

AN ASSESSMENT ON THE USE OF THE DEBYE-HÜCKEL EQUATION FOR THE THERMODYNAMIC MODELING OF AQUEOUS SYSTEMS CONTAINING POLYMERS AND SALTS

K. C. Nascimento Alves and P. A. Pessoa Filho *

Departamento de Engenharia Química, Escola Politécnica da Universidade de São Paulo, USP,
Caixa Postal 61548, 05424-970, São Paulo - SP, Brazil.
E-mail: pedro.pessoa@poli.usp.br

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Abstract - In this work, a study on the role of the long-range term of excess Gibbs energy models in the modeling of aqueous systems containing polymers and salts is presented. Four different approaches on how to account for the presence of polymer in the long-range term were considered, and simulations were conducted considering aqueous solutions of three different salts. The analysis of water activity curves showed that, in all cases, a liquid-phase separation may be introduced by the sole presence of the polymer in the long-range term, regardless of how it is taken into account. The results lead to the conclusion that there is no single exact solution for this problem, and that any kind of approach may introduce inconsistencies.

Keywords: Thermodynamics; Gibbs energy; Aqueous solutions; Polymer; Salt.

INTRODUCTION

Aqueous systems containing polymers and salts have gained increasing attention due to the use of aqueous two-phase systems in separating mixtures of compounds of biological origin. Aqueous two phase systems, as suggested by their denomination, are systems in which two liquid aqueous phases coexist in equilibrium. These systems can be formed by adding to water pairs of neutral polymers (such as polyethylene glycol and dextran), a polymer and a neutral salt (such as polyethylene glycol and ammonium sulfate), a neutral polymer and a polyelectrolyte (such as polyethylene glycol and sodium polyacrylate), and single polymers whose aqueous solutions have a low cloud point (and can be used to induce phase separation). The fact that both phases are aqueous provides a suitable environment for these compounds, and the composition difference (which results in different phase properties) provides the driving force for the uneven distribution of

biomolecules. Just to quote a few examples, one can cite the extraction of toxins from the fermentation broth of *Clostridium perfringens* (Cavalcanti et al., 2006), the separation of cell lineages rich in anthocyanins (Edahiro et al., 2005) and the partitioning of antibiotics (Bora et al., 2005) as uses of this technique. Despite promising reports on the use of these systems on pilot and industrial scales, they are still mainly used for pre-treatment and characterization of biomolecule mixtures on the laboratory scale (Hatti-Kaul, 2001).

Although they have been used for almost fifty years, the modeling of phase equilibria in aqueous two-phase systems remains an active field of investigation. While many models have been proposed in the last decades, no single model has been found to adequately represent all possible kinds of systems. Some models are specifically developed for two-polymer systems – for instance, the modified Flory-Huggins equation by Pessoa Filho and Mohamed (2004) – but other models are used

*To whom correspondence should be addressed

without extensive changes, such as virial-like equations (Tada et al., 2004) and other excess Gibbs energy models. Equations are also tailored for the modeling of salt-polymer systems: these usually consist of a long-range term (usually the Debye-Hückel equation or a modification thereof) and a short range-term, such as virial-like equations (Haraguchi et al., 2007), lattice models (Foroutan and Mohammadlou, 2008) or other excess Gibbs energy models (Madeira et al., 2005). Specific models can also be found for polymer-polyelectrolyte systems (Pessoa Filho and Maurer, 2008) and single polymer systems (Rangel-Yagui et al., 2004).

The general pattern of equilibrium diagrams of aqueous two-phase systems is depicted in Figure 1, which shows the coexistence of two equilibrium phases: an aqueous phase containing an appreciable fraction of polymer 1 (and a small fraction of either polymer 2 or salt) and an aqueous phase containing an appreciable fraction of polymer 2 or salt (and a small fraction of polymer 1).

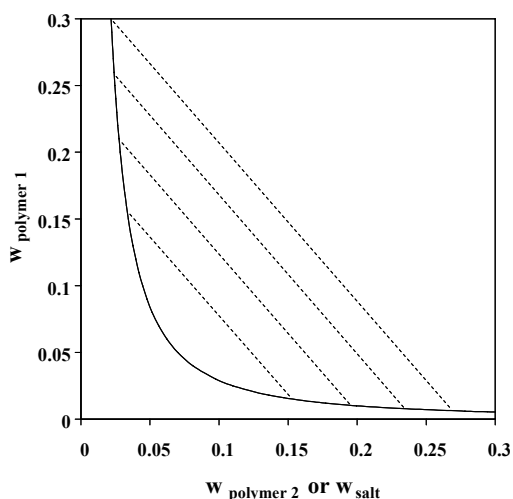


Figure 1: General pattern of phase equilibrium diagrams of aqueous two-phase systems. Binodal curve (—) and tie-lines (----).

A controversial issue is posed by the presence of a long-range term in those models developed for salt-polymer systems. This term accounts for the coulombic interactions between ions and depends on medium properties (mass density and permittivity), which are usually considered constant. The validity of the Debye-Hückel equation is limited to low ionic strengths, but these models are often used for highly concentrated salt solutions – since the same thermodynamic model must be used to describe the whole phase diagram. Moreover, in the salt-poor phase, the fraction of polymer (which serves as a co-solvent for the salt, changing the medium properties and hence the coulombic interactions among ions) is

high, whereas the salt-rich phase contains a small fraction of polymer, which means that the medium properties, in this case, are approximately those of water itself.

