CMC vs. T
	$C_{12}SO_3Na$	CMC vs. T	$C_{12}SO_3Na$	CMC vs. T
			$C_{14}SO_3Na$	CMC vs. T
			$CnSO_3Na$ (n=5-18)	CMC vs. n
Potassium carboxylates	C_8COOK	CMC vs. T	C_8COOK	CMC vs. T
	$C_{14}COOK$	CMC vs. T	$C_{10}COOK$	CMC vs. T
			$C_{12}COOK$	CMC vs. T
			$C_{14}COOK$	CMC vs. T
			CnCOOK (n=5-17)	CMC vs. n

(ii) Sodium Alkyl Sulfonates ($C_nH_{2n+1}SO_3^-Na^+$)

The two approaches used for sodium alkyl sulphates can also be applied to the sodium alkyl sulphonates ($CnSO_3Na$). The same assumptions on $u_{CH2Na,1}$ and $u_{CH2Na,2}$ for sodium alkyl sulphates are adopted for sodium alkyl sulfonates.

First Approach

All available CMC values for sodium alkyl sulfonates, as shown in Table 7.5, are fitted to 4 interaction parameters $u_{CH2SO3,1}$, $u_{CH2SO3,2}$, $u_{SO3H2O,1}$, $u_{SO3H2O,2}$ ($u_{NaH2O,2}$=0.0).

The correlation results are presented in figures 7.3-7.4 with solid lines. The obtained interaction parameters are given in Table 7.6. Both temperature and chain length effects are described satisfactorily.

Second Approach

The CMC data of three surfactants (C_8SO_3Na, $C_{10}SO_3Na$, and $C_{12}SO_3Na$) (Table 7.5) are used to re-estimate the 4 unknown interaction parameters: $u_{CH2SO3,1}$, $u_{CH2SO3,2}$, $u_{SO3H2O,1}$, $u_{SO3H2O,2}$. The parameter estimation results are presented in figures 7.3-7.4 with dotted lines and in Table 7.6.

The CMC values of $C_{14}SO_3Na$ and $CnSO_3Na$ (n=5-12) are calculated using these parameters. Figures 7.3-7.4 show the calculations with dashed lines. As can be seen, the model can extrapolate well the CMC values, except for the short alkyl chain surfactant solutions.

Table 7.6 Parameter estimation results (bold numbers) of two approaches for sodium alkyl sulfonates (in K). All other parameters can be found in Table 7.1

	CH_2~SO_3^-(a)	H_2O~SO_3^-(a)	CH_2~Na^+(c)	Na^+~H_2O(w)
First approach	$u_{aCH2,1}$=**249.4** $u_{aCH2,2}$=**1.321**	$u_{wa,1}$=**384.6** $u_{wa,2}$=**0.0**	$u_{CH2c,1}$=4500* $u_{CH2c,2}$=0	$u_{cw,1}$=–1145.8 $u_{cw,2}$=0
Second approach	$u_{aCH2,1}$=**–369.03** $u_{aCH2,2}$=**1.247**	$u_{wa,1}$=**499.81** $u_{wa,2}$=**1.467**	$u_{CH2c,1}$=4500* $u_{CH2c,2}$=0	$u_{cw,1}$=–1154.39 $u_{cw,2}$=–1.439

* fixed value

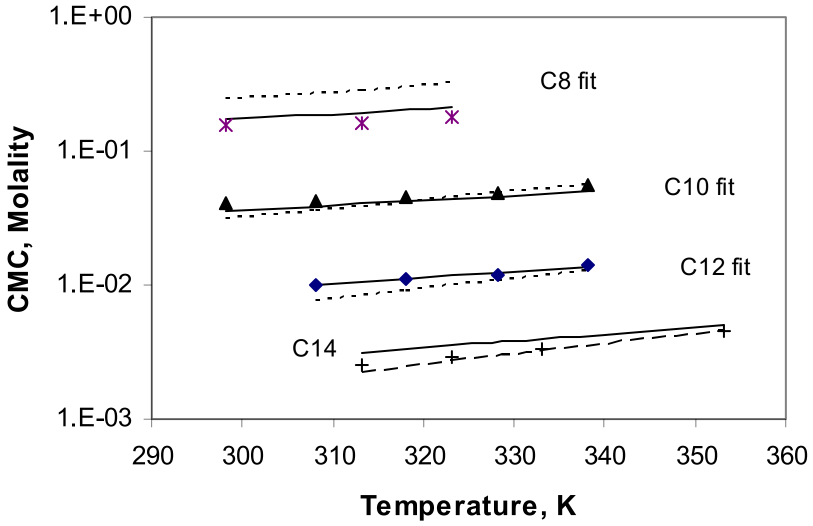


Figure 7.3 Results for C_8SO_3Na (C8 fit), $C_{10}SO_3Na$ (C10 fit) and $C_{12}SO_3Na$ (C12 fit) and $C_{14}SO_3Na$ (C14) at different temperatures. Points: experimental CMC values. Solid lines: fitting results with the first approach, dotted lines: fitting results with the second approach, dashed lines: calculation results.

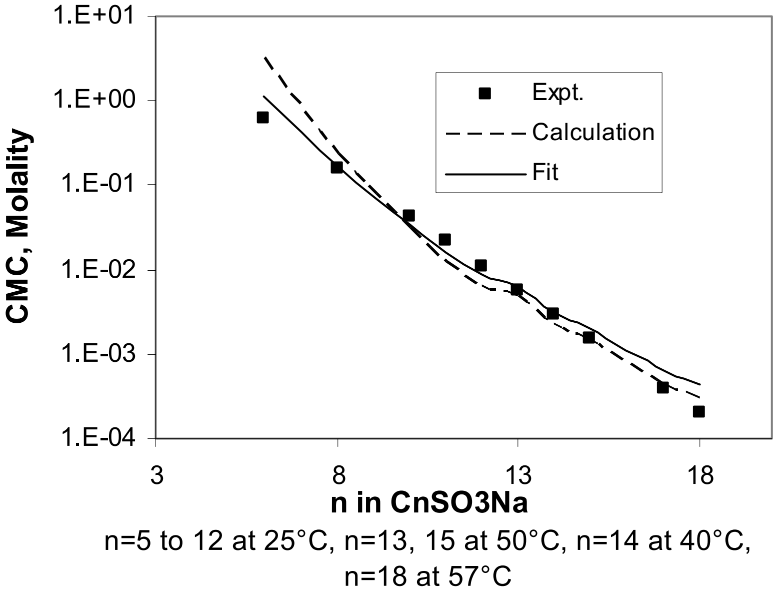


Figure 7.4 Results for sodium alkyl sulfonates with different carbon numbers in alkyl chain. Points: experimental CMC values for C_nSO_3Na, n=5 to 18 at different temperatures. Solid line: fitting results with the first approach, dashed line: calculation results.

(iii) Potassium Carboxylates ($C_nH_{2n-1}OO^-K^+$)

All CMC data of selected potassium carboxylates (Table 7.5, first approach) are simultaneously fitted. The interaction parameters between K^+ and H_2O obtained by the mean activity coefficient data correlation for KCl+H_2O solution (Table 6.10, Chapter 6) are used. The fitting results are presented in figures 7.5-7.6 with solid lines. The obtained interaction parameters are given in Table 7.7. The model overestimates the CMC values for potassium carboxylates with short alkyl chains (figure 7.5) using five adjustable parameters (shown in Table 7.7).

As observed from the parameter estimation results in Table 7.7, the interaction parameter between K^+ and CH_2 has a large value. Thus, this interaction parameter was set as: $u_{CH2K,1}$=4500, $u_{CH2K,2}$=0.0.

Then, CMC data of C_7COOK and $C_{13}COOK$ systems (Table 7.5, second approach) are fitted to four unknown interaction parameters: $u_{CH2COO,1}$, $u_{CH2COO,2}$, $u_{COOH2O,1}$, $u_{COOH2O,2}$. The parameter estimation results are presented in figure 7.5 with dotted lines, and Table 7.7.

Using the obtained interaction parameters, the CMC of C_9COOK, $C_{11}COOK$, $C_{15}COOK$, and CnCOOK (n=5-17) are calculated with the modified Achard method. The calculations are shown in figures 7.5-7.6 with dashed lines. The model overestimates the CMC of short alkyl chain potassium carboxylates.

Table 7.7 Parameter estimation results (bold numbers) of potassium carboxylates (in K). All other parameters can be found in Table 7.1

	CH_2~ COO^-(a)	H_2O~ COO^-(a)	CH_2~ K^+(c)	K^+~H_2O(w)
First approach	$u_{aCH2,1}$=**–176.47** $u_{aCH2,2}$=**15.35**	$u_{wa,1}$=**289.56** $u_{wa,2}$=**8.962**	$u_{CH2c,1}$=**3220** $u_{CH2c,2}$=0	$u_{cw,1}$=–654.555 $u_{cw,2}$=7.831
Second approach	$u_{aCH2,1}$=**–91.75** $u_{aCH2,2}$=**5.846**	$u_{wa,1}$=**420.83** $u_{wa,2}$=**–1.962**	$u_{CH2c,1}$=4500* $u_{CH2c,2}$=0	$u_{cw,1}$=–654.555 $u_{cw,2}$=7.831

* fixed value

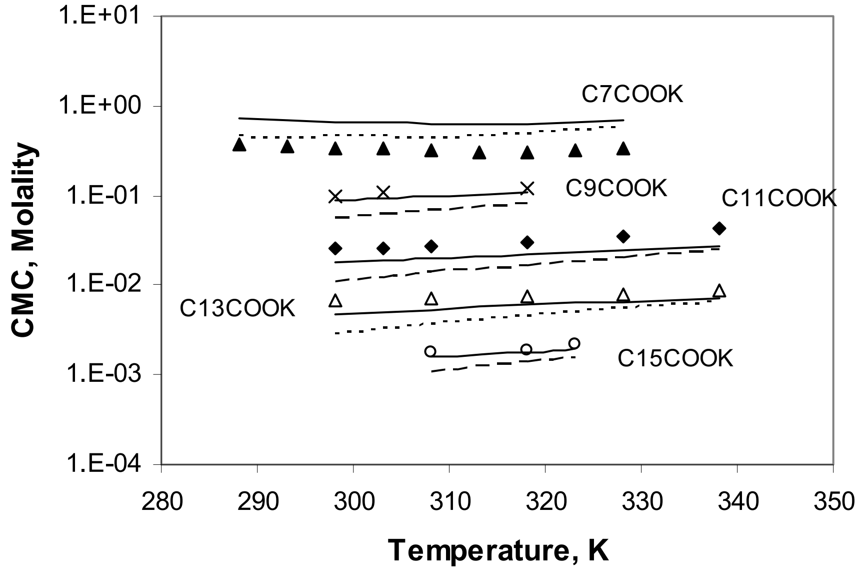


Figure 7.5 Results for C_7COOK, C_9COOK, $C_{11}COOK$, $C_{13}COOK$ and $C_{15}COOK$ at different temperatures. Points: experimental CMC values. Solid lines: fitting results with the first approach, dotted lines: fitting results with the second approach, dashed lines: calculation results.

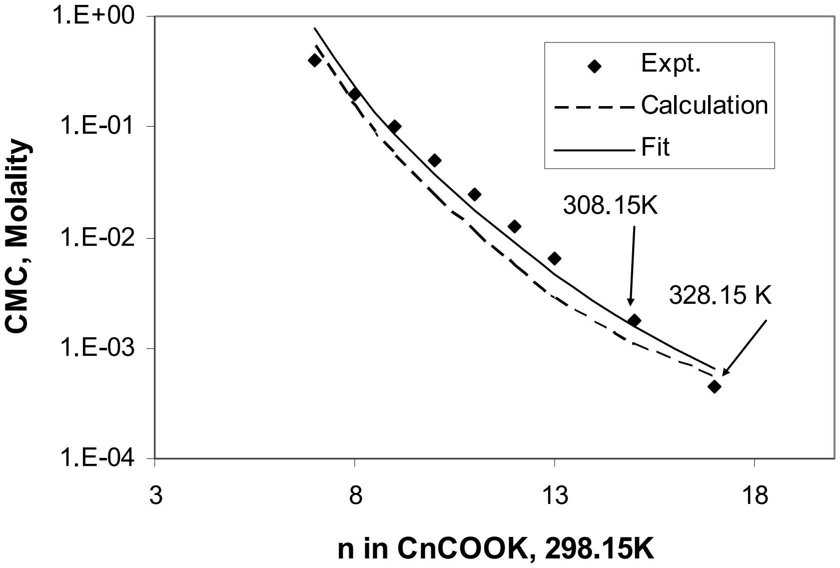


Figure 7.6 Results for potassium carboxylates with different carbon numbers in alkyl chain. Points: experimental CMC values at 298.15 K. Solid line: fitting results with the first approach, dashed line: calculation results

7.3.2 Prediction of CMC for Sodium Carboxylates

With the interaction parameters obtained from the CMC data for potassium carboxylates (CnCOOK) systems (Table 7.7) and the mean activity coefficient data correlation for NaCl+H_2O system (Table 6.10, Chapter 6), the CMC values of sodium carboxylate ($C_nH_{2n-1}COO^-Na^+$, abbr. CnCOONa) solutions are predicted with the modified Achard model, as shown in figure 7.7. As can be seen, the prediction results are rather poor. But the prediction shows CMC increases with increasing temperature. The interaction parameters used in the prediction are summarized in Table 7.8 labelled with 'Pred.'. For comparison, the CMC data of sodium carboxylates are also fitted with the modified Achard model and presented in figure 7.7 and Table 7.8 labelled with 'Fitting'.

As discussed in Chapter 6, the modified Achard method can simultaneously correlate the mean activity coefficients of five short chain sodium carboxylate (CnCOONa, n=1-5) solutions. The interaction parameters obtained for these sodium carboxylates can be used to predict the CMC of long chain sodium carboxylates (CnCOONa, n=7-18) with the modified

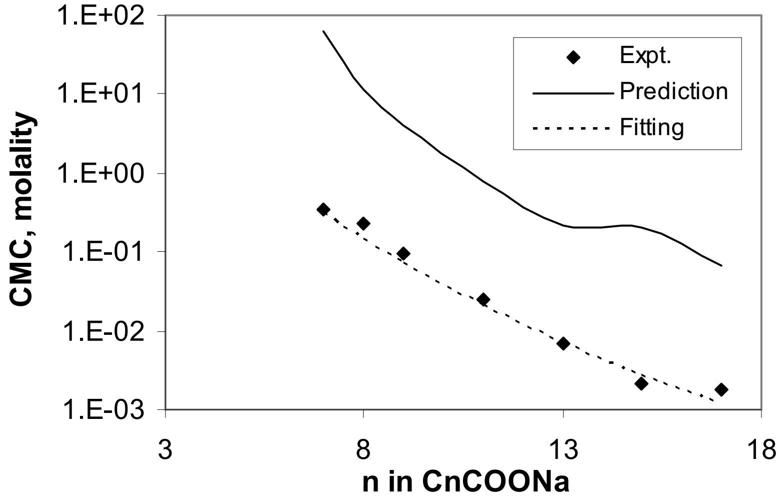
Achard model. However, the calculation in the CMC prediction is diverged with those interaction parameters in Table 6.11, Chapter 6. Some negative CMC values are obtained.

