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MEASUREMENT AND PREDICTION OF DENSITIES AND VISCOSITIES OF AQUEOUS BINARY AND TERNARY SOLUTIONS AT TEMPERATURES FROM 20 TO 60 °C

by

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Thesis submitted in fulfilment of the requirements

for the degree of Master of Science

2007

ACKNOWLEDGEMENT

I would like to extend my deepest appreciation to my main supervisor, Associate Professor Seng Chye Eng for his excellent guidance, invaluable suggestions, encouragement, patience and tolerance during my period of study. At the same time, I want to express my thanks to my co-supervisors, Professor Teng Tjoon Tow and Associate Professor Mahamad Hakimi Ibrahim for their assistance, help and advices.

I greatly thank all the staff and friends in School of Chemical Sciences for their help. I highly appreciate the cooperation from all the technicians and lab assistants who provide their valuable help. Special thanks to Mr. Koo Sieak Koon, Mr. Kanthasamy, Mr. Tan Chiat Soon and Ms. Yeap Pei Koon for their help and encouragement throughout the study.

Lastly, I would like to thank my family members for their concern and support throughout my research study.

Pang Fong Meng

2007

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NOMENCLATURE

(CF)	charge fraction, $m_i z_i$ / CH
(CH)	total charge, $\Sigma\ m_i z_i$
(ISF)	ionic strength fraction, $m_i z_i^{\ 2}$ / 2I
$\Delta\eta$	viscosity deviations
A	empirical adjustable parameter of equation (1.38)
A, B	parameters of equation (1.2)
Ă, D	parameters of equation (1.28)
$A`$, $B`$	calibration constants in equation (3.1)
A’, B’ and C’	parameters of equation (1.3)
A’’, B’’	constants of equation (1.25)
a_1, a_2, a_3, a_4	temperature dependent parameters of equation (1.5)
a_j	polynomial coefficient
A_v	Debye-Hückel coefficient
B(p’)	density function
b, h	parameters of equation (1.35a)
b_i, e_i	polynomial coefficients of equation (1.4)
b_{ref}, h_{ref}	values of b and h at the reference temperature T_{ref}
c	concentration (molarity)
$c_{i,id}$	molar concentration of the ideal dilute solution
d_1,d_2	parameters of equation (1.19)
Ë	average non-dimensional free energy parameter
E'	activation energy for viscous flow of equation (1.39)
E(vis)	activation energy for viscous flow
g	acceleration due to gravity
h	average height of the liquid in the tube
k, m’	constants of equation (1.1)
k_1, k_2	viscometer constants
m	molality
M	molar mass
m_i	molality of solute i

$m_i°$	molality of solute i in aqueous binary solution with the same water activity as the aqueous multicomponent solution
m^j	molality of the solute j in mixed solution
m_{o1}	molality of binary solute 1 having the same viscosity as the mixed solution
m_{o2}	molality of binary solute 2 having the same viscosity as the mixed solution
m_{oi}	molality of binary solute i having the same density (viscosity) as the mixed solution
NSOLU	total number of solute species
$ø_i, ø_2$	volume fractions of component i and the solute
P	applied pressure differential
p’	weight fraction of solute
R	gas constant
T	temperature
t’	flow time
V	volume parameter
V	molar volume of holes
V^E	excess molar volumes
w	mass fraction of solute
x	mole fraction of solute
Y_i	appropriate weighting factor
y_i	molality fraction of solute i
α’, β’	parameters of equation (1.15)
β	non-linear adjustable constant for the mole fraction
ΔG^*	free activation energy constant
η	absolute viscosity
$\eta°$	viscosity of the pure solvent
η_1	pure solvent dynamic viscosity
$\eta_{b,i}$	viscosities of the binary solution at the total molality of the mixed solution
η_i	viscosity of the component i
η_{id}	dynamic viscosity of ideal dilute solution

η_o	viscosity of pure water
η_{rel}	relative viscosity
η_{sp}	specific viscosity
ρ	density
ρ_i	density of the pure component i
ρ_i°	density of the aqueous binary solution with the molality of m_i°
ρ_{iI}	density of the binary solution i with the same ionic strength as the mixed solution
ρ_o	density of water
ρ_{rel}	relative density
σ_c	apparent viscosity rates
τ	oscillating period
ψ_C, ψ_2, ψ_{12}	dimensionless numbers
Φ_v	apparent molal volume
Φ_{vI}	apparent molal volume of the solute i with the same ionic strength as the mixed solution.
τ	shear stress
τ_c	shear stress of equation (1.39)
ν	kinematic viscosity
ν_A, ν_B, ν	kinematic viscosities of the pure components and the liquid mixture
ν_{AB}, ν_{BA}, ν_{AAAB}, ν_{AABB}, ν_{BBBA}	adjustable parameters of equation (1.34)