The effect of the presence of a polymeric solvent on the Debye-Hückel equation and modifications thereof is investigated in this work. The paper presents a theoretical framework, showing how the long-range term of excess Gibbs energy may be accounted for in the modeling of aqueous two-phase systems. The water activity of aqueous solutions containing a polymer and a salt at concentrations similar to those found in aqueous two-phase systems is evaluated considering different approaches to the problem.

THEORETICAL FRAMEWORK

The excess Gibbs energy (G^E) of a system consisting of a salt dissolved in a solvent is usually written as:

$$G^E = G^{E-LR} + G^{E-SR} \quad (1)$$

wherein the acronyms LR and SR represent long and short range, respectively. The separation in these terms is maintained in the derived properties, such as the chemical potential and activity. For the long range term, the most extensively used expression was presented by Debye-Hückel, which can be written in Pitzer's version as (Pitzer, 1980):

$$\frac{G^{E-LR}}{n_s M_s RT} = -\frac{4I}{b_s} A_\phi \ln(1 + b_s \sqrt{I}) \quad (2)$$

In this equation, b_s is a constant (dependent on the solvent), M_s is the solvent molar mass (expressed in $\text{kg}\cdot\text{mol}^{-1}$), n_s is the amount of solvent, and I is the ionic strength, defined in the molality scale (solute concentration expressed in terms of quantity of solute per kilogram of solvent) by:

$$I = \frac{1}{2} \sum_i m_i z_i^2 \quad (3)$$

wherein m_i is the molality of ion i , and z_i is its valence. The term A_ϕ in the previous Equation (2) is given by:

$$A_\phi = \frac{1}{3} \left(\frac{e^2}{4\pi\epsilon_0\epsilon_s k_B T} \right)^{3/2} (2\pi N_A V \rho_s)^{1/2} \quad (4)$$

wherein e is the electron charge ($1.60218 \cdot 10^{-19}$ C), ϵ_0 is the vacuum permittivity (8.85419×10^{-12} $\text{C}^2 \cdot \text{N}^{-1} \cdot \text{m}^{-2}$),

ϵ_s is the solvent relative permittivity, N_{AV} is Avogadro's number ($6.02205 \times 10^{23} \text{ mol}^{-1}$), ρ_s is the solvent mass density (expressed in $\text{kg} \cdot \text{m}^{-3}$) and k_B is the Boltzmann constant ($1.38066 \cdot 10^{-23} \text{ J} \cdot \text{K}^{-1}$). It must be stressed that A_ϕ is not dimensionless, but has units of $\text{kg}^{1/2} \cdot \text{mol}^{-1/2}$.

Although the excess Gibbs energy is the fundamental property, the theoretical reasoning behind the Debye-Hückel equation actually yields the activity coefficient of the salt, and the activity coefficient of the solvent (and hence the excess Gibbs energy) is obtained through the Gibbs-Duhem equation. Demonstrations of the Debye-Hückel equation can be found in textbooks, such as Tester and Modell (1997). If the solvent is unique – for instance, water in an aqueous solution of a single salt – the resulting expressions for the activity coefficient of the solvent is:

$$\ln \gamma_s^{\text{LR}} = 2A_\phi M_s \frac{I^{3/2}}{1 + b_s \sqrt{I}} \quad (5)$$

The solvent activity is given by:

$$a_s = \exp(-M_s \sum_{i \neq w} m_i) \cdot \gamma_s^{\text{LR}} \cdot \gamma_s^{\text{SR}} \quad (6)$$

The exponential term is related to the ideal mixture contribution to the activity. The use of the previous equations poses no problem for a single solvent. However, in aqueous two-phase systems containing a salt and a polymer, the role of these substances in the long range term is often unclear, and different procedures can be found in the literature.

The most common approach is to consider that the solvent is simply water: the polymer is just another solute with no net charge, and the solvent-dependent properties that appear in the previous equations (M_s , ϵ_s and ρ_s) are those for pure water. In this case, the parameter A_ϕ is not a function of system composition, and the previous equations can be used straightforwardly. The use of this approach is extensively documented, and has the main advantage of simplicity; just to mention some references, Haraguchi et al (2004) and Hagtalah and Joda (2009) adopt this methodology. However, if one considers that, in aqueous two-phase systems, the polymer-rich phase usually has a low concentration of the salt (which is exactly the situation for which the long-range term was derived), one can see that simply ignoring the influence of the polymer in this situation is at least an ambiguous procedure: the long-range term is added in order to make the infinite dilution limit correct, but because

of the description adopted, this limit is no longer physically correct.

A second approach is to consider that the polymer plays the role of a second solvent in the long-range term. If one considers the very demonstration of the Debye-Hückel term (Tester and Modell, 1997), one can see that the term solvent is actually related to the medium – whatever it is. Thus, in a dilute solution of a salt in polymer + water, the medium wherein the coulombic interactions occur is actually the mixture polymer + water. Therefore, by this reasoning, the requisite medium properties should be those of the mixture. However, this choice entails some decisions as to exactly how the polymer will be considered. These questions are by no means trivial, and arise from the fact that the Debye-Hückel equation is obtained within the McMillan-Mayer framework. In this framework, the solvent is considered to be simply the medium wherein interactions take place. However, in aqueous two-phase systems, one has two different phases with two-different polymer/water proportions – that is to say, two different solvents.