For non-electrolyte solutions, UNIFAC method can give satisfied prediction results for similar systems. However, sodium carboxylate aqueous solution is an electrolyte solution. The strong hydrogen bonding and hydration effects may be the reasons for the poor prediction with the modified Achard model.

Table 7.8 Interaction parameters for sodium carboxylates (in K)*

Surfactant	$u_{CH2a,1}$	$u_{CH2a,2}$	$u_{CH2c,1}$	$u_{aw,1}$	$u_{aw,2}$	$u_{cw,1}$	$u_{cw,2}$	Note
CnCOONa	-91.75	5.846	4500^{**}	420.83	-1.962	-1154.4	-1.439	Pred.
	-434.86	74.83	4500^{**}	764.45	96.54	-1154.4	-1.439	Fitting

*subscripts: w: water; c: Na^+, a: COO^-; CH2: CH_2 main group, $u_{ww} = -700$ K, $u_{CH2CH2} = -129.4$ K.
** fixed value



n=7-17, n=7,8 at 20°C, n=9,11,14 at 25°C, n=15,17 at 50°C

Figure 7.7 CMC prediction results for sodium carboxylates CnCOONa (n=7-17) with different hydrocarbon chain length at several temperatures. The prediction shows CMC increases with increasing temperature.

7.4 CMC Calculation of Surfactant Mixtures

As an example to use and evaluate regular solution method (Rubingh, 1979, Holland, 1986) discussed in Chapter 3, CMC of sodium alkyl sulphates (AS) and alkyl trimethylammonium bromides (TAB) ternary surfactant mixtures were calculated in this method based on the work of Murphy et al. (2002). This method is often applied to mixed surfactant systems and treats the micelles or aggregates as a separated pseudo-phase. The pseudo micelle phase is considered as non-ideal liquid mixtures. Regular solution method is used to describe activity coefficient of surfactants in the non-ideal liquid mixtures (pseudo micelle phase).

Extending equation (3.63) to ternary mixture of surfactants, CMC can be calculated as:

$$\frac{1}{\mathrm{CMC_{mix}}} = \frac{\alpha_1}{\gamma_1 \mathrm{CMC}_1} + \frac{\alpha_2}{\gamma_2 \mathrm{CMC}_2} + \frac{\alpha_3}{\gamma_3 \mathrm{CMC}_3} \tag{7.12}$$

where $\mathrm{CMC_{mix}}$, CMC_1, CMC_2, CMC_3 are the CMC values of the mixed surfactants, surfactant 1, surfactant 2 and surfactant 3, respectively; α_1, α_2 and α_3 are the mole fractions of the respective surfactants in aqueous solution (aqueous phase) and γ_1, γ_2 and γ_3 are the activity coefficients of surfactants 1, 2 and 3 in pseudo micelle phase. The activity coefficients are calculated by:

$$\ln \gamma_1 = \left(\beta_{12} x_2^2 + \beta_{13} x_3^2 + (\beta_{12} + \beta_{13} - \beta_{23}) x_2 x_3\right) / RT \tag{7.13}$$

$$\ln \gamma_2 = \left(\beta_{12} x_1^2 + \beta_{23} x_3^2 + (\beta_{12} + \beta_{23} - \beta_{13}) x_1 x_3\right) / RT \tag{7.14}$$

$$\ln \gamma_3 = \left(\beta_{13} x_1^2 + \beta_{23} x_2^2 + (\beta_{23} + \beta_{13} - \beta_{12}) x_1 x_2\right) / RT \tag{7.15}$$

where β_{12}, β_{13} and β_{23} are the interaction parameters between surfactants 1 and 2, 1 and 3, and 2 and 3, respectively, and they are obtained by fitting CMC of binary surfactant systems; x_1, x_2 and x_3 are the compositions of surfactants 1, 2 and 3 in pseudo micelle phase.

Based on these equations, CMC values of ternary surfactant mixtures are calculated for cationic surfactants: octyl- (C8), decyl- (C10), dodecyl- (C12), tetradecyl- (C14) and hexadecyl- (C16) trimethylammonium bromide (TAB), and anionc surfactants: sodium octyl- (C8), decyl- (C10), dodecyl- (C12), tetradecyl- (C14) and hexadecyl- (C16) sulphates. The interaction parameters between these surfactants are taken from Murphy et al. (2002). Based on the work of Murphy et al., compositions of surfactants 1, 2 and 3 in aqueous phase (α_1, α_2 and α_3) and pseudo micelle phase (x_1, x_2 and x_3) are approximated as:

Aqueous phase composition: $\alpha_1 = \alpha_2 = \alpha_3 = 1/3$

Pseudo micelle phase: $x_1 = x_2 = x_3 = 1/3$

because the three components in an experimental sample are very similar, as shown in Tables 7.9-7.10. If the compositions of surfactant in micelle phase are not available, a method proposed by Holland (1986) can be used to calculate them.

By equations (7.12)-(7.15), CMC of ternary surfactant mixtures are calculated and presented in Tables 7.9-7.10, and figure 7.8. In these tables, experimental CMC are from conductivity measurements (Murphy et al. 2002). These results show that the regular solution method can predict well the CMC of ternary surfactant mixture using experimental binary interaction parameters. However, these calculations only show an ideal case because the surfactant compositions in aqueous and micelle phase are equal for these ternary surfactant systems through the special designed experiments in the work of Murphy et al. (2002).

Table 7.9 CMC calculation results using the regular solution method for alkyl trimethylammonium bromides at 303 K (Molality, ×10^{-3})*

Surfactants 1/2/3	CMC_1	CMC_2	CMC_3	β_{12}	β_{13}	β_{23}	CMC, exp.	CMC, cal.	Dev.%
C12/C10/C8	16.03	48	290	-0.7	-1.4	-0.7	27.00	34.65	28.3
C14/C10/C8	3.08	48	290	-1.6	-2.4	-0.7	7.00	8.60	22.9
C16/C10C8	0.8	48	290	-3.1	-3.9	-0.7	1.90	2.36	24.0
C14/C12/C8	3.08	16.03	290	-0.8	-2.1	-2.7	6.77	7.69	13.6
C16/C12/C8	0.8	16.03	290	-3.3	-3.9	-2.9	1.89	2.28	20.7
C16/C14/C8	0.8	3.08	290	-1.0	-3.8	-2.4	1.83	1.90	4.0
C14/C12/C10	3.08	16.03	48	-0.9	-2.5	-0.8	6.80	7.36	8.2
C16/C12/C10	0.8	16.03	48	-3.2	-3.7	-0.6	1.70	2.25	32.4
C16/C14/C10	0.8	3.08	48	-0.9	-2.9	-2.1	1.90	1.88	1.0
Average Dev.									17.2

* experimental CMC, β_{12}, β_{13} and β_{23}: from Murphy et al. (2002)

Table 7.10 CMC calculation results using the regular solution method for sodium alkyl sulphates at 318 K (Molality, ×10^{-3})*

Surfactants 1/2/3	CMC_1	CMC_2	CMC_3	β_{12}	β_{13}	β_{23}	CMC, exp.	CMC, cal.	Dev.%
C12/C10/C8	7.8	25	150	-1.4	-2.4	-1.1	14.20	17.17	20.9
C14/C10/C8	1.61	25	150	-2.2	-2.3	-2.0	4.30	4.50	4.6
C16/C10/C8	0.4	25	150	-3.1	-3.6	-1.0	1.49	1.18	20.9
C14/C12/C8	1.61	7.8	150	-0.6	-2.7	-1.4	3.60	3.97	10.3
C16/C12/C8	0.4	7.8	150	-2.6	-3.4	-1.7	1.60	1.14	28.8
C16/C14/C8	0.4	1.61	150	-0.9	-3.3	-2.8	1.30	0.96	26.2
C14/C12/C10	1.61	7.8	25	-1.9	-2.4	-1.3	3.50	3.80	8.7
C16/C12/C10	0.4	7.8	25	-1.9	-4.7	-0.6	0.96	1.12	17.2
C16/C14/C10	0.4	1.61	25	-2.1	-4.8	-1.8	1.40	0.95	32.2
C16/C14/C12	0.4	1.61	7.8	-0.5	-0.9	-1.4	1.10	0.92	16.0
Average Dev.									18.6

* experimental CMC, β_{12}, β_{13} and β_{23}: from Murphy et al. (2002)

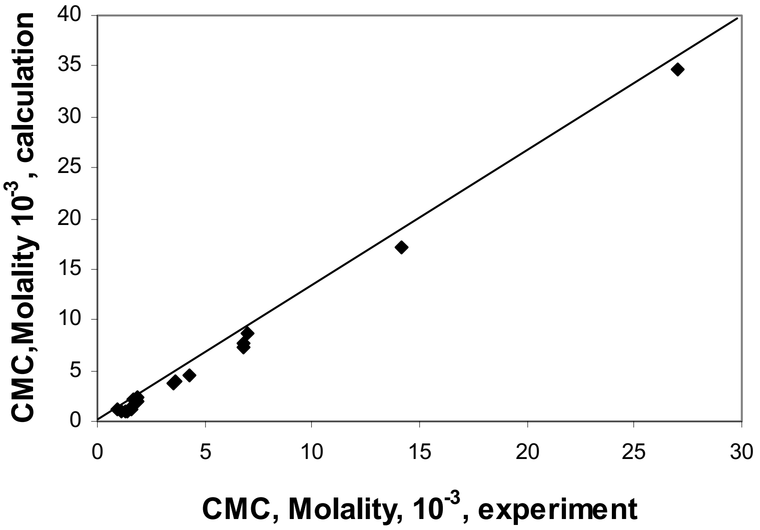


Figure 7.8 Calculated vs. experimental CMC for the ternary surfactant systems shown in Tables 7.9-7.10. Experimental CMC are from Murphy et al. (2002).

As can be seen from equations (7.12)-(7.15) and section 3.5, the regular solution method focused on activity coefficient of surfactants inside micelle (pseudo micelle phase). Micelles are considered as non-ideal liquid mixtures. The cationic and anionic surfactants in micelle phase are treated as non-dissociation components. The electrostatic properties of ionic surfactants in aqueous and micelle phase are not taken into account, even the CMC of mixed surfactants are obtained by conductive measurement (Murphy et al., 2002). In aqueous phase, activity coefficients of surfactant are set to unity.

In sections 7.2 and 7.3, activity coefficients of surfactant in aqueous phase were studied using modified Achard model. This model could be used to calculate the activity coefficient in equation (7.12). However, in the framework of regular solution method for mixed surfactants, ionic surfactants are treated as non-dissociated component. The necessary interaction parameters of non-dissociated cations and anions are not available for the modified Achard model. Therefore, the CMC of mixed surfactants are not calculated by the modified Achard model. In aqueous phase, activity coefficient is set to 1.0 in the regular solution method for mixed surfactants.

Using the modified Achard model, however, CMC of pure surfactants in aqueous solution, such as sodium alkyl sulphates, can be extrapolate to different temperatures. Based on the CMC of pure surfactants, the CMC of mixed surfactants at different temperatures can be calculated using equation (7.12) if the binary interaction parameters of surfactants can be used at different temperatures.

In principle, other activity coefficient model, such as UNQUAC and UNIFAC can be used to calculate the activity coefficients of surfactant in micelle phase. But the necessary interaction parameters of non-dissociated ionic surfactants or groups are not available for these models.

7.5 Summary

Based on Chen’s thermodynamic treatment (Chen et al., 2001) for the micelle formation of ionic surfactant solution, the modified Achard method can successfully correlate the CMC values of three surfactant families. Using the CMC data of a few surfactant + H_2O systems (two or three systems), the group interaction parameters of the modified Achard model are determined. Using these group interaction parameters, the modified Achard model can calculate the CMC values of other ionic surfactants in the same surfactant family. The modified Achard model has some potential in predicting the CMC of ionic surfactant solutions. However, the CMC prediction results for sodium carboxylates + H_2O systems are poor using the interaction parameters determined from potassium carboxylates+H_2O systems and NaCl+H_2O system.

Using regular solution method (Rubingh, 1979, Holland, 1986), CMC values of alkyl trimethylammonium bromides (at 303 K) and sodium alkyl sulphates (at 318 K) are predicted successfully based on experimental binary interaction parameters reported by Murphy et al. (2002).

Chapter 8 Correlations of Important Properties of Surfactant Solutions

In this chapter, some correlations of important properties of surfactants and surfactant solutions, e.g. the hydrophilic–lipophilic balance (HLB), the Krafft point, the cloud point and detergency are presented. Some new correlations for the aggregation number, the toxicity, the bio-concentration factor and the HLB of specific surfactant families are developed in this work. A calculation map of these properties is also presented.

8.1 Introduction

A number of properties are of interest to certain applications of surfactant solutions, e.g. the cloud point, the Krafft point, the hydrophilic-lipophilic balance (HLB), the aggregation number (n_g), and the phase inversion temperature (PIT). They are often related to emulsification and solubility, wetting, dispersing, foaming and detergency. Some of them, e.g. HLB, have no solid thermo-physical origin, but are widely used in industrial applications. These properties give a fast, less expensive and perhaps unique way to classify the abilities of surfactants.

A lot of experimental investigations have been carried out for these important properties. However, such data are scattered in many different journals and books and are somewhat difficult to retrieve. van Os and co-workers (1993) have compiled many types of physico-chemical properties for non-ionic, cationic and anionic surfactants during the period 1970-1991. Mukerjee and Mysels (1971) published a CMC data collection, and evaluated the CMC values for hundreds of surfactants. Grieser and Drummond (1988) collected data on micelle aggregation numbers. Hinz (1986) edited a thermodynamic data collection for biochemistry and biotechnology which include a chapter on experimental data of surfactant solutions.

Laughlin (1994) summarized the research history of surfactant solutions since the end of the 19th century. In this book, different theoretical concepts are comprehensively described and compared. The journal 'Current Opinion in Colloid & Interface Science' (Current Chemistry Ltd, London, UK) is now publishing review papers on different aspects of surfactant solutions, including thermodynamic theories.

Empirical correlations are often of interest to engineers so that many important properties of surfactant solutions can be estimated using one or two key properties (e.g. CMC, *K*ow). The investigated properties in this chapter are HLB, Krafft point, cloud point, aggregation number, detergency and toxicity.

In this study, many of the correlation results are directly collected from the literature. Some new correlations have been also developed for certain surfactant families.

8.2 The Hydrophilic-Lipophilic Balance (HLB)

In 1949, Griffin introduced the parameter HLB (hydrophilic - lipopholic balance) to characterise the effectiveness of polyoxyethylene surfactants as emulsifiers based on their molecular structures (Laughlin, 1994). As a consequence, the HLB number is nowadays mostly used as a parameter to compare one surfactant with others and to classify surfactants in a scale that varies from 1 to 40. The lower numbers indicate high solubility in oil (hydrophobic), while the higher numbers indicate high solubility in water (hydrophilic). The HLB should be considered as an empirical selection method that provides some general trends, but cannot be used for fine-tuning formulation. HLB value is often reported for the various surfactant products.