No theoretical solution has yet been found for this problem (and no exact conversion from the McMillan and Mayer to the Lewis and Randall approach has been developed), so one must resort to empirical approaches. Two different procedures can thus be followed. Firstly, one can consider not only that A_ϕ is a function of composition, but also that the “solvent” which appears in the molality definition is actually the polymer + water mixture. Thus:

$$n_s M_s = n_w M_w + n_p M_p \quad (7)$$

and:

$$\ln \gamma_w^{\text{LR}} = 2A_\phi M_w \frac{I^{3/2}}{1 + b_s \sqrt{I}} - \quad (8)$$

$$\frac{4I}{b_s} n_s M_s \ln(1 + b_s \sqrt{I}) \left(\frac{\partial A_\phi}{\partial n_w} \right)_{n_p}$$

A second approach is to keep the dependency of A_ϕ , but to consider that the molality refers only to water. In this case, the last equation is slightly changed:

$$\ln \gamma_w^{\text{LR}} = 2A_\phi M_w \frac{I^{3/2}}{1 + b_s \sqrt{I}} - \quad (9)$$

$$\frac{4I}{b_s} n_w M_w \ln(1 + b_s \sqrt{I}) \left(\frac{\partial A_\phi}{\partial n_w} \right)_{n_p}$$

There are theoretical arguments against either choice. In the first case, if one considers that molality refers to both the polymer and water, one obtains the following expression for the ideal activity term in a salt-free polymer solution:

$$\ln a_w^{\text{ID}} = -\frac{n_p}{(n_w + n_p)} \quad (10)$$

This expression results in a non-zero value for water activity in the limit $n_w \rightarrow 0$. On the other hand, considering only water as the solvent for the calculation of molality would result in unsymmetrical expressions for the activity coefficient for polymer and water – substances that, in this case, play the same role. One should note that these expressions should be the same despite the fact that the polymers considered are usually solid at room temperature.

Finally, it must be stressed that, in some cases, when the polymer is taken into account for the long-range term calculation, the variation of A_ϕ with n_w (or n_p) in Equations (8) and (9) is neglected. This procedure (with the Fowler-Guggenheim version of the Debye-Hückel equation) can be found, for instance, in Wu et al. (1996), Zafarani-Moattar and Sadeghi (2002), and Forouthan and Khomami (2009). While this may seem to be a mathematically inconsistent procedure, the Gibbs-Duhem equation is fulfilled – provided this dependency is also neglected in the analogous equation for the polymer activity coefficient. Finally, a model can be found wherein the value of A_ϕ is kept constant equal to that of water, while the polymer is accounted for in the molality calculation (Pazuki et al., 2009).

As one can see, there are theoretical arguments for pro and against any possible choice for accounting for the long-range interactions in this case. Therefore, one must examine the results of calculations using these terms in order to assess which is the best methodology.

MODELING

Four different approaches for the long-range term were evaluated. In the first one (henceforth referred to as Model 1) the Debye-Hückel equation was considered according to the expression presented by Pitzer (1980), i.e., Equation (5), considering that only water is the solvent. In the second one (Model 2), the equation was modified by considering the influence of polymer upon the medium properties and upon the molality, Equation (8). The medium properties were calculated according to Wu et al. (1996):

$$\rho_s = \rho_w \cdot \phi_w + \rho_p \cdot \phi_p \quad (11)$$

$$\varepsilon_s = \varepsilon_w \cdot \phi_w + \varepsilon_p \cdot \phi_p \quad (12)$$

wherein ϕ_w and ϕ_p correspond to the salt-free volume fractions of water and polymer, respectively. These fractions are calculated through:

$$\phi_p = \frac{w_w / \rho_w}{w_w / \rho_w + w_p / \rho_p} \quad (13)$$

and $\phi_w = 1 - \phi_p$.

In this case, the expression for the derivative in Equation (8) is given by:

$$\left(\frac{\partial A_\phi}{\partial n_w} \right)_{n_p} = A_\phi \left(\frac{1}{2} \left(\frac{\rho_w - \rho_p}{\rho_s} \right) - \frac{3}{2} \left(\frac{\varepsilon_w - \varepsilon_p}{\varepsilon_s} \right) \right) \frac{\phi_w \phi_p}{n_w} \quad (14)$$

The third approach (Model 3) is identical to Model 2 except that the polymer is considered not to change the molality expression (Equation 9). Finally, the last approach (Model 4) is identical to Model 3, except that the term containing the derivative is not considered in the calculations, i.e., the activity coefficient of water is given by:

$$\ln \gamma_w^{\text{LR}} = 2A_\phi M_w \frac{I^{3/2}}{1 + b_s \sqrt{I}} \quad (15)$$

but the properties of polymer are taken into account in the calculation of A_ϕ .

The short-range term was neglected in the calculations of a_w , which is equivalent to assigning the value of 1.0 to γ_w^{SR} .