The surfactant HLB number is calculated directly from the relative weight of the hydrophilic and lipophilic parts of the surfactant. For instance, the HLB number of polyethoxylate non-ionic surfactants is linearly related to the percent of ethylene oxide group, EO (CH_2CH_2O), in the molecule. Using the Griffin's equation (Schick, 1987), HLB of polyethoxylate can be calculated as following.

$$\mathrm{HLB} = (\%\mathrm{EO})/5 \tag{8.1}$$

Such a HLB number cannot take into account the formulation effects that are known to be relevant, such as the nature, structure or branching of the hydrophobic group, the temperature effect, etc. Moreover, surfactants with the same HLB number can sometimes exhibit quite different behaviours.

The great importance of HLB is due to two practical uses (Bergen et al. 1998): first, the numerical value of HLB permits one to predict the kind of emulsion that can be formed, such as oil/water (O/W) if HLB>8 or water/oil (W/O) if HLB<8; second, the HLB values in surfactant mixtures are additive as follows:

$$\mathrm{HLB} = \sum_i w_i \left(\mathrm{HLB}\right)_i \tag{8.2}$$

where w_i is the weight fraction of surfactant *i*, $(\mathrm{HLB})_i$ is the HLB value of surfactant *i*. The HLB in a surfactant mixture is an average of all pure surfactant HLB numbers with a numerical weight factor identical to the weight fraction w_i. This is a useful equation in the design of emulsions.

An alternative method for characterizing emulsifying agents is the phase inversion temperature (PIT). With nonionic surfactants, below this temperature range the surfactant is soluble in water and above this range it is soluble in oil (Marszall, 1987). Thus, the PIT is the temperature at which the surfactant shifts its preferential solubility from water to oil, as the temperature is increased.

Different methods have been developed to relate HLB to the properties of surfactants or surfactant solutions. Most of them are empirical correlations. However, Bergen et al. (1998) made an effort to examine the possible relation between HLB and the parameters of equation of state of a lattice fluid. In our work, the relation between HLB and CMC is of interest since CMC can be obtained from thermodynamic considerations. Some estimation methods for HLB are presented here.

(1) *Davies's Method for Estimating HLB*

Davies et al. (1963) suggested a group-contribution method for estimating HLB of surfactants directly from their structure. The HLB is calculated from the following equation:

$$\text{HLB}=7+\sum(\text{hydrophilic group numbers})+\sum(\text{lipophilic group numbers}) \qquad (8.3)$$

where the summations are over all (hydrophobic and lipophilic) groups. Group numbers (i.e. group contribution parameters) are estimated for various groups of surfactant molecules, e.g., CH_3, $-CH_2$, -COO-, $-CH_2CH_2O-$, etc., as listed in Table 8.1. For many cases, Davies has shown that the HLB numbers calculated from this equation are in satisfactory agreement to the experimental data. However, this equation is based on the assumption that each individual group has the same hydrophilic or hydrophobic contribution in all situations, thus the equation fails in some cases.

For a given structure, the HLB is calculated by substituting the group number (listed Table 8.1) into equation (8.3). For example, the HLB of $C_{12}H_{25}OSO_3Na$ (SDS) is

$$\text{HLB}=7+38.7+12\times(-0.475)=40.0$$

The literature HLB number is also 40 for SDS (Becher, 1987).

Table 8.1 HLB group values (Davies et al., 1963)

Hydrophilic group	Group number	Lipophilic group	Group number
$-SO_4Na^+$	38.7	-CH-	–0.475
$-COO^-H^+$	21.1	$-CH_2-$	–0.475
$-COO^-Na^+$	19.1	CH_3-	–0.475
N(tertiary amine)	9.4	=CH-	–0.475
Ester (sorbitan ring)	6.8	$-CF_2-$	–0.870
Ester (free)	2.4	$-CF_3-$	–0.870
-COOH	2.1	Derived groups	
OH (free)	1.9	$-(CH_2-CH-O)-$	0.33
-O-	1.3	$-(CH_2-CH-(CH_3)-O)-$	–0.15
OH (sorbititan ring)	0.5		

(2) *General Correlations Between CMC and HLB*

By regressing experimental data for ionic and nonionic surfactant solutions at 25ºC, some researchers (Lin and Marszall, 1976, 1977, Wang, 1986) derived a series of relationships for CMC and HLB or effective number of carbon atoms in chain (n_{eff}), as shown in Table 8.2.

Table 8.2 Correlations of CMC (molality) and HLB or effective number of carbon atoms in chain (n_{eff}) at 25ºC

No	Correlation	Surfactant	Ref.
1	logCMC=–37.14 + 0.866HLB	Sodium alkyl sulfates	Ref. 1
2	logCMC=1.665 – 0.314 n_{eff} (1) n_{eff}=12.32+0.3635x (2) n_{eff}=15.98+1.11x –0.15x^2 (3) n_{eff}=17.6+0.44x x=number of group OCH_2CH_2	 (1)$C_{12}H_{25}(OCH_2CH_2)_xOSO_3Na$ (2)$C_{16}H_{33}(OCH_2CH_2)_xOSO_3Na$ (3)$C_{18}H_{37}(OCH_2CH_2)_xOSO_3Na$	Ref. 1
3	logCMC=1.775 – 0.291 n_{eff} (1) n_{eff}=10.15+0.85x (2) n_{eff}=12.18+0.95x x=number of group OCH_2CH_2	 (1)$C_{10}H_{21}(OCH_2CH_2)_xN(CH_3)_3Cl$ (2)$C_{12}H_{25}(OCH_2CH_2)_xN(CH_3)_3Cl$	Ref. 1
4	logCMC=1.855 – 0.305 n_{eff} (1) n_{eff}=10.15+0.85x (2) n_{eff}=12.18+0.95x (3) n_{eff}=16.17+1.2x x=number of group OCH_2CH_2	 (1)$C_{10}H_{21}(OCH_2CH_2)_xNC_5H_5Cl$ (2)$C_{12}H_{25}(OCH_2CH_2)_xNC_5H_5Cl$ (3)$C_{16}H_{33}(OCH_2CH_2)_xNC_5H_5Cl$	Ref. 1
5	logCMC= –16.287 + 0.734 HLB logCMC = 3.109 – 0.647n n=carbon number	$C_nF_{2n+1}COONa$	Ref. 2

Ref. 1: Lin and Marszall (1976, 1977)
Ref. 2: Wang, 1986

(3) *Correlation Between HLB and Partition Coefficient*

Davies et al. (1963) have shown that the distribution constant ($K=C_w/C_0$) of alcohol ethoxylates is related to HLB as:

$$HLB=7 + 0.36 \ln(C_w/C_0) \qquad (8.4)$$

where C_w and C_0 are the concentrations of the surfactant in water and oil (heptane) phases, respectively. If the oil is *n*-octanol, then *K* is equal to octanol-water partition coefficient (*K*ow) (Birdi, 1999). However, only very few experimental *K*ow data of surfactants are available. There is no further investigations in the literature for the relationship of HLB with *K*ow.

8.3 Correlations of the Krafft Point

Surfactants have unusual solubility behaviour as their solubilities exhibit a rapid increase above a certain temperature, known as the Krafft point or Krafft temperature, as shown schematically in Figure 8.1. This solubility behaviour is mostly observed for ionic surfactants. This behaviour is explained due to the fact that non-associated surfactants have a limited solubility, whereas micelles are able to solubilize non-polar materials in aqueous solutions. Below the Krafft point the surfactant molecules are non-associated and thus solubility is limited. When the temperature is raised, the solubility increases very slowly until the Krafft point is reached. At the Krafft point, micelles are formed and a large increase in solubility is therefore observed. It is desirable to make a formulation above the Krafft temperature if complete solubilization is required. For example, many wash powders, which contain mixed surfactants, have good detergency at higher temperatures.

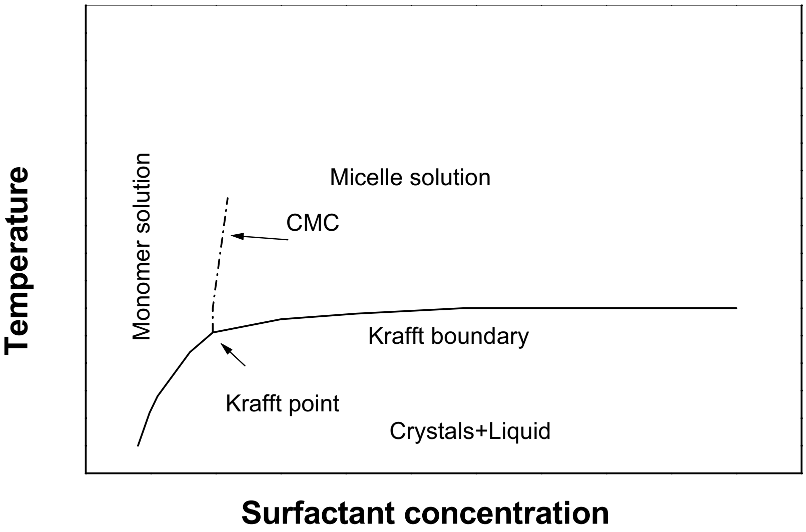


Figure 8.1 Schematic diagram of the Krafft point of surfactant solution

The Krafft point depends on complex three-phase equilibrium and the counter ion of the surfactant. The chain length of the hydrophobic part and the presence of electrolytes do also influence the Krafft point of ionic surfactants. The addition of electrolytes increases the Krafft point.

Surfactants with a high Krafft temperature have ionic head groups or have compact highly polar head-groups and long straight alkyl chains. Lower Krafft point temperature can be obtained with branched alkyl chains or bulkier hydrophobic groups (e.g. two alkyl chains). If the surfactant solution exhibits surface-activity based characteristics, such as wetting, the solution would be used below or near its Krafft point, whereas if high solubility is required, the solution need to be used at temperatures above the Krafft point.

Several estimation methods have been proposed for Krafft point. Huibers (1996a) used quantitative structure-property relationships (QSPR) to correlate the Krafft point with molecule structure information and obtain a predictive relation for the Krafft points of 44 surfactants. In our study, correlations between Krafft point and molecular structure or CMC are presented.

(1) *Correlation of Gu et al.* (1992)

In the work of Gu et al., (1992), the Krafft points (KP, ºC) are correlated with the structure of different surfactant molecules. In the case of ionic ethoxylated surfactants of type $C_nH_{2n+1}(OCH_2CH_2)_mSO_4^-Na^+$, the dependence between the KP and the molecular structure units can be expressed as

$$\mathrm{KP} = k_c n_c - 9m_{EO} - k_i \tag{8.5}$$

where n_c is the number of hydrocarbon groups in alkyl chain, n_c = 16, 18, m_{EO} is the number of ethylene oxide unit (OCH_2CH_2) in $C_nH_{2n+1}(OCH_2CH_2)_mSO_4^-Na^+$ molecule, m_{EO}=1~4. In the equation k_c and k_i are constants depending on the ionic headgroup, which are given in Table 8.3.

For surfactants with a single straight hydrocarbon chain, the KP can also be related to the number of hydrocarbon groups, n_c (n_c = 10~18) by

$$\mathrm{KP} = k_c n_c - k_i \tag{8.6}$$

where k_i and k_c are the values listed in Table 8.3.

Table 8.3 Constants k_c and k_i of ionic surfactants for equations (8.5)–(8.6)

No	Type of surfactant	k_c	k_i
1	$C_nH_{2n+1}SO_4^-Na^+$	5.5	44
2	$2\text{-}MeC_nH_{2n}SO_4^-Na^+$	5.5	61
3	$C_nH_{2n+1}[OCH_2CH(CH_3)]_2SO_4^-Na^+$	5.5	69
4	$C_nH_{2n+1}OCH_2CH(SO_4^-Na^+)CH_3$	5.5	60
5	$C_nH_{2n+1}(OC_2H_4)_mSO_4^-Na^+$	5.5	44
6	$Na^+O_4^-S(CH_2)_nSO_4^-Na^+$	5.5	52
7	$Li^+O_4^-S(CH_2)_nSO_4^-Li^+$	5.5	45
8	$K^+O_4^-S(CH_2)_nSO_4^-K^+$	5.5	43
9	$C_nH_{2n+1}SO_3^-Na^+$ (even n)	5.5	29
10	$C_nH_{2n+1}SO_3^-Na^+$ (odd n)	5.5	34
11	$C_nH_{2n+1}COO(CH_2)_2SO_3^-Na^+$	5.5	44
12	$C_nH_{2n+1}OOC(CH_2)_2SO_3^-Na^+$	5.5	41
13	$C_nH_{2n+1}CHCH_3C_6H_4SO_3^-Na^+$	5.5	24
14	$C_nH_{2n+1}CH(SO_3^-Na^+)CH_2OH$	5.5	-6
15	$C_nH_{2n+1}CH(SO_3^-Na^+)COOH$	5.5	-3
16	$C_nH_{2n+1}CH(SO_3^-Na^+)COONa$	5.5	-1
17	$C_nH_{2n+1}CH(Py^+)COO^-$ (Py^+=pyridinium)	5.5	41
18	$(C_nH_{2n+1}SO_4^-)_2Ca^{2+}$	11	85
19	$(C_nH_{2n+1}SO_4^-)_2Mg^{2+}$	11	115
20	$(C_nH_{2n+1}SO_4^-)_2Mn^{2+}$	11	121
21	$(C_nH_{2n+1}SO_4^-)_2Cu^{2+}$	11	113
22	$(C_nH_{2n+1}SO_4^-)_2Zn^{2+}$	11	121

8.4 Correlations of the Cloud Point

Surfactants in aqueous solution show miscibility gab with a lower and/or an upper critical solution temperature. When heating (or cooling) a non-ionic aqueous solution, a separation into two phases occurs at a certain temperature as the surfactant “drop out of” the solution indicated by the cloud boundary as shown in Figure 8.2. This temperature is called the cloud point, as this mixture becomes cloudy when the separation process starts. The cloud point is also sometimes called a lower (or upper) consolute temperature (point).

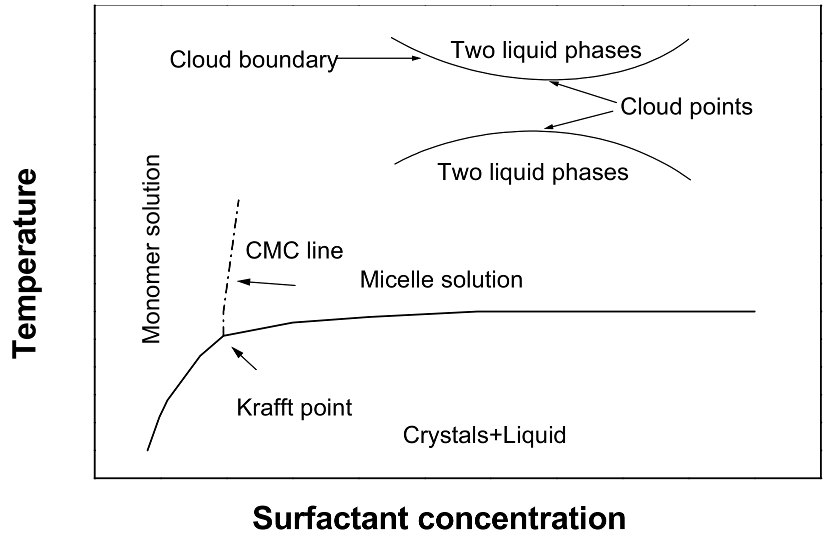


Figure 8.2 Schematic diagram of cloud points (upper or lower critical solution temperature) for surfactant solutions

The phase behaviour (cloud boundary) of surfactant solutions has been widely investigated. Chernik (2000) reviewed the phase studies of surfactant + water systems for typically used non-ionic and ionic surfactants. Garcia-Lisbona et al. (1998) used a simplified version of the statistical associating fluid theory (SAFT) to examine the liquid-liquid immiscibility of aqueous alkyl polyoxyethylene surfactant solutions. Rudolph et al. (2000) investigated the phase behaviour of the water + alkyl polyoxyethylene system. Based on Rudolph's measurements at pressures up to 100MPa and over a temperature range 315 – 355 K, the Peng-Robinson equation of state with the Wong-Sandler mixing rules and the UNIQUAC model were used to model the system. Lai et al. (1999) used UNIQUAC model to correlate the liquid-liquid equilibrium data for three binary systems (water + alcohol ethoxylates), ranging from their lower consolute solution temperature to 70°C at atmospheric pressure. Huibers et al. (1997b) developed a quantitative structure-property relationship (QSPR) to estimate the cloud point of pure nonionic surfactant of alkyl ethoxylates. Below, some correlations are presented.

(1) *Correlation by Gu and Sjöblom* (1992)

Gu and Sjöblom (1992) developed a linear relationship between the cloud point (CP) and the logarithm of the ethylene oxide number for nonionic surfactants:

$$\mathrm{CP} = A\log(n_{EO}) - Bn_C - C \tag{8.7}$$

where CP is the cloud point with unit in K, n_{EO} is the ethylene oxide unit for alkyl ethoxylates, alkylpenyl ethoxylates and methyl capped alkyl ethoxylate esters (n_{EO}=5-8) and n_{C} is the alkyl carbon number for linear alkyl ethoxylates (n_{C}=6-16). In the equation, *A*, *B* and *C* are empirical constants depending on the surfactants as shown in Table 8.4.

Table 8.4 Constants *A*, *B*, *C* for equation (8.7)*

No	Type of surfactant	*A*	*B*	*C*
1	$C_nH_{2n+1}(OC_2H_4)_mOH$	220	5.5	55
2	$C_nH_{2n+1}C_6H_4(OC_2H_4)_mOH$	278	5.5	171
3	$C_nH_{2n+1}COO(C_2H_4O)_mCH_3$, n=9, 11	152	0.0	87

* subscript m: ethylene oxide unit n_{EO}, subscript n: alkyl carbon number n_C

(2) *Correlation of Huibers et al.* (1997b)

Huibers et al. (1997b) re-calculated the empirical relationship of equation (8.7) (Gu and Sjöblom, 1992) with a larger data set and obtained a new set of coefficients for the linear alkyl ethoxylates:

$$\mathrm{CP} = 87.1\log n_{EO} - 5.78n_C - 40.7 \tag{8.8}$$

Based on the correlation, it is found that the carbon number (n_{c}) is an inadequate descriptor for modelling the cloud point except for linear alkyl ethoxylates. Huibers et al. (1997b), thus further developed a correlation using several topological descriptors from connectivity or topology of molecules to get better regression results for the cloud point. The correlations of topological method can be found in the work of Huibers et al. (1997b).

8.5 Correlations of the Detergency

The detergency is described as (Zimoch et al., 2000):

$$D = \frac{Y - C}{A - C}\% \tag{8.9}$$

where D is the detergency, Y and C are the average whiteness degree of the investigated test fabric after and before washing, respectively, and A is the average whiteness of the investigated fabric, not soiled.

Detergency is a complex physicochemical process, which occurs at the interface between fabrics contaminated with soil and surfactant aqueous solutions. Many parameters affect the detergency during a washing process. The efficiency of washing depends on the properties of washed fabrics, type and composition of soil, composition of washing bath and washing conditions. The wetting of the hydrophilic fabrics and emulsifications of soil deposited on the fabrics play a crucial role in the effectiveness of washing.

In practice, the washing ability is measured using the standard, tedious and time-consuming experiments in which swatches of standard soiled fabrics are washed in specially designed washing device. Carroll (1993) investigated the physical characteristics of detergency. Miller et al. (1993) studied the solubilization mechanism of detergency. But, their investigations and theories cannot be generalized for complex washing system.

Correlation methods are often used to shorten the period of time to determine the optimal formulations of washing agents. Zimoch et al. (2000) and Lindgren et al. (1994) modelled the detergency with physical properties of surfactants. Some of their results are presented here.

(1) *Correlations of Zimoch et al.* (2000)

Zimoch et al. investigated the relations of detergency with surface tension and HLB using three standard test swatches: Krefeld 10C (cotton fabric), Krefeld 20C (65% polyester and 35% cotton mixed cloth) and Krefeld 30C (polyester) for alcohol ethoxylate surfactants. Correlation results are presented as follows:

Krefeld 10C:

$$\ln D = 1.72 \ln DP - 5.55 DP^2 - 0.0501 \gamma_{CMC} + 0.0176 T \tag{8.10}$$

Krefeld 20C:

$$\ln D = 0.0352 CP + 1.76 DP - 7.87 \times 10^{-3} DP^2 - 0.135 \gamma_{CMC} + 0.0186 T \tag{8.11}$$

Krefeld 30C:

$$\ln D = 0.144 DP - 0.554 HLB + 0.0204 T \tag{8.12}$$

where *D* is the detergency, *DP* is the distribution of the polyoxyethylene chain in the products, *CP* is the cloud point, γ_{CMC} is the surface tension at the critical micelle concentration (CMC), HLB is the hydrophilic lipophilic balance, *T* is the temperature (°C). *CP* and γ_{CMC} were measured for the mixed alcohol ethoxylate surfactants.

The *DP* is calculated as

$$DP = \frac{1}{n} \sum_{i=1}^{n} w_i^2 n_{EO} \times 100 \tag{8.13}$$

where *n* is the number of surfactants in mixture, w_i is the weight per cent of surfactant *i*, n_{EO} is the oxyethylene unit.

These correlations are in agreement with the washing theory. The positive coefficients for temperature in equations (8.10)-(8.12) reflect the positive effect of temperature on detergency of ethoxylates, i.e. increasing washing temperature results in better washing effect (larger detergency (D) value in equations (8.10)-(8.13)). The negative coefficients with the surface tension related to the positive effect of surfactant surface activity on detergency. The presence of two terms containing *DP* (or HLB) with positive and negative coefficients reflects the existence of maximum detergency.

8.6 New Developed Correlations

In this section some new developed correlations are presented. These new correlations focused on general and environmental properties of the priority surfactant families in the guidelines of the Danish environmental research programme (mentioned in Chapter 1).

8.6.1 Correlation of HLB with CMC

(1) *Correlations for Polyoxyethylene Sodium Alkyl Sulfates*

The polyoxyethylene sodium alkyl sulfates ($C_nH_{2n+1}(OC_2H_4)_mSO_4^-Na^+$) are nontoxic, biodegradeable, and industrial useful surfactants. However, no correlation between HLB and CMC could be found in the literature. Such a correlation was developed in our work using the experimental data presented in Table 8.5. An excellent linear relationship is obtained as shown in equation (8.14) and figure 8.3.

$$\log \mathrm{CMC} = -28.726 + 0.666\,\mathrm{HLB},\ r^2=0.999 \tag{8.14}$$

where r^2 is the correlation coefficient.

Table 8.5 HLB and CMC data (Lin et al.,1976)

	$C_nH_{2n+1}(OC_2H_4)_mSO_4^-Na^+$		CMC, 25ºC	HLB
No.	n	m	Molality	
1	12	0	8.10E-03	40
2	12	1	4.20E-03	39.57
3	12	2	3.10E-03	39.38
4	12	3	2.80E-03	39.24
5	12	5	1.90E-03	39.05
6	14	0	2.10E-03	39.05
7	16	0	4.00E-04	38.1
8	16	1	2.20E-04	37.62
9	16	2	1.40E-04	37.34
10	16	3	1.00E-04	37.15
11	16	4	1.00E-04	37.15
12	18	0	1.10E-04	37.15
13	18	1	1.10E-04	37.15
14	18	2	7.00E-05	36.91
15	18	3	5.00E-05	36.63
16	18	4	4.00E-05	36.53

* HLB and CMC data are from Lin et al. (1976)

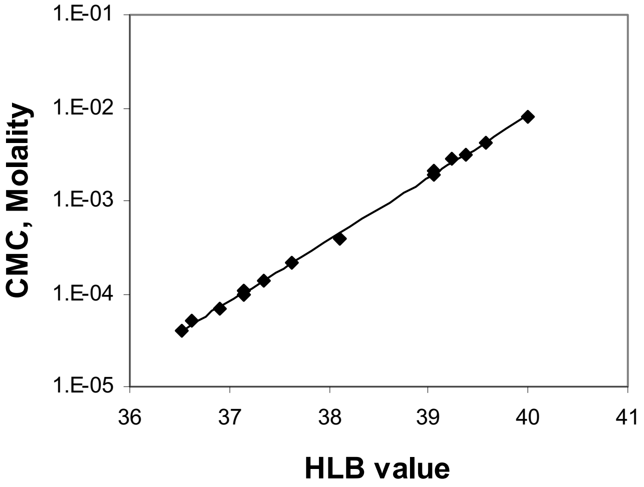


Figure 8.3 CMC of the polyoxyethylene sodium alkyl sulfates as a function of HLB

8.6.2 Correlation of CMC with the Krafft Point

In the correlations of Gu et al. (1992), i.e. equations (8.5)-(8.6), the KP is correlated with the hydrocarbon groups in the alkyl chain and the number of ethylene oxide unit. However, the KP can also be correlated to CMC. Taking advantage of the correlation results of Gu et al. (1992), the Krafft point is correlated to CMC by

$$\mathrm{KP} = -(k_c / B)\log \mathrm{CMC} + k_c A - k_i, \quad r^2=0.988 \qquad (8.15)$$

where k_c and k_i are given in Table 8.3., CMC is the critical micelle concentration in molality scale (25ºC), r^2 is the average correlation coefficient of these correlations, and the constants A and B are given in Table 8.6. The experimental data of Krafft point and CMC from Brandrup et al. (1975) and van Os et al. (1993) were used. The results for two surfactant families are given in Figure 8.4.

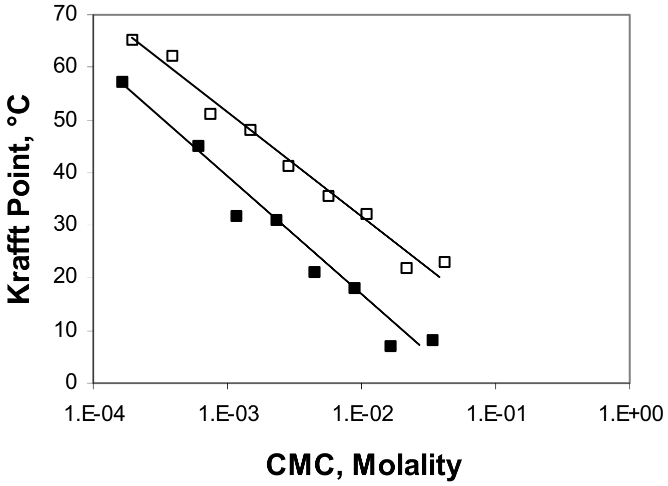


Figure 8.4 Relationship between CMC and Krafft points (equation 8.15). White and black squares: experimental data of sodium alkyl sulfonates and sodium alkyl sulfates, respectively.

Table 8.6 Constants *A*, *B* of ionic surfactants

No	Surfactant	*A*	*B*
1	$C_nH_{2n-1}OO^-Na^+$, n=12-18	1.96	0.296
2	$C_nH_{2n-1}OO^-K^+$, , n=12-18	1.96	0.296
3	$C_nH_{2n+1}SO_4^-Na^+$, n=10-18	1.43	0.290
4	$C_nH_{2n+1}SO_3^-Na^+$ n=10-18	1.53	0.290
5	$C_nH_{2n+1}CHCH_3C_6H_4SO_3^-Na^+$, n=10-16	-0.456	0.215
6	$C_nH_{2n+1}CH(SO_3^-Na^+)CH_2OH$	2.529	0.364
7	$C_nH_{2n+1}CH(SO_3^-Na^+)COONa$	1.514	0.240
8	$C_nH_{2n+1}OOC(CH_2)_2SO_3^-Na^+$	1.108	0.30

8.6.3 Correlation of Aggregation Number with CMC

In surfactant solutions, the micelle formation process is a gradual self-association of surfactant molecules. Around the critical micelle concentration, the amount of the associated surfactant group (aggregates) in solution is so high that the properties of the solution are rapidly changed. Around the CMC, the average number (aggregation number) of surfactant molecules in each aggregate can be measured by light scattering method. After CMC, the micelles (aggregates) continue to grow with increasing concentration of the surfactant. Finally, phase separation occurs. Grieser and Drummond (1988) have collected experimental aggregation number data. In our study, empirical relationships between aggregation number and CMC are regressed for several surfactant families, as shown in Table 8.7 using the data from van Os et al. (1993). The correlation results are also given in figures 8.5 and 8.6. In figure 8.5, the regression line is extended to low CMC values reported by van Os et al. (1993) to observe the extrapolated aggregation number. But no aggregation number data have been reported for the low CMC values.

Table 8.7 Correlations for aggregation number (n_g) vs. CMC (in molality, 25ºC)

No	Surfactant	Correlation	r^2
1	$C_nH_{2n+1}SO_4Na$	n_g=8.333–21.92logCMC, n=8–18	0.986
2	$C_{12}H_{25}(OCH_2CH_2)_mOH$	logn_g= – 3.2604 – 1.24597logCMC, m=4–12	0.96
3	$C_{16}H_{33}(OCH_2CH_2)_mOH$	logn_g= – 9.25699 – 2.05724logCMC, m=7–21	0.975
4	$C_9H_{19}C_6H_4(OCH_2CH_2)_mOH$	logn_g= – 4.160 – 1.553logCMC, m=10–50	0.98

* r^2 is the correlation coefficient

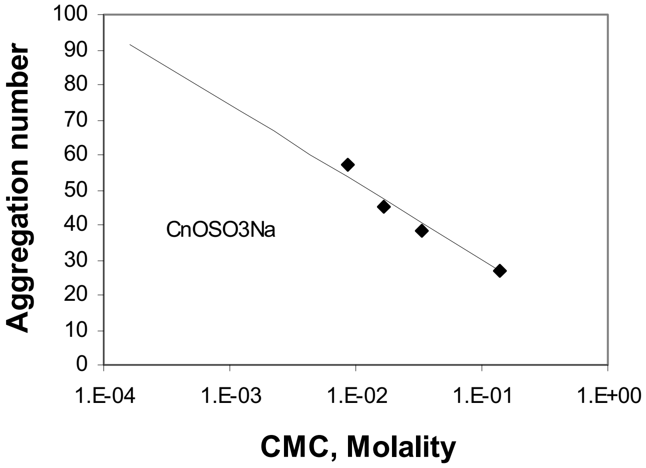


Figure 8.5 Correlation results for $C_nH_{2n+1}SO_4Na$ (CnOSO3Na). Points: experimental data from van Os et al. (1993) at 25°C. Line: regression result.