RESULTS AND DISCUSSION

As a model system, three different kinds of salts were considered: a 1-1 salt (NaCl), a 2-1 salt (Na_2SO_4) and a 2-2 salt (MgSO_4). Polyethylene glycol with an average molar mass of 4000 $\text{g}\cdot\text{mol}^{-1}$ was considered in all calculations. Since the Debye-Hückel equation depends only on the charge and number of each ionic species, these results would be the similar for other salts of the same type. For each salt, curves of water activity considering only the ideal and the long-range term (as a function of salt concentration at definite polymer/water proportions) were obtained. The value of water activity was considered for this study because it is the easiest experimentally accessible activity in a ternary system containing water, polymer and salt – even though

reliable data on these systems are scarce, especially if phase separation occurs.

All calculations were performed at 298.2 K. The following values of polymer properties were used (Wu et al., 1996):

$$\varepsilon_p = 2.20$$

$$\rho_p = 833.4 \text{ kg.m}^{-3}$$

The permittivity of water was calculated from the

expression of Bradley and Pitzer (1979), and water specific volume was calculated from the expression of Saul and Wagner (1987); at 298.2 K these values are $\varepsilon_w = 78.34$ and $\rho_w = 997.0 \text{ kg.m}^{-3}$. The permittivity of the polymer is much lower than that of water, which means that the long-range term will be comparatively more important at high polymer concentrations.

In Figures 2 to 4, curves of water activity as functions of salt concentration are presented. Each of these curves was obtained considering a definite polymer/water ratio.

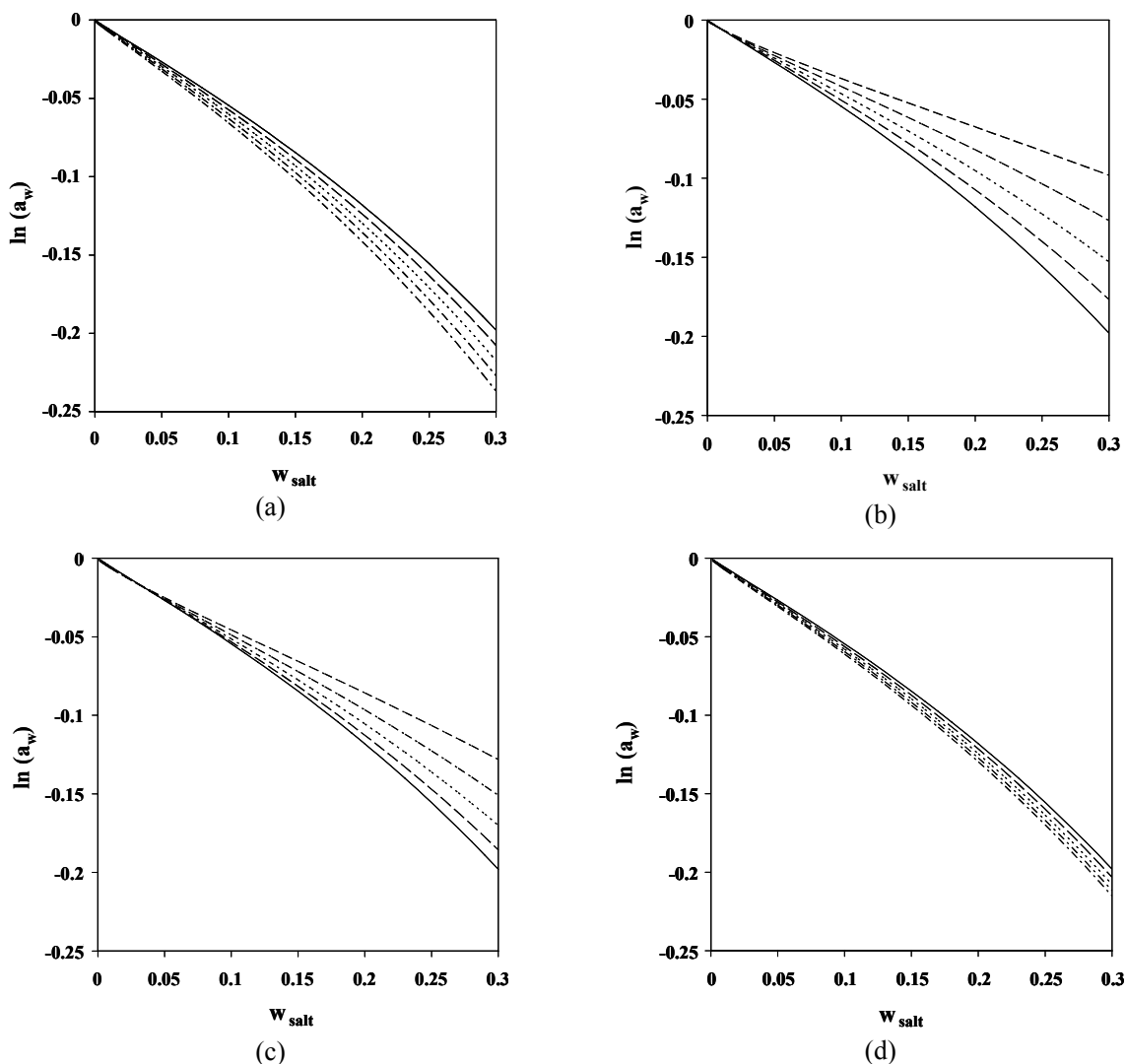


Figure 2: Water activity (a_w) calculated using the Debye-Hückel equation for aqueous solutions of NaCl and polyethylene glycol at 298.2 K. Curves are drawn for constant polymer to water ratios: (—) 0 %; (---) 5 %; (.....) 10 %; (-·-·-) 15 % and (- - - -) 20%. (a) model 1, (b) model 2, (c) model 3 and (d) model 4.