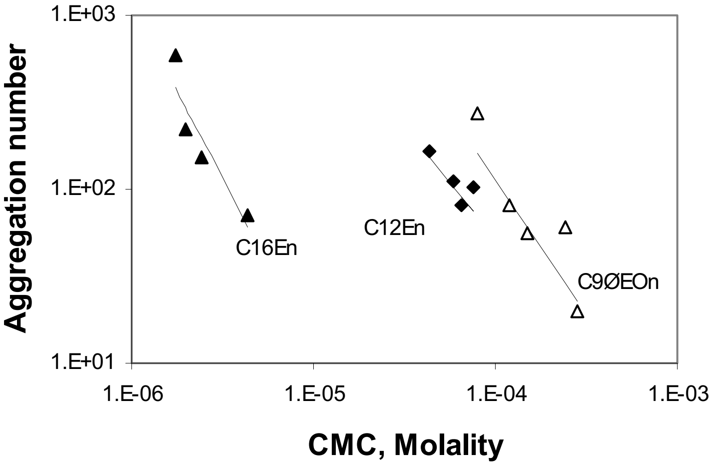


Figure 8.6 Correlation results for $C_{12}H_{25}(OCH_2CH_2)_mOH$ (C12En), $C_{16}H_{33}(OCH_2CH_2)_mOH$ (C16En), $C_9H_{19}C_6H_4(OCH_2CH_2)_mOH$ (C9ØEOn). Points: experimental data from van Os et al. (1993) at 25°C. Lines: regression results.

8.6.4 Correlation of *K*ow with HLB

The relationship of *K*ow and HLB is investigated in this section. Davies et al. (1963) proposed a linear correlation for HLB and partition coefficient, i.e. equation (8.4). Birdi (1999) suggested that this partition coefficient could be replaced by the octanol-water partition coefficient (*K*ow). In chapter 4, the *K*ow has been investigated by UNIFAC and commercial software. Because HLB can be easily obtained or calculated for surfactants, a correlation for HLB and *K*ow is very helpful for practical applications even if *K*ow cannot be easily measured for surfactants.

Both HLB and *K*ow are parameters to describe the hydrophobic and hydrophilic properties of a chemical. HLB is an approximated parameter and often used for surfactants, and *K*ow is a strict thermodynamic parameter. The HLB value is a summation of the contributions from the hydrophobic and the hydrophilic groups. As can be seen from Table 8.1, hydrophilic groups have a positive contribution to HLB, and hydrophobic groups give a negative contribution. The chemicals with longer hydrophilic chain will have larger HLB. Oppositely, the longer hydrophilic group chain a chemical has, the lower *K*ow value a chemical will have.

All HLB values for alcohol ethoxylates ($R(CH_2CH_2O)_nOH$, C_mE_n) are directly calculated by group contribution method using equation (8.3). *K*ow values are taken from the prediction results in Chapter 4. Using the HLB and the predicted *K*ow values from ClogP software and UNIFAC VLE 1 (see Appendix A) for alcohol ethoxylates, linear relations are developed, as shown in Table 8.8. Figures 8.7 and 8.8 show the comparisons of model calculations and predicted *K*ow from ClogP and UNIFAC VLE 1. As can be seen from figures 8.7-8.8, equations A, B, C and D are in good agreement with predicted *K*ow values from ClogP and UNIFAC VLE 1.

Table 8.8 Correlations between log*K*ow and HLB for alcohol ethyoxylates *

No	Source of log*K*ow values	Correlation equation	r^2**
A	ClogP software	$\log Kow = -3.05751 + 0.61999 n_C + 0.1940\text{HLB}$	0.999
B	ClogP software	$\log Kow = 8.5624 + 0.43264 n_{EO} - 1.1130\text{HLB}$	0.998
C	UNIFAC VLE 1	$\log Kow = 9.05947 - 0.08492 n_C - 1.11858\text{HLB}$	0.999
D	UNIFAC VLE 1	$\log Kow = 7.46141 - 0.05685 n_{EO} - 0.94101\text{HLB}$	0.997

* n_C: number of alkyl group (CH_2), n_C=4-16, n_{EO}: the number of oxyethylene group (OCH_2CH_2), n_{EO}=1-30
** r^2 is the correlation coefficient

The correlations of Table 8.8 show that the effect of equation D is in agreement with the above analysis, i.e. increasing hydrophilic chain (n_{EO} number in equation D) will give larger HLB but smaller *K*ow. However, the coefficients for HLB in equation B indicates different effects, i.e. increasing n_{EO} number in equation does not give smaller *K*ow. In Chapter 4, figures 4.3-4.4, 4.8-4.10 show that ClogP and UNIFAC VLE 1 have opposite trends with increasing hydrophilic group number. The coefficients of n_{EO} in equations B and D have opposite signs and reflect the different trends. It further demonstrates that UNIFAC VLE 1 is a good method to predict the *K*ow for surfactants, as discussed in Chapter 4.

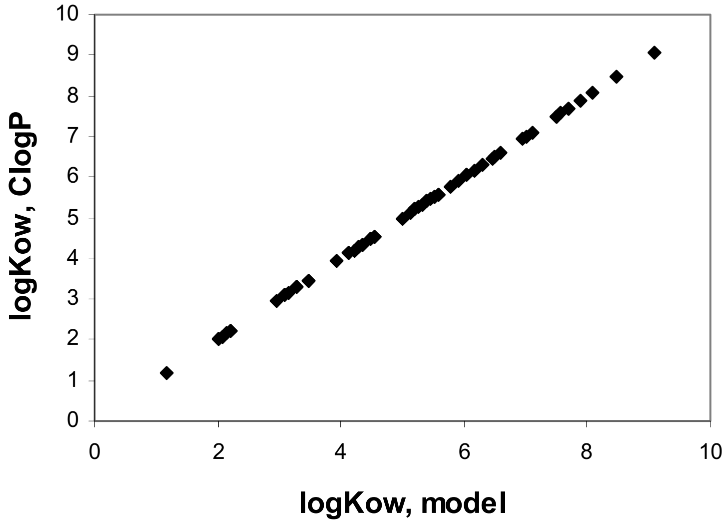


Figure 8.7 Scatter plot of the equation A and B (model) vs. ClogP for log*K*ow values of alcohol ethoxylates

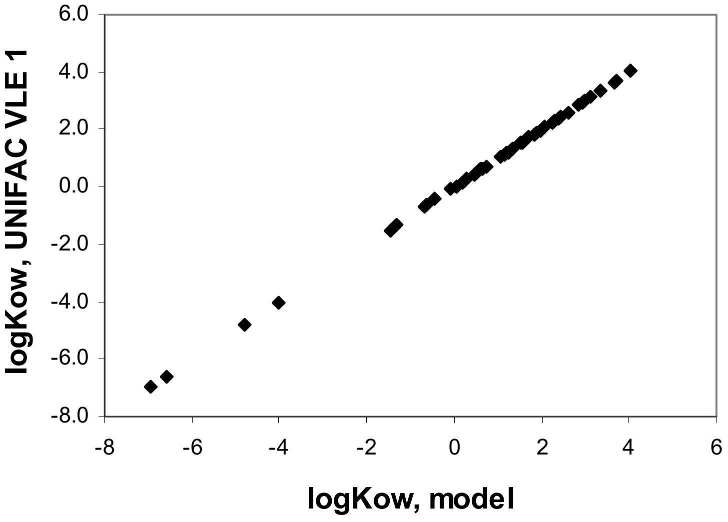


Figure 8.8 Scatter plot of the equation C and D (model) vs. UNIFAC VLE 1 for log*K*ow values of alcohol ethoxylates

Table 8.9 gives log*K*ow calculation results for alcohol ethoxylates using the equations in Table 8.8 and compares with few experimental *K*ow data. As can be seen, the equations C and D produce very stable *K*ow values and are in good agreement with UNIFAC VLE 1. Equations A and B match well ClogP values except for C3E1.

Based on these correlations, the log*K*ow value can be easily calculated from HLB and one structural parameter n_C or n_{EO}. These correlations provide the basis to set up correlation for *K*ow and environmental properties which is given in the next section.

Table 8.9 log*K*ow calculation results for alcohol ethoxylates using equations in Table 8.8

Compound	Exp.*	ClogP	Eq. A	Eq. B	VLE1*	Eq. C	Eq. D
C1E1	-0.77	-0.75	-0.74	-0.75	-0.83	-0.82	-0.83
C2E1	-0.28	-0.22	-0.21	-0.22	-0.38	-0.37	-0.39
C2E2	-0.54	-0.15	-0.15	-0.16	-0.75	-0.74	-0.75
C3E1	0.05	0.09	0.32	0.31	0.07	0.07	0.06
C4E1	0.8	0.84	0.84	0.84	0.51	0.52	0.51
C4E2	0.56	0.91	0.91	0.90	0.15	0.15	0.14
C6E1	1.86	1.90	1.90	1.89	1.41	1.41	1.40
C6E2	1.7	1.96	1.96	1.96	1.04	1.04	1.03
Mean Dev.%		33	91	87	36	36	35

*Exp.: experimental data from Sangster (2001), VLE1: original UNIFAC VLE 1 (Hansen et al., 1991).

In Table 8.9,

$$\text{Mean Dev.\%} = \frac{1}{n}\sum_{1}^{n}\frac{\left|\log K\text{ow}^{\text{Exp}} - \log K\text{ow}^{\text{Cal}}\right|}{\left|\log K\text{ow}^{\text{Exp}}\right|}\%, \; n \text{ is the total number of data.}$$

8.6.5 Correlation of *K*ow with Environmental Properties

As presented in Table 2.6 (Chapter 2), Denmark consumes about 20,000 tons surfactants as cleaning products in 1998; Europe markets need 1.7 million tons surfactants annually. All these consumed surfactants will finally enter our nature. Therefore, the environmental effects of surfactants have been heavily debated in public. The Danish Environmental Protection Agency (EPA) has systematically investigated and published reports about the environmental effects of surfactants. Modelling work for the environmental effects of surfactants will help EPA to evaluate the newly released surfactants. In our work, the correlations of *K*ow and environmental effects are developed.

(1) *Correlation of Kow with Bio-concentration Factor (BCF)*

The bio-concentration factor (BCF) is a description of bioaccumulation of chemical in aquatic organisms, normally fish, and calculated as:

$$\mathrm{BCF} = \frac{\text{mean measured concentration in fish}}{\text{mean measured concentration in water}}$$

BCF shows the accumulation of chemicals in aquatic organisms, and indicates the amount of chemical concentrated in organisms during 54-72 hours. For example, BCF is 799 for $C_{14}E_7$ at 26°C (Madsen et al., 2001). It means the concentration of $C_{14}E_7$ in aquatic organisms is around 800 times higher than in water.

For alcohol ethoxylates, a relation of BCF and *K*ow is obtained as:

$$\log \mathrm{BCF} = 0.97209 + 0.38957 \log \mathrm{Kow} + 0.01912 (\log \mathrm{Kow})^2, \; r^2=0.8 \tag{8.16}$$

where r^2 is the correlation coefficient. The correlation results of equation (8.16) are also given in Table 8.10 and figure 8.9. In Table 8.10, log*K*ow values are calculated by equation D in Table 8.8. Using equations A, B and C in Table 8.8 can obtain similar results. But equations C and D are reliable for alcohol ethyoxylates based on the analysis in section 8.6.4.

As can be seen, correlation equation (8.16) is in good agreement with the experimental BCF values and gives correct BCF trend, i.e. the BCF value in fish will decrease with increasing hydrophilic group (OCH_2CH_2) number of alcohol ethoxylates.

Table 8.10 Experimental and model calculation results for whole body BCF of alcohol ethyoxylates in fish. Experimental BCF values are from Madsen et al., (2001)

Surfactant/species	logBCF, exp.	logBCF, cal.	log*K*ow
$C_{12}E_4$, Carp (Cyrinus carpio)	2.49	2.30	2.98
$C_{12}E_8$, Carp	2.35	1.60	1.51
$C_{12}E_{16}$, Carp	0.63	0.45	-1.441
$C_{13}E_4$, Fathead minnow	2.37	2.53	3.43
$C_{13}E_8$, Fathead minnow	1.62	1.81	1.96
$C_{14}E_4$, Fathead minnow	2.37	2.77	3.877
$C_{14}E_7$, Bluegill subfish	2.90	2.20	2.77
$C_{14}E_8$, Fathead minnow	1.98	2.02	2.402
$C_{14}E_{11}$, Fathead minnow	1.20	1.51	1.296
$C_{14}E_{14}$, Fathead minnow	0.70	1.05	0.19
$C_{16}E_8$, Fathead minnow	2.59	2.46	3.296

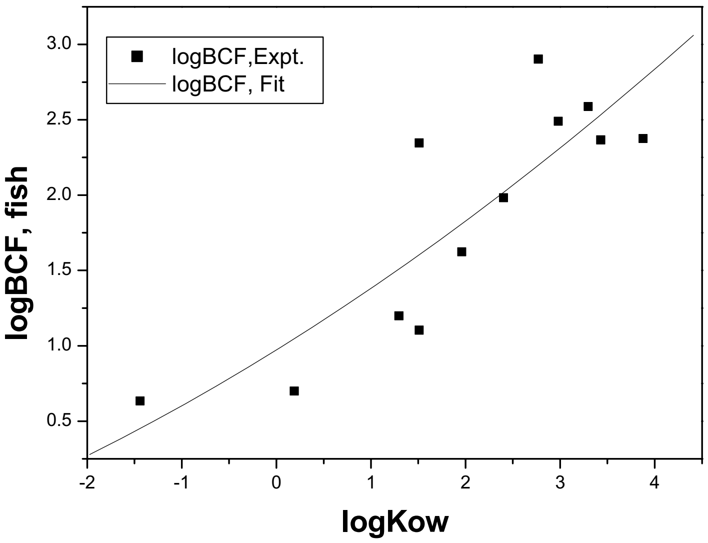


Figure 8.9 Equation (8.16) calculation results for whole body BCF of alcohol ethoxylates in fish using the log*K*ow as correlation parameter. Experimental BCF values are from Madsen et al. (2001).

(2) *Correlation of Kow with Toxicity*

Toxicity is a very important property and often used to establish regulations in chemical management. Using *K*ow to correlate and predict toxicity has a long history (Schultz, 2003). *K*ow is one of the standard parameters for EPA to evaluate the toxicity of chemicals. In our work, a new correlation model for toxicity and *K*ow of alcohol ethoxylates is developed.