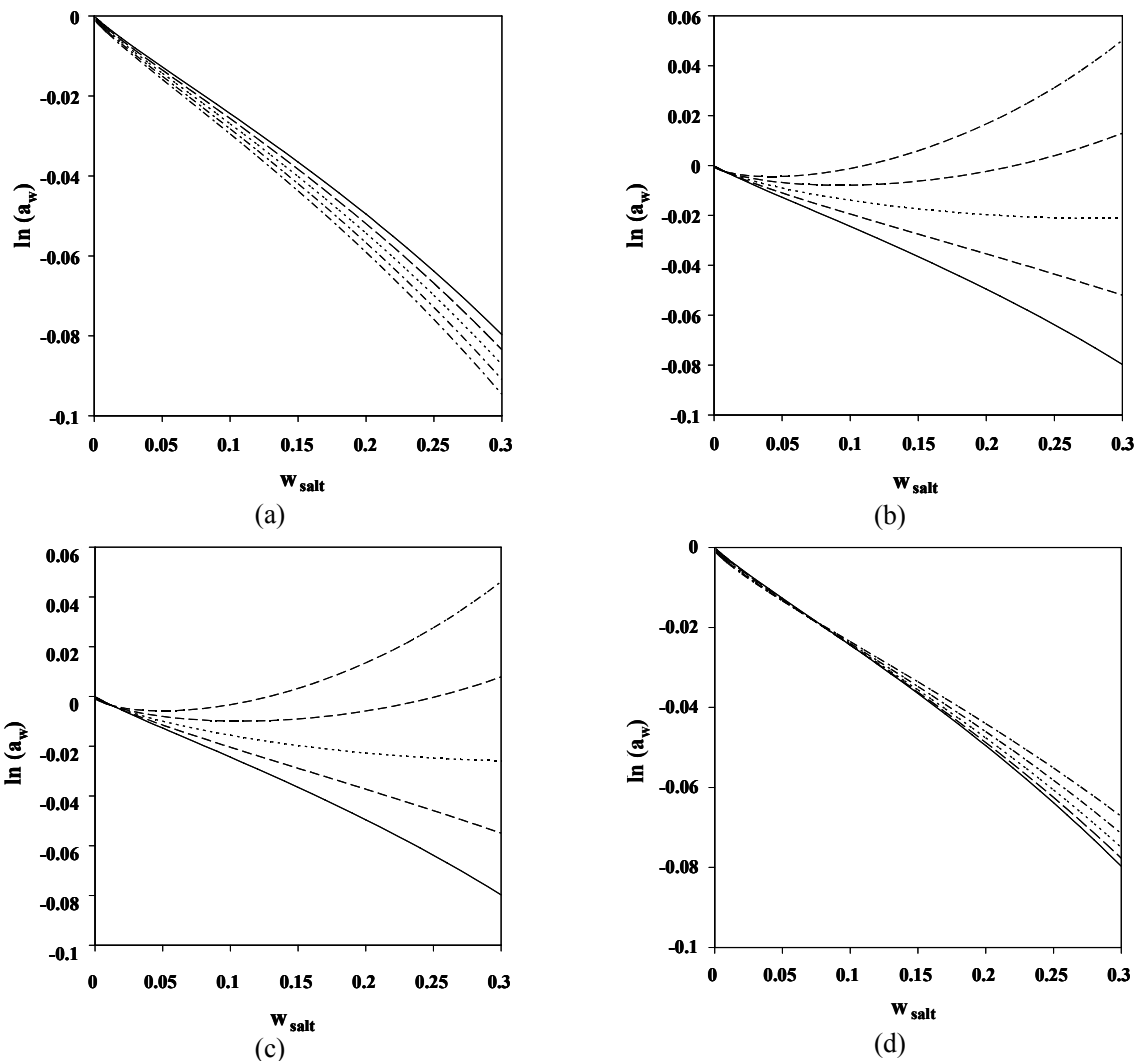
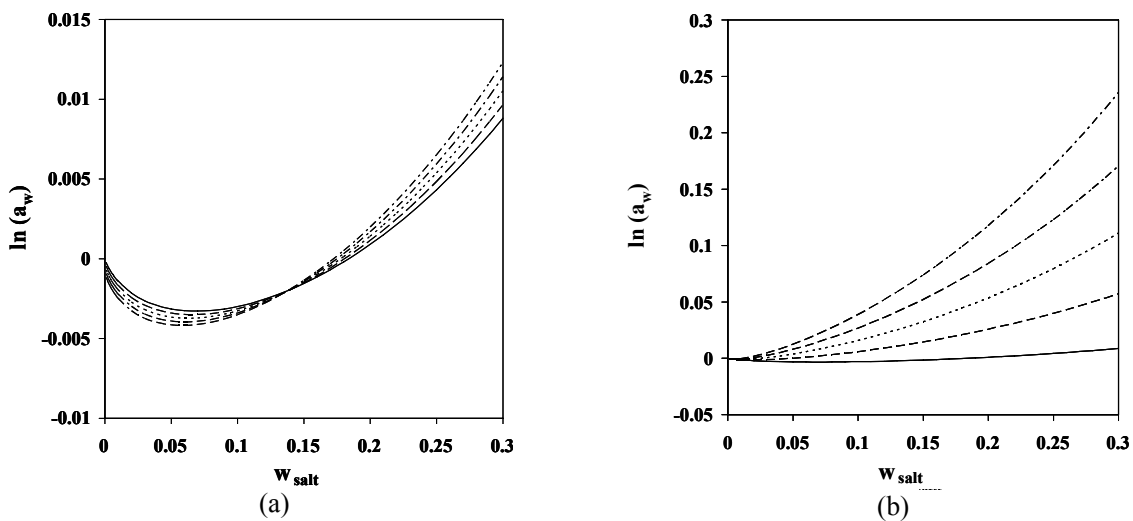


Figure 3: Water activity (a_w) calculated using the Debye-Hückel equation for aqueous solutions of Na_2SO_4 and polyethylene glycol at 298.2 K. Curves are drawn for constant polymer to water ratios: (—) 0 %; (---) 5 %; (.....) 10 %; (-·-·-) 15 % and (- - - -) 20%. (a) model 1, (b) model 2, (c) model 3 and (d) model 4.



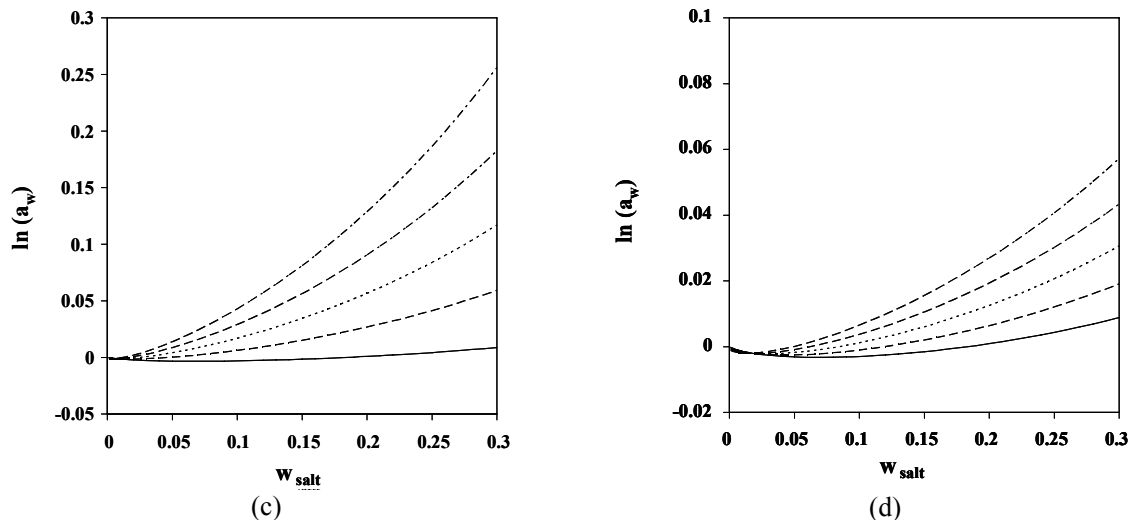


Figure 4: Water activity (a_w) calculated using the Debye-Hückel equation for aqueous solutions of $MgSO_4$ and polyethylene glycol at 298.2 K. Curves are drawn for constant polymer to water ratios: (—) 0 %; (---) 5 %; (.....) 10 %; (-·-·-) 15 % and (- - - -) 20%. (a) model 1, (b) model 2, (c) model 3 and (d) model 4.

A first conclusion that can be drawn from these Figures is that both models 2 and 3 result in analogous behavior. The difference between them lies only in the definition of molality, and this choice does not result in expressive differences.

On the other hand, there are significant differences between either model 1 or model 4 and models 2 and 3. These differences are strongly dependent on the salt type. Let one consider, for instance, the system containing $NaCl$ (Figure 2). The behavior of model 1 is coherent with the expected behavior – when the salt concentration increases, the water concentration decreases, and consequently so does the water activity. The behavior of model 4 is similar, except that differences in water activity for a same salt concentration are smaller than for model 1. However, for models 2 and 3 the behavior is different: at relatively lower salt concentrations, the curves of water activity show an inversion, and – for higher salt concentrations – the water activity is higher for higher polymer proportions than for lower ones. This behavior is compatible with a liquid phase separation: systems wherein the activity of a certain compound increases upon decreasing its concentration are inherently unstable. Nevertheless, one would not expect that long-range interactions could result in phase separation. If one thinks of the reasoning behind the equations, this calculated phase separation has no physical meaning.

In order to analyze the reasons for this behavior, one can separately consider the ideal mixture and the

long-range contributions to water activity. The ideal mixture term always decreases when the salt concentration increases. However, the long-range activity coefficient always increases with increasing salt concentration. When the polymer is taken into account in the long-range term, the value of A_ϕ increases, and this is the reason why, for a same system, the water activity calculated using model 4 is always higher than that calculated using model 1. Moreover, since A_ϕ decreases with increasing water/polymer ratio, the derivatives in Equations (8) and (9) are negative, and the overall contribution of this term is positive – which makes the calculated water activity for models 2 and 3 even higher than for model 4.