Toxicity to algae, invertebrates, fish and rat data are taken from the collection of Madsen et al. (2001) for alcohol ethoxylates which includes C_iE_j, i=9~18, j=1~30. *K*ow data are calculated by UNIFAC VLE 1 (see Appendix A) and compared with correlation equation D in Table 8.8. The comparison between UNIFAC VLE 1 and equation D is given in figure 8.10. Figure 8.10 shows the simple equation D can be used to replace UNIFAC VLE 1 in the *K*ow calculation for alcohol ethoxylates. Based on the toxicity and *K*ow data, linear correlations are obtained and given in Table 8.11 and figures 8.11-8.14.

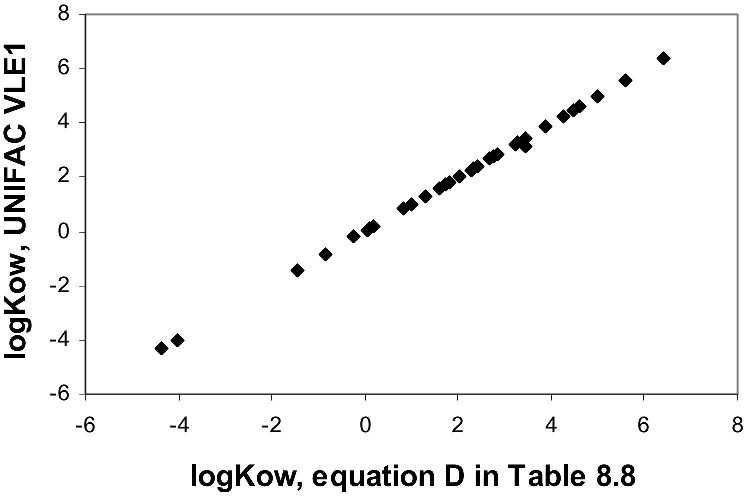


Figure 8.10 Scatter plot of log*K*ow values from the equation D in Table 8.8 and UNIFAC VLE 1 for alcohol ethoxylates used in toxicity correlations.

Table 8.11 Correlations of *K*ow and toxicity (EC50: mg/l, LD50: g/kg)

Species	Correlation equation	Figures	r^2
Algae	$\log 1/\mathrm{EC50} = -1.13599 + 0.4507\log\mathrm{Kow}$	8.11	0.67
Invertebrates	$\log 1/\mathrm{EC50} = -0.71905 + 0.18504\log\mathrm{Kow}$	8.12	0.52
Fish	$\log 1/\mathrm{EC50} = -0.55571 + 0.1776\log\mathrm{Kow}$	8.13	0.76
Rat	$\log \mathrm{LD50} = 0.04356 + 0.18631\log\mathrm{Kow}$	8.14	0.88

In the equations of Table 8.11, EC50 is the concentration of a chemical causing a defined effect to 50% of a group of test organisms (e.g. immobilization or growth inhibition), LD50 is the dosage causing death to 50% of the exposed animals after a single administration.

As can be seen in figures 8.11-8.14, experimental toxicity data are rather scattered with plot against *K*ow. However, *K*ow does capture qualitatively the trend of the experimental toxicity data. The scattered experimental data indicate this toxicity cannot be correlated alone with *K*ow.

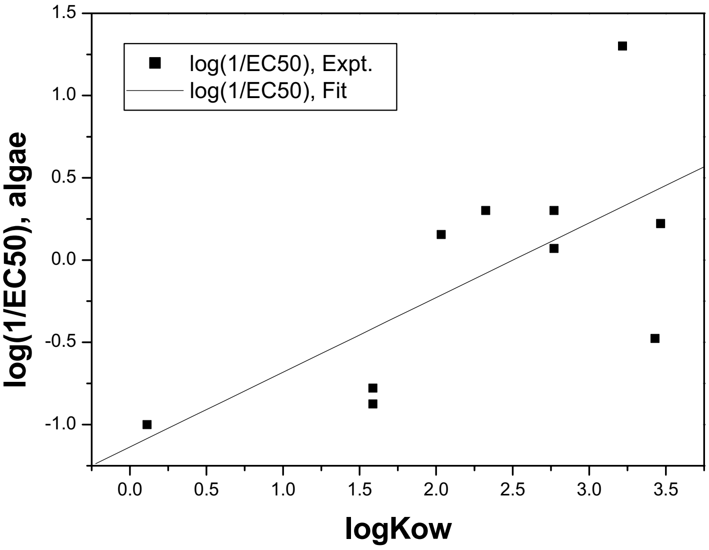


Figure 8.11 Correlation results of *K*ow and toxicity (EC50) of alcohol ethoxylates to algae. Experimental EC50 data are from Madsen et al. (2001)

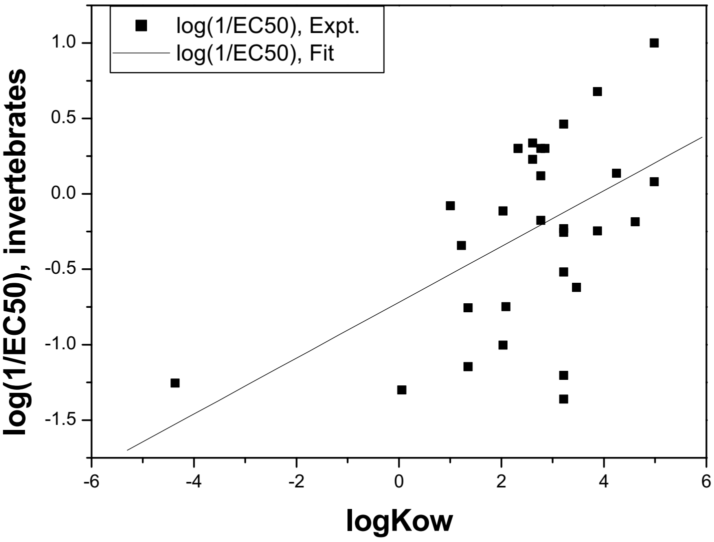


Figure 8.12 Correlation results of *K*ow and toxicity EC50 of alcohol ethoxylates to invertebrates. Experimental EC50 data are from Madsen et al. (2001)

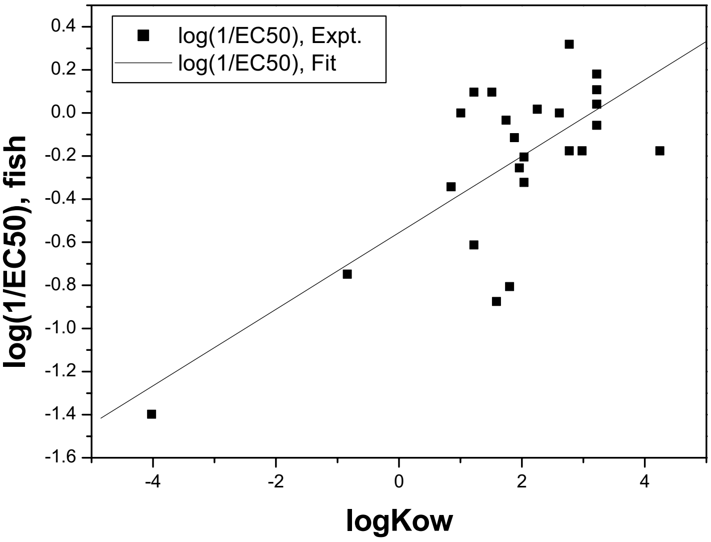


Figure 8.13 Correlation results of *K*ow and toxicity EC50 of alcohol ethoxylates to fish. Experimental EC50 data are from Madsen et al. (2001).

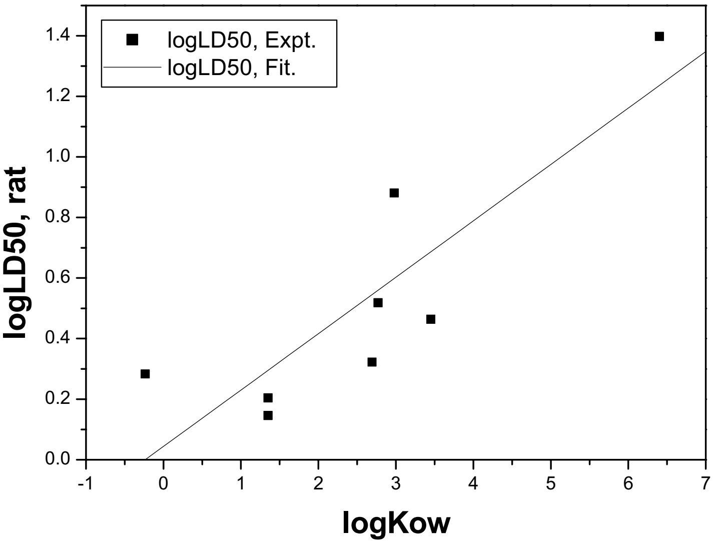


Figure 8.14 Correlation results of *K*ow and toxicity LD50 of alcohol ethoxylates to rat. Experimental EC50 data are from Madsen et al. (2001).

8.7 Conclusions

Correlation equations are obtained for the estimation of the HLB, the Krafft point, the cloud point, and the detergency of surfactants. Some new correlations for the aggregation number, the toxicity, the bio-accumulation factor and the HLB of specific surfactant families have been developed.

Based on the correlations, many important properties for practical applications can be easily calculated using only the information of surfactant molecular structures. The calculation methods for these properties are summarized in figure 8.15.

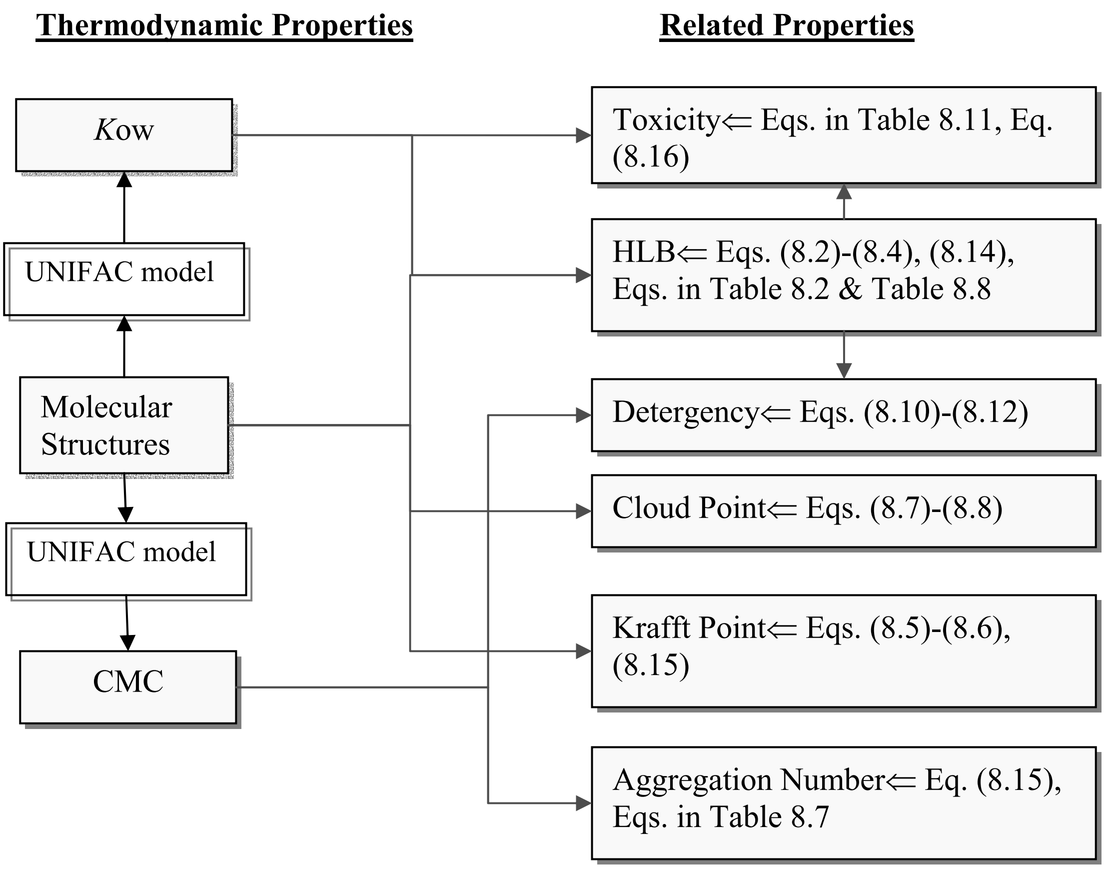


Figure 8.15 Map of calculation methods of thermodynamic and related properties.

Chapter 9 Conclusions and Future Work

9.1 Conclusions

This thesis has addressed the modelling of surfactant solutions. The main conclusions are summarised here:

(1) The thermodynamic framework of Chen et al. (1996, 2001) for non-ionic and ionic surfactant solutions is adopted. Based on this, the CMC of non-ionic and ionic surfactant solutions is investigated with the UNIFAC model.

(2) The CMC of a specific family of non-ionic surfactant solutions (alcohol ethoxylates) is first correlated and then predicted with the UNIFAC model. A new UNIFAC functional group (OCH_2CH_2) is introduced and the necessary interaction parameters are obtained directly from the CMC data (correlation) or from vapour-liquid equilibrium data (prediction). The trends of CMC against both the hydrophobic and hydrophilic chain length are well represented.

(3) The octanol-water partition coefficients of phthalates and non-ionic surfactant (alcohol ethoxylates) are predicted with different UNIFAC models and three commercial tools, known with the abbreviations ACD, ClogP and KowWin. UNIFAC VLE1 is the best among the methods investigated and very close to some of these commercial tools.

(4) In order to describe the CMC of ionic surfactant solutions, an electrolyte UNIFAC model proposed by Achard et al. (1994 a, b) is used and modified to correlate the mean ionic activity coefficients of organic electrolyte solutions. The structural parameters of ions are directly calculated with the ionic radii of Marcus's without using hydration number.

(5) It has been found that the ratio of structural parameters (R and Q) for ions in the Achard's method (and other) is $Q/R>1$ and does not follow the physically correct limitation $Q/R\leq1$ in the Flory-Huggins theory. The physical derivation of UNIQUAC/UNIFAC is not correct with the ratio $Q/R>1$. The effects of Q/R for electrolyte UNIQUAC/UNIFAC have been studied through comparing combinatorial and residual terms of UNIQUAC model. A new set of normalization factors is derived to yield a ratio $Q/R\leq1$ for ions.

(6) Using the new structural parameters of ions, the mean activity coefficients of electrolyte solutions and organic electrolyte solutions are successfully correlated with the modified Achard model. Similar behaviour as the electrolyte NRTL model is observed. For investigated systems, the model has better correlation results than that of the extended UNIQUAC. For organic electrolyte solutions, the model simultaneously captures the mean activity coefficients of five sodium carboxylate systems with four interaction parameters and is in good agreement with experimental values.

(7) The modified Achard model was used for calculating the CMC of sodium alkyl sulphates, sodium alkyl sulfonates and potassium carboxylates surfactant solutions. The model can successfully capture the effects of different alkyl chain lengths and temperatures. However, the CMC prediction results for sodium carboxylates are poor.

(8) Semi-empirical relationships for the hydrophilic-lipophilc balance (HLB), the Krafft point, the cloud point and the detergency are presented.

(9) New correlations for the aggregation number, the HLB, the toxicity and bio-concentration factor of some specific surfactants are developed.