The results for systems containing Na_2SO_4 show an even greater influence of the long-range term. Considering models 2 and 3, for systems containing higher polymer/water proportions, at some intermediate salt concentrations the water activity passes through a minimum, and at higher salt concentrations it increases with increasing salt concentration. Model 4 also shows an inversion, and at high salt concentrations the water activity increases with increasing polymer/water ratio. The reason for this behavior is that the relative importance of the long-range term increases upon increasing the electric charge of the ions: the water activity for 2-1 salts (Figure 3) is thus much more affected by the changes in the value of A_ϕ than for 1-1 salts (Figure 2).

In this context, one can expect an even higher effect for MgSO_4 , and it indeed occurs (Figure 4). In this case, models 2 and 3 result in a value of water activity greater than 1.0 for almost all salt concentrations, and model 4 results in water activities higher than 1.0. But the most surprising finding is that even model 1 presents a behavior compatible with a liquid-phase separation – that is to say, in this case even the original Debye-Hückel equation is unsuitable. For a 2-2 salt, the ideal term is the same as for a 1-1 salt, but the ionic strength increases in a 4-fold proportion. The relative importance of the long-range term, therefore, is much higher.

One must be very careful not to draw any inconsequential conclusion in the analysis of these results. There is no reason to criticize the Debye-Hückel equation itself – it is obtained through a theoretical reasoning and is exact for dilute salt solutions (ionic strengths up to 0.1 mol.kg^{-1}). What is questionable is the use of the long-range term so far beyond its range of validity.

Some criticisms can be made of these results. Firstly, they refer to a specific single term, viz. the Pitzer version of the Debye-Hückel equation. Actually, using the original Debye-Hückel term would result in even higher water activities: the term $1 + b_s \sqrt{I}$ in Equation (5), which is the main difference between both approaches, is always greater than 1.0, and thus the activity coefficient of water will be even higher for the original Debye-Hückel equation.

Secondly, dissociation equilibria were ignored in the calculations. Of course these equilibria do occur, although they are not so pronounced for the salts herein considered. However, one must be aware that dissociation equilibria are not often accounted for in calculations – and the aim of this work is not to provide a new (correct) model, but to simply verify the applicability of the models as they are used. Finally, only a single chain size of PEG was considered, and results may be diverse for different chain sizes. This is true to some extent: choosing another chain size would change the ideal mixture term in Equation (6). This effect is, nevertheless, very small: the dominant contribution to the ideal mixture term arises from the presence of the ions. The polymer chain-size has no effect on the value of A_ϕ (it alters the salt-free volume fractions) and therefore the main conclusion would not change by modifying this parameter.

When modeling the phase equilibrium in aqueous two-phase systems (the main situation wherein the

problems previously presented arise), if modified long-range terms are used (models 2 to 4), the short-range term must be able to overcome the effect of the long-range term. A fine tuning of the parameters for the short-range term will be necessary, and one can foresee that this may be a complex procedure. This is a probable reason why this kind of modification – which should be sought after due to physical consistency reasons – has not received widespread attention in the literature. On the other hand, although model 1 also results in abnormal behavior in some cases (such as for a 2-2 salt), their results make this model more suitable for the modeling of aqueous two-phase systems. A line of constant water activity intercepts the curves in both systems with high polymer proportion and low salt concentration and systems with low polymer proportion and higher salt concentration – which is roughly the compositions of the two phases that exist in this kind of phase equilibrium.

Thus, for the whole phase diagram of aqueous two-phase systems, the short-range term will eventually be responsible for the quality of the modeling of experimental data – and the fact that these data can be modeled is extensively demonstrated in the literature, as previously shown. Even 2:2 salts can be well correlated with the original Debye-Hückel equation, regardless of the anomalous behavior of the long-range term. Just to present a single example, let us consider a Pitzer-like equation for the short-range term:

$$\frac{G^{\text{E-SR}}}{n_w M_w RT} = \sum_{i \neq w} \sum_{j \neq w} \lambda_{ij} m_i m_j \quad (16)$$

with the parameter λ_{ij} (not dependent on ionic strength) considered to be an adjustable one. The fitting of data for the aqueous two-phase system sodium carbonate (considering the partial ionization of the carbonate ion) and PEG 8000 at 298.15 K (Zaslavksky, 1995) using either model 1 or model 2 for the long-range term results in approximately the same behavior, as can be seen in Figure 5.

The only adjustable parameter (related to the pair polymer-salt) assumes the value $9.287 \text{ kg.mol}^{-1}$ when using model 1 and $9.773 \text{ kg.mol}^{-1}$ when using model 2. The fact that the overall result is similar, which confirms that even this simple short-range term can correct the anomalous behavior of model 2, may be the reason why the behavior presented herein has not been previously reported in the literature.

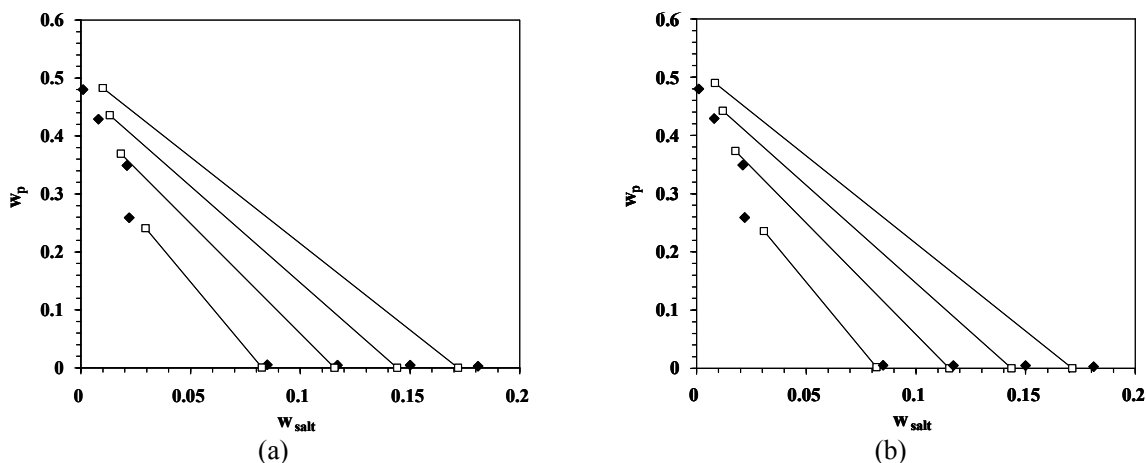


Figure 5: Phase diagrams calculated using model 1(a) and model 2(b). Full diamonds: experimental data; empty squares: modeling; continuous line: calculated tie-lines.

CONCLUSIONS

The long-range term is often maintained in excess Gibbs energy models developed for aqueous two-phase systems for consistency reasons. The results presented in this paper show that its use for modeling concentrated salt solutions containing polymers may introduce inconsistencies as well: in some cases, the long-range term predicts a liquid phase-separation that is not consistent with the physics underlying the equation. Nevertheless, upon introducing the short-range term, aqueous two-phase systems may be well correlated. No single recipe is currently available to overcome the questions posed by the use of different forms of the long-range term: any approach introduces inconsistencies, either theoretically or as a direct result of its application.

ACKNOWLEDGMENTS

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NOMENCLATURE

Latin Letters

A_ϕ	parameter of the Debye-Hückel equation defined by Equation (4)	$\text{kg}^{1/2} \cdot \text{mol}^{1/2}$
a_s	solvent activity	
a_w^{ID}	term of water activity	

b_s	related to the ideal solution parameter of Pitzer's version of the Debye-Hückel equation	$\text{kg}^{1/2} \cdot \text{mol}^{-1/2}$
e	electron charge	$1.60218 \times 10^{-19} \text{ C}$
G^E	excess Gibbs energy	$\text{J} \cdot \text{mol}^{-1}$
$G^{\text{E-LR}}$	long range contribution of the excess Gibbs energy	$\text{J} \cdot \text{mol}^{-1}$
$\underline{G}^{\text{E-LR}}$	extensive long range contribution of the excess Gibbs energy	J
$G^{\text{E-SR}}$	short range contribution of the excess Gibbs energy	$\text{J} \cdot \text{mol}^{-1}$
$\underline{G}^{\text{E-SR}}$	extensive short range contribution of the excess Gibbs energy	J
I	ionic strength	$\text{mol} \cdot \text{kg}^{-1}$
k_B	Boltzmann constant	$1.38066 \times 10^{-23} \text{ J} \cdot \text{K}^{-1}$
m_i	molality of species i	$\text{mol} \cdot \text{kg}^{-1}$
M_p	polymer molar mass	$\text{kg} \cdot \text{mol}^{-1}$
M_s	solvent molar mass	$\text{kg} \cdot \text{mol}^{-1}$
M_w	water molar mass	$\text{kg} \cdot \text{mol}^{-1}$
N_{AV}	Avogadro's number	$6.02205 \times 10^{23} \text{ mol}^{-1}$
n_p	amount of polymer	mol
n_s	amount of solvent	mol
n_w	amount of water	mol
T	absolute temperature	K
w_p	polymer mass fraction	
w_{salt}	salt mass fraction	
w_w	water mass fraction	
z_i	electric charge of species i	

Greek Letters

ε_p	polymer relative permittivity	
ε_s	solvent relative permittivity	
ε_w	water relative permittivity	
ε_0	vacuum permittivity	8.85419×10^{-12} $C^2 \cdot N^{-1} \cdot m^{-2}$
ϕ_p	polymer volume fraction	
ϕ_w	water volume fraction	
γ_s^{LR}	long range term of solvent activity coefficient	
γ_s^{SR}	short range term of solvent activity coefficient	
γ_w^{LR}	long range term of water activity coefficient	
γ_w^{SR}	short range term of water activity coefficient	
λ_{ij}	parameter in Equation (16)	$kg \cdot mol^{-1}$
ρ_p	polymer mass density	$kg \cdot m^{-3}$
ρ_s	solvent mass density	$kg \cdot m^{-3}$
ρ_w	water mass density	$kg \cdot m^{-3}$

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