9.2 Future Work

As described in Chapter 3, thermodynamic understanding of surfactant solutions is rather limited. The work described so far is an effort toward such understanding. Based on the work presented in previous chapters, it seems appropriate to suggest some directions for future efforts as following.

As shown in chapters 5 and 7, CMC of alcohol ethoxylates, sodium alkyl sulphates, sodium alkyl sulfonates and sodium (potassium) carboxylates can be correlated and predicted by UNIFAC or modified Achard model. Thus, it is very interesting to extend the UNIFAC and modified Achard model developed in this work to different single surfactant solutions, especially for sodium alky ether sulphates and sodium alky benzene sulphates. In practical applications, CMC of mixed surfactant solutions are very important. The correlation results for different single surfactant solutions will help to establish a basis to extend these models to mixed surfactant solutions.

As described in Chapter 6, the structural parameters (Q, R) of ions used by many UNIQUAC or UNIFAC based electrolyte models do not follow Flory-Huggins theory, which results in UNIQUAC and UNIFAC having no physical meanings. Based on this point, a new method was proposed to calculate Q and R parameters of ions from ionic radii. The new Q and R calculation method can be further investigated in several directions: (1) optimization of standard segment for structural parameter estimation; (2) investigation of the effects of different Q and R ratios in mean activity coefficient correlation of electrolyte solutions. From these investigations, a new UNIQUAC or UNIFAC-based electrolyte model could be developed for electrolytes, especially for organic electrolyte solutions or ionic liquids.

Based on the UNIFAC and modified Achard model for non-ionic and ionic surfactant solutions, CMC of mixed surfactants could be investigated. In order to carry out this work, mixing rule for mixed surfactant solutions should be first selected or developed based on existing methods. Meanwhile, an electrolyte model for mixed solvents and multiple ions should be found or developed.

In Chapter 7, environmental properties of surfactant, such as BCF, EC50 and LD50, were correlated with *K*ow for alcohol ethoxylates. This correlation method can be extended to other surfactant families, such as sodium alkyl sulphates, etc. As a necessary step, the octanol-water partition coefficient of ionic surfactants should be first investigated using modified Achard method proposed in this work.

Appendix A The UNIFAC Method

A.1 Basic Equations

The activity coefficient of component *i*, γ_i, is expressed in terms of the UNIFAC model as follows:

$$\ln \gamma_i = \ln \gamma_i^C + \ln \gamma_i^R$$

where $\ln \gamma_i^C$ and $\ln \gamma_i^R$ are, respectively, the combinatorial part and the residual part of the model.

The following formula of the UNIFAC model is useful for computer implementation (Fredenslund, et al. 1980).

Combinatorial Part:

$$\ln \gamma_i^{\mathrm{C}} = 1 - RI_i + \ln RI_i - q_i \frac{z}{2}\left(1 - \frac{RI_i}{QI_i} + \ln \frac{RI_i}{QI_i}\right) \tag{A1}$$

Residual Part:

$$\ln \gamma_i^{\mathrm{R}} = q_i\left(1 - \ln QI_i\right) - \sum_k \left[\theta_{\mathrm{k}} \frac{S_{ki}}{\eta_k} - G_{ki} \ln \frac{S_{ki}}{\eta_k}\right] \tag{A2}$$

where the sum over *k* are over all main groups in the system.

$$RI_i = \frac{r_i}{\sum_j x_j r_j} \qquad QI_i = \frac{q_i}{\sum_j x_j q_j} \tag{A3}$$

where the sums over *j* are over all components in system, r_{i} and q_{i} are the molecular volumes and surface areas calculated from the group values (R_{k} and Q_{k}) provided by Bondi (1968) using equation (A4).

$$r_i = \sum_k \upsilon_k^{(i)} R_k \, , \qquad q_i = \sum_k \upsilon_k^{(i)} Q_k \tag{A4}$$

where $\upsilon_k^{(i)}$ is the number of groups of type *k* in molecule *i*, the sums over *k* are over all main groups in the system.

$$G_{ki} = Q_k \upsilon_k^{(i)}, \quad \theta_k = \sum_i G_{ki} x_i \tag{A5}$$

$$S_{ki} = \sum_m G_{mi}\tau_{mk}\,, \qquad \eta_k = \sum_i S_{ki}x_i \tag{A6}$$

$$\tau_{mk} = \exp\left(-\frac{a_{mk}}{T}\right) \tag{A7}$$

where the sum *m* is over all main groups in the system. In equation (A6), the unit of group interaction parameter a_{mk} is in K. The coordination number *z* is set equal to 10.

A.2 Existing UNIFAC Models

Since the UNIFAC method has been introduced (Fredenslund et al., 1977), several different versions (group interaction parameter tables and changing in the combinatorial and residual part) have been proposed. Among these, the following five versions are used in this work: the original UNIFAC VLE 1 (Hansen et al., 1991), UNIFAC LLE 1 (Magnussen et al., 1981), UNIFAC VLE 2 (Hansen et al., 1992), Modified UNIFAC VLE 3 (Larsen et al., 1987) and water-UNIFAC (Chen et al., 1993). They are summarised in Table A.1.

Table A.1 The five UNIFAC models considered in this work

Model	Volume fraction RI_i calculation in combinatorial part	Temperature dependency of the interaction parameters	Data used in parameter estimation	Refs.
Original UNIFAC VLE 1	$RI_i = \frac{r_i}{\sum_j x_j r_j}$	$a \neq f(\text{T})$	VLE	a
UNIFAC LLE 1	$RI_i = \frac{r_i}{\sum_j x_j r_j}$	$a \neq f(\text{T})$	LLE	b
UNIFAC VLE 2	$RI_i = \frac{r_i}{\sum_j x_j r_j}$	$a_{ji} = a_{ji,1} + a_{ji,2}(T - T_0)$	VLE	c
Modified UNIFAC VLE 3	$RI_i = \frac{r_i^{2/3}}{\sum_j x_j r_j^{2/3}}$	$a_{ji} = a_{ji,1} + a_{ji,2}(T - T_0) + a_{ji,3}(T \ln\frac{T_0}{T} + T - T_0)$	VLE & H^E	d
Water- UNIFAC	$RI_i = \frac{r_i}{\sum_j x_j r_j}$	$a \neq f(\text{T})$	VLE & $\gamma^{\infty,aq}$	e

In Table A.1, VLE indicates Vapor-Liquid Equilibrium, LLE denotes Liquid-Liquid Equilibrium, H^E is the Excess enthalpy, and $\gamma^{\infty,aq}$ is the activity coefficient at infinite dilute for aqueous solutions.

References for Table A. 1

a). Hansen, H. K., P. Rasmussen, A. Fredenslund, M. Schiller, and J. Gmehling, "Vapor-Lquid Equilibria by UNIFAC Group Contribution 5. Revision and Extension," *Ind. Eng. Chem. Res.*, **30**, 2352 (1991).

b). Magnussen, T., P. Rasmussen, and A. Fredenslund, "UNIFAC Parameters Table for Prediction of Liquid – Liquid Equilibria," *Ind. Eng. Chem. Process Des. Dev.*, **20**, 133 (1981).

c). Hansen, H. K., B. Coto, and B. Kuhlmann, *UNIFAC with Linearly Temperature-dependent Group Interaction Parameters*. SEP 9212 (Internal Report); Department of Chemical Engineering, Technical University of Denmark, Lyngby, Denmark, (1992).

d). Larsen, B. L., P. Rasmussen, and A. Fredenslund, "A Modified UNIFAC Group Contribution Modle for Prediction of Phase Equilibria and Heats of Mixing," *Ind. Eng. Chem. Res.*, **26**, 2274 (1987).

e). Chen, F., J. H. Andersen, and H. Tyle, "New Developments of the UNIFAC Model for Environmental Application," *Chemosphere*, **26**, 1325 (1993).

Appendix B Micelle Formation Equation in Ionic Surfactant Solutions

In this appendix, some basic equations in electrolyte solutions are given by following the work of Zerres and Prausnitz (1994). From these basic equations, a further explanation is given for the thermodynamic treatment of micelle formation in ionic surfactant solutions.

In solutions with strong electrolytes, we can assume complete dissociation of an electrolyte E into cations C and anions A:

$$E \rightarrow \nu_C C + \nu_A A \tag{B.1}$$

where ν_C and ν_A are the stoichiometric coefficients and

$$\nu = \nu_C + \nu_A \tag{B.2}$$

For any species k, the mole fraction x_k, based on the assumption of complete dissociation, is related to the mole numbers n by:

$$x_k = \frac{n_k}{\sum_l n_l} \tag{B.3}$$

The sum includes all ionic and molecular species.

The chemical potential μ_E of the electrolyte is related to those of the ions by:

$$\mu_E = \nu_C \mu_C + \nu_A \mu_A \tag{B.4}$$

Based on the complete-dissociation mole fractions, the activity coefficient of cations (γ_C) and anions (γ_A) are introduced as:

$$\mu_E = \nu_C \left(\mu_C^0 + RT \ln\left(x_C \gamma_C\right)\right) + \nu_A \left(\mu_A^0 + RT \ln\left(x_A \gamma_A\right)\right) \tag{B.5}$$

where superscript 0 denotes the standard (or reference) state.

Regardless of the solvent, the standard state for the cation is a hypothetical ideal dilute solution in water when x_C=1, at system temperature and pressure. Similarly, the standard state for the anion is a hypothetical ideal dilute solution when x_A=1. In the hypothetical ideal dilute solution, γ_C=γ_A=1 for all x. For an ionic species, it is a pseudo-pure component.

In the equations above, cations and anions appear as separate species. However, only the chemical potential of the electrically neutral salt is experimentally accessible. This follows from the condition of electroneutrality for every phase.

If we use the mean ionic activity coefficient, denoted by subscript ±, for the chemical potential of salt, we write:

$$\mu_E = \nu\mu_\pm = \nu_C\mu_C + \nu_A\mu_A \tag{B.6}$$

$$\mu_\pm = \mu_\pm^0 + RT\ln\left(\gamma_\pm x_\pm\right) \tag{B.7}$$

where $\gamma_\pm$ and $x_\pm$ are defined by:

$$\gamma_\pm = \left(\gamma_C^{\nu_C}\gamma_A^{\nu_A}\right)^{1/\nu} \tag{B.8}$$

$$x_\pm = \left(x_C^{\nu_C}x_A^{\nu_A}\right)^{1/\nu} \tag{B.9}$$

For the chemical potential in the standard state

$$\nu\mu_\pm^0 = \nu_C\mu_C^0 + \nu_A\mu_A^0 \tag{B.10}$$

For liquid-liquid equilibrium, the condition for the phase equilibrium in aqueous single electrolyte system is given by:

$$\mu_w' = \mu_w'' \tag{B.11}$$

$$\mu_E' = \mu_E'' \tag{B.12}$$

where superscript ′ and ′′ denote the two liquid phases; subscript *w* and *E* denote the water and electrolyte.

With the definition of the mean ionic properties (equations (B.6)-(B.10)), equation (B.12) can be replaced by:

$$\mu_\pm' = \mu_\pm'' \tag{B.13}$$

Using equation (B.7), the equations for liquid-liquid phase equilibrium are:

$$\left(\mu_w^0 + RT\ln\left(\gamma_w x_w\right)\right)' = \left(\mu_w^0 + RT\ln\left(\gamma_w x_w\right)\right)'' \tag{B.14}$$

$$\left(\mu_\pm^0 + RT\ln\left(\gamma_\pm x_\pm\right)\right)' = \left(\mu_\pm^0 + RT\ln\left(\gamma_\pm x_\pm\right)\right)'' \tag{B.15}$$

In equation (B.14), the chemical potential of water in the standard state is at pure liquid water at system temperature and pressure.

Using the defined standard-state chemical potentials, the equations of liquid-liquid equilibrium simplify to:

$$(x_w \gamma_w)^{'} = (x_w \gamma_w)^{''} \tag{B.16}$$

$$(x_{\pm} \gamma_{\pm})^{'} = (x_{\pm} \gamma_{\pm})^{''} \tag{B.17}$$

For convenience, we define x_I as the sum of the mole fractions of cation and anion as:

$$x_I = x_C + x_A \tag{B.18}$$

Based on equation (B.9) and (B.18), we can obtain:

$$x_{\pm}^{\nu} = \left(\nu_C^{\nu_C} \nu_A^{\nu_A} x_I / \nu\right)^{\nu} \tag{B.19}$$

Using equation (B.19), equation (B.17) can be re-written as:

$$(x_I \gamma_{\pm})^{'} = (x_I \gamma_{\pm})^{''} \tag{B.20}$$

Using the equilibrium relation for the micelle solution system, the equilibrium between free monomeric surfactant in the aqueous solution and the aggregated surfactants in the micelle particles can be given as:

$$(x_I \gamma_{\pm})_{aq} = (x_I \gamma_{\pm})_{micelle} \tag{B.21}$$

where the subscripts "*aq*" and "*micelle*" represent the aqueous solution and the micelle particles, respectively. In the micelle particles, the ionic headgroups of the surfactant molecules, together with their counter ions, remain immersed in the aqueous solution at the micelle-aqueous solution interface.

At and above the critical micelle concentration, we can assume that the micelle particles have only surfactant molecules. The mole fraction of surfactant molecules in the micelle is unity.

Appendix C Van der Waals Parameters of Local Composition Models

This appendix is largely reported by the work of Abrams and Prausnitz (1975). The structural parameters R and Q of UNIQUAC model are, respectively, the van der Waals volume and area of the molecule relative to those of a standard segment.

$$R_k = \frac{V_{wk}}{V_{ws}} \tag{C.1}$$

$$Q_k = \frac{A_{wk}}{A_{ws}} \tag{C.2}$$

where V_{wk} and A_{wk} are the van der Waals volume and area of the molecule given by Bondi (1968), V_{ws} and A_{ws} are the van der Waals volume and area of a standard segment. The choice of a standard segment is somewhat arbitrary. However, it is defined as a sphere such that for a linear poly-methylene molecule of infinite length, the identity

$$\frac{Z}{2}(R - Q) = R - 1 \tag{C.3}$$

is satisfied because Q/R=1.0 for the standard segment (monomer). The coordination number Z is set equal to 10. The volume of the standard sphere in terms of its radius R_{ws} is given by

$$V_{ws} = \frac{4}{3}\pi\, R_{ws}^3 \tag{C.4}$$

and the area by

$$A_{ws} = 4\pi\, R_{ws}^2 \tag{C.5}$$

The van der Waals volume and area of an n-mer of poly-methylene are n times the volume and area of a methylene group as given by Bondi; that is

$$V_{wk} = \mathrm{n}(10.23)\mathrm{cm}^3/\mathrm{mole} \tag{C.6}$$

$$A_{wk} = \mathrm{n}(1.35)\times 10^9\,\mathrm{cm}^2/\mathrm{mole} \tag{C.7}$$

Substitution of equations (C.1), (C.2), and (C.4) to (C.7) into (C.3) yields:

$$\frac{10}{2}\left(\frac{V_{wk}}{V_{ws}} - \frac{A_{wk}}{A_{ws}}\right) = \frac{V_{wk}}{V_{ws}} - 1 \tag{C.8}$$

$$4\frac{V_{wk}}{V_{ws}} = 5\frac{A_{wk}}{A_{ws}} - 1 \tag{C.9}$$

$$4\frac{n(10.23)}{\frac{4}{3}\pi R_{ws}^3} = 5\frac{n\left(1.35\times 10^9\right)}{4\pi R_{ws}^2} - 1 \tag{C.10}$$

$$4\frac{(10.23)}{\frac{4}{3}\pi R_{ws}^3} = 5\frac{\left(1.35\times 10^9\right)}{4\pi R_{ws}^2} - \frac{1}{n} \tag{C.11}$$

As $n \to \infty$, $\frac{1}{n} \to 0$ and we obtain

$$4\frac{(10.23)}{\frac{4}{3}\pi R_{ws}^3} = 5\frac{\left(1.35\times 10^9\right)}{4\pi R_{ws}^2} \tag{C.12}$$

$R_{ws} = 1.81867\times 10^{-8}$ cm/molecule

or $R_{ws} = 1.81867\times 10^{-8} \times 6.023\times 10^{23} = 10.95\times 10^{15}$ cm/mole

Substitution the R_{ws} value into equations (C.4) and (C.5) yields a standard segment volume and area.

$$V_{ws} = \frac{4}{3}\pi \times \left(1.818\times 10^{-8}\right)^3 \times 6.023\times 10^{23} = 15.17\ \text{cm}^3/\text{mole} \tag{C.13}$$

$$A_{ws} = 4\pi \times \left(1.818\times 10^{-8}\right)^2 \times 6.023\times 10^{23} = 2.50\times 10^9\ \text{cm}^2/\text{mole} \tag{C.14}$$

Equations (C.1) and (C.2) then become

$$R_k = V_{wk}/15.17 \tag{C.15}$$

$$Q_k = A_{wk}/(2.5\times 10^9) \tag{C.16}$$

Equations (C.15) and (C.16) are the ones typically used in UNIQUAC and UNIFAC models.

Appendix D Structural Parameters of Ions

The structural parameters of ions are calculated from the ionic radii from Marcus (1997) using equations (6.56) and (6.57) of Chapter 6.

Table D 1. Structural parameters of ions

Ion, *k*	Ionic radii, Å	R_k	Q_k
Li^+	0.69	0.3285	0.4761
Na^+	1.02	1.0612	1.0404
K^+	1.38	2.6281	1.9044
Rb^+	1.49	3.3080	2.2201
Cs^+	1.70	4.9130	2.8900
Cu^+	0.96	0.8847	0.9216
Ag^+	1.15	1.5209	1.3225
Au^+	1.37	2.5714	1.8769
Tl^+	1.50	3.3750	2.2500
H_3O^+	1.30	2.1970	1.6900
NH_4^+	1.48	3.2418	2.1904
Be^{2+}	0.35	0.0429	0.1225
Mg^{2+}	0.72	0.3732	0.5184
Ca^{2+}	1.00	1.0000	1.0000
Sr^{2+}	1.13	1.4429	1.2769
Ba^{2+}	1.36	2.5155	1.8496
Ra^{2+}	1.43	2.9242	2.0449
V^{2+}	0.79	0.4930	0.6241
Cr^{2+}	0.82	0.5514	0.6724
Mn^{2+}	0.83	0.5718	0.6889
Fe^{2+}	0.78	0.4746	0.6084
Co^{2+}	0.75	0.4219	0.5625
Ni^{2+}	0.69	0.3285	0.4761
Cu^{2+}	0.73	0.3890	0.5329
Zn^{2+}	0.75	0.4219	0.5625
Pd^{2+}	0.86	0.6361	0.7396
Ag^{2+}	0.89	0.7050	0.7921
Cd^{2+}	0.95	0.8574	0.9025
Sn^{2+}	0.93	0.8044	0.8649
Sm^{2+}	1.19	1.6852	1.4161
Eu^{2+}	1.17	1.6016	1.3689
Yb^{2+}	1.05	1.1576	1.1025
Pt^{2+}	0.80	0.5120	0.6400
Hg^{2+}	1.02	1.0612	1.0404

Table D 1. *Continued*

Ion, k	Ionic radii, Å	R_k	Q_k
Pb^{2+}	1.18	1.6430	1.3924
Al^{3+}	0.53	0.1489	0.2809
Sc^{3+}	0.75	0.4219	0.5625
Ti^{3+}	0.67	0.3008	0.4489
V^{3+}	0.64	0.2621	0.4096
Cr^{3+}	0.62	0.2383	0.3844
Mn^{3+}	0.65	0.2746	0.4225
Fe^{3+}	0.65	0.2746	0.4225
Co^{3+}	0.61	0.2270	0.3721
Ga^{3+}	0.62	0.2383	0.3844
Y^{3+}	0.90	0.7290	0.8100
Rh^{3+}	0.67	0.3008	0.4489
In^{3+}	0.79	0.4930	0.6241
Sb^{3+}	0.77	0.4565	0.5929
La^{3+}	1.05	1.1576	1.1025
Ce^{3+}	1.01	1.0303	1.0201
Pr^{3+}	1.00	1.0000	1.0000
Nd^{3+}	0.99	0.9703	0.9801
Pm^{3+}	0.97	0.9127	0.9409
Sm^{3+}	0.96	0.8847	0.9216
Eu^{3+}	0.95	0.8574	0.9025
Gd^{3+}	0.94	0.8306	0.8836
Tb^{3+}	0.93	0.8044	0.8649
Dy^{3+}	0.91	0.7536	0.8281
Ho^{3+}	0.90	0.7290	0.8100
Er^{3+}	0.89	0.7050	0.7921
Tm^{3+}	0.88	0.6815	0.7744
Yb^{3+}	0.87	0.6585	0.7569
Lu^{3+}	0.86	0.6361	0.7396
Au^{3+}	0.79	0.4930	0.6241
Tl^{3+}	0.88	0.6815	0.7744
Bi^{3+}	1.02	1.0612	1.0404
Ac^{3+}	1.18	1.6430	1.3924
U^{3+}	1.04	1.1249	1.0816
Np^{3+}	1.02	1.0612	1.0404
Pu^{3+}	1.01	1.0303	1.0201
Am^{3+}	1.00	1.0000	1.0000
Cm^{3+}	0.98	0.9412	0.9604
Bk^{3+}	0.96	0.8847	0.9216
Cf^{3+}	0.95	0.8574	0.9025
Zr^{4+}	0.72	0.3732	0.5184

Table D 1. *Continued*

Ion, *k*	Ionic radii, Å	R_k	Q_k
Sn^{4+}	0.69	0.3285	0.4761
Ce^{4+}	0.80	0.5120	0.6400
Hf^{4+}	0.71	0.3579	0.5041
Th^{4+}	1.00	1.0000	1.0000
Pa^{4+}	0.96	0.8847	0.9216
U^{4+}	0.97	0.9127	0.9409
Np^{4+}	0.95	0.8574	0.9025
Pu^{4+}	0.93	0.8044	0.8649
F^-	1.33	2.3526	1.7689
Cl^-	1.81	5.9298	3.2761
Br^-	1.96	7.5296	3.8416
I^-	2.20	10.6480	4.8400
At^-	2.28	11.8524	5.1984
OH^-	1.33	2.3526	1.7689
HS^-	2.07	8.8698	4.2849
HSe^-	2.05	8.6152	4.2025
O_2^-	1.58	3.9443	2.4964
ClO^-	2.10	9.2610	4.4100
BrO^-	2.30	12.1670	5.2900
IO^-	2.50	15.6251	6.2500
CN^-	1.91	6.9679	3.6481
NCO^-	2.03	8.3655	4.1209
SCN^-	2.13	9.6636	4.5369
$SeCN^-$	2.25	11.3907	5.0625
N_3^-	1.95	7.4149	3.8025
HF_2^-	1.72	5.0885	2.9584
HO_2^-	1.80	5.8320	3.2400
BO_2^-	2.40	13.8240	5.7600
AlO_2^-	2.60	17.5761	6.7600
ClO_2^-	2.50	15.6251	6.2500
NO_2^-	1.92	7.0779	3.6864
AsO_2^-	2.90	24.3891	8.4100
NO_3^-	1.79	5.7354	3.2041
ClO_3^-	2.00	8.0000	4.0000
BrO_3^-	1.91	6.9679	3.6481
IO_3^-	1.81	5.9298	3.2761
VO_3^-	1.82	6.0286	3.3124
ClO_4^-	2.40	13.8240	5.7600
BrO_4^-	2.50	15.6251	6.2500
IO_4^-	2.49	15.4383	6.2001
MnO_4^-	2.40	13.8240	5.7600

Table D 1. *Continued*

Ion, k	Ionic radii, Å	R_{k}	Q_{k}
TcO_4^-	2.50	15.6251	6.2500
ReO_4^-	2.60	17.5761	6.7600
BH_4^-	1.93	7.1891	3.7249
BF_4^-	2.30	12.1670	5.2900
$B(OH)_4^-$	2.30	12.1670	5.2900
$Al(OH)_4^-$	2.90	24.3891	8.4100
HCO_2^-	2.04	8.4897	4.1616
HCO_3^-	1.56	3.7964	2.4336
HSO_3^-	1.70	4.9130	2.8900
$HseO_3^-$	2.10	9.2610	4.4100
HSO_4^-	1.90	6.8590	3.6100
$HseO_4^-$	2.10	9.2610	4.4100
$H_2PO_4^-$	2.00	8.0000	4.0000
O^{2-}	1.40	2.7440	1.9600
S^{2-}	1.84	6.2295	3.3856
Se^{2-}	1.98	7.7624	3.9204
Te^{2-}	2.21	10.7939	4.8841
O_2^{2-}	1.73	5.1777	2.9929
S_2^{2-}	2.80	21.9521	7.8400
CO_3^{2-}	1.78	5.6398	3.1684
$C_2O_4^{2-}$	2.10	9.2610	4.4100
SiO_3^{2-}	2.14	9.8004	4.5796
SO_3^{2-}	2.00	8.0000	4.0000
SeO_3^{2-}	2.39	13.6520	5.7121
TeO_3^{2-}	2.50	15.6251	6.2500
SO_4^{2-}	2.30	12.1670	5.2900
SeO_4^{2-}	2.43	14.3490	5.9049
TeO_4^{2-}	2.60	17.5761	6.7600
CrO_4^{2-}	2.40	13.8240	5.7600
MoO_4^{2-}	2.54	16.3871	6.4516
WO_4^{2-}	2.70	19.6831	7.2900
MnO_4^{2-}	2.50	15.6251	6.2500
$S_2O_3^{2-}$	2.50	15.6251	6.2500
$S_2O_4^{2-}$	2.60	17.5761	6.7600
$S_2O_6^{2-}$	2.80	21.9521	7.8400
$S_4O_6^{2-}$	3.10	29.7911	9.6100
$S_2O_8^{2-}$	2.90	24.3891	8.4100
HPO_4^{2-}	2.00	8.0000	4.0000
SiF_6^{2-}	2.59	17.3740	6.7081
PO_4^{3-}	2.38	13.4813	5.6644

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List of Symbols

a	Activity
a_0	Head group area at the head-tail interface
a_{ij}	Energy parameter in UNIFAC
A	Average whiteness of the investigated fabric, not soiled
A_{ws}	van der Waals surface area
$A_{\o}$	Debye-Hückel parameter
BCF	Bio-concentration factor
C	Concentration; average whiteness degree, before washing
C_i	Critical micelle concentration of pure surfactant i, in equation (3.6), (3.7)
C^*	Critical micelle concentration of mixed micelle solution
CCP	Critical packing parameter
CMC	Critical micelle concentration
CMC^0	Critical micelle concentration of pure component
CP	Cloud point
C_P	Constant-pressure heat capacity
EC50	Concentration of a chemical causing a defined effect to 50% of a group of test organisms (e.g. immobilization or growth inhibition)
D	Detergency
DP	Distribution of the polyoxyethylene chain in a product
n_g	Aggregation number
g^*_{mic}	Free energy of micellization
g^E	Molar excess Gibbs energy
G	Gibbs energy
G^E	Molar excess Gibbs energy
h	Hydration number
H	Enthalpy
HLB	Hydrophilic-lipophilic balance

I	Ionic strength
k	Chemical reaction equilibrium constant
k_B	Boltzmann's constant
K	Chemical reaction equilibrium constant
$K\mathrm{ow}$	*n*-Octanol-water partition coefficient
KP	Krafft point
l_c	Critical tail chain kength
LD50	Dosage causing death to 50% of the exposed animals after a single administration
m	Molality
M	Cation
n	Carbon number; group number
NRTL	Nonrandom, two-liquid equation
Nh_k	Hydration number of ions k
P	Pressure
P	A number depends on the shape of micelles
PIT	Phase inversion temperature
P^0	Vapour pressure of pure component
Q_k	Surface area parameter in UNIQUAC
$Q_k^{'}$	Surface area parameter of hydrated species
r	Radius
R	Gas constant
R_k	Volume parameter in UNIQUAC
$R_k^{'}$	Volume parameter of hydrated species
R_{ws}	Radius standard sphere
T	Absolute temperature
S	Entropy; Free surfactant molecules
$\mathrm{S_n}$	Surfactant molecules in a micelle, having an aggregation number n
SATF	Statistical association fluid theory

sh	Shape variable of surfactant solution
u_{ij}	Energy parameter in UNIQUAC
UNIFAC	Universal functional activity coefficient model
UNIQUAC	Universal quasi-chemical equation
V_{ws}	van der Waals volume
v	Tail chain volume
x	Liquid phase mole fraction
X	Anion
y	Vapour phase mole fraction
Y	Average whiteness degree, after washing
w	Weight fraction
Z	Ionic valence; coordination number

Greek Symbols

α	System dependent (adjustable) parameter; mole fraction of surfactant in aqueous solution
β	Molecular interaction parameter; system parameter
ϕ	Osmotic coefficient
γ	Activity coefficient
$\gamma*$	Unsymmetrically normalized activity coefficient
μ	Chemical potential
μ_1^{M0}	Chemical potential of surfactant 1 in pure micelles
μ_1^{M}	Chemical potential of surfactant 1 in mixed micelle
ν	Ionic charge
ρ	‘Closet approach’ parameter in Pitzer-Debye-Hückel theory
σ	Adjustable parameter

Superscripts

0	Standard state

cmc	Critical micelle concentration
H	Hydrated standard state
mon	Monomer
LR	Long-range interaction
MR	Middle range interaction
o	Octanol
p	Structure parameter of micelle
PDH	Pitzer-Debye-Hückel equation
SR	Short-range interaction
w	Water
∞	Infinite dilution

Subscripts

aq	Aqueous solution
cmc	Critical micelle concentration
$crit$	Critical micelle concentration
g	Aggregates
i	Component i
$liquid$	Liquid phase
m	Surfactant molecule inside micelle
mic	Micelle
$micelle$	Micelle phase
mon	Monomer
s	Free surfactant molecule
T	Total surfactant mixture
t	Overall concentration
$vapour$	Vapour phase
w	Water
ws	van der Waals
∞	Infinite dilution