SUKATAN DAN RAMALAN KETUMPATAN DAN KELIKATAN BAGI SISTEM LARUTAN AKUEUS BINARI DAN TERNARI DARIPADA SUHU 20 HINGGA 60 °C

ABSTRAK

Ketumpatan dan kelikatan bagi sistem larutan akueus binari dan ternari 1-propanol + H_2O, 2-propanol + H_2O, urea + H_2O, 1-propanol + natrium klorida + H_2O, 1-propanol + urea + H_2O, 2-propanol + natrium klorida + H_2O dan 2-propanol + urea + H_2O telah ditentukan dalam seluruh julat komposisi dan pada julat suhu 20 hingga 60 °C. Tenaga pengaktifan bagi larutan akueus 1-propanol dan 2-propanol telah dikira dan nilainya ialah 17.93 and 22.15 kJ mol^{-1} masing-masing. Persamaan polinomial dan suatu persamaan berdasarkan Hukum Power dan Teori Kadar Mutlak Erying telah diguna untuk mengkorelasikan kelikatan larutan akueus 1-propanol dan 2-propanol. Sisihan peratusan penyimpangan mutlak purata (AAD) bagi korelasi ini adalah 0.771 % dan 1.235 % bagi sistem larutan akueus 1-propanol dan 2-propanol masing-masing. Data ketumpatan telah dikorelasi oleh persamaan polinomial. Ralat purata bagi semua sistem yang dikaji ialah 3.80292×10^{-4}. Ketumpatan dan kelikatan menurun dengan kenaikan suhu bagi semua sistem yang dikaji.

Nilai-nilai isipadu molar lebihan (V^E) dan kelikatan dinamik lebihan ($\Delta\eta$) telah dikira dari data sukatan larutan akueus 1-propanol dan 2-propanol. Nilai-nilai ini telah dikorelasi sebagai fungsi pecahan mol dengan persamaan Redlich-Kister. Nilai bagi isipadu molar lebihan adalah negatif manakala kelikatan dinamik lebihan didapati adalah positif dalam seluruh julat komposisi dan suhu.

Pengubahsuaian persamaan kekuatan ionik telah digunakan untuk meramal ketumpatan bagi sistem larutan akueus ternari. Nilai ketumpatan ramalan adalah bersetuju dengan nilai ketumpatan eksperimen, dengan peratusan ralat purata 0.29 %. Persamaan penambahan berdasarkan kekuatan ionik larutan campuran telah digunakan untuk meramal kelikatan larutan akueus ternari. Percubaan telah dibuat untuk mengubahsuai persamaan kekuatan ionik dengan menggunakan jumlah kemolalan sebagai ganti kekuatan ionik. Peratusan ralat purata ramalan kelikatan bagi sistem yang dikaji adalah 1.63 %.

MEASUREMENT AND PREDICTION OF DENSITIES AND VISCOSITIES OF AQUEOUS BINARY AND TERNARY SOLUTIONS AT TEMPERATURES FROM 20 TO 60 °C

ABSTRACT

Densities and viscosities of the binary and ternary aqueous solution of 1-propanol + H_2O, 2-propanol + H_2O, urea + H_2O, 1-propanol + sodium chloride + H_2O, 1-propanol + urea + H_2O, 2-propanol + sodium chloride + H_2O and 2-propanol + urea + H_2O systems were measured over the whole composition range at temperatures between 20 and 60 °C. The energies of activation for viscous flow for aqueous solutions of 1-propanol and 2-propanol were calculated and found to be 17.93 and 22.15 kJ mol^{-1}, respectively. A polynomial equation and an equation based on the Power Law and Erying's absolute rate theory were used to correlate the viscosity data of the aqueous solutions of 1-propanol and 2-propanol. The average absolute deviation percentage errors (AAD) of these correlations were found to be 0.771 % and 1.235 % for aqueous solutions of 1-propanol and 2-propanol, respectively. The density data were correlated by the polynomial equation. The average standard deviation for the systems studied is 3.80292×10^{-4}. The densities and viscosities decrease with increase in temperatures for all the systems studied.

The values of excess molar volumes (V^E) and viscosity deviations ($\Delta\eta$) were calculated from the measured data of 1-propanol and 2-propanol aqueous solutions. These values were correlated as a function of mole fraction by using the Redlich-Kister equation. The excess volumes are negative whereas the viscosity deviations are all positive over the entire composition range at all temperatures for the systems studied.

The modified form of the ionic strength additive equation was used to predict the densities of the aqueous solution of the ternary systems. The predicted and observed densities are in good agreement, with an overall average percent error of 0.29 %. An additivity equation based on the ionic strength of the mixed solution was used for the viscosity prediction of the viscosity of the aqueous ternary solutions. An attempt was made to modify the ionic strength additive equation by using total molality instead of ionic strength. The overall average error for the viscosity prediction for the systems studied is 1.63 %.

CHAPTER ONE

INTRODUCTION

Many industrial processes involve with systems of aqueous solution containing more than one solute. The basic properties of the aqueous solutions most commonly used are density, solubility, viscosity, vapor pressure and thermal conductivity. A knowledge of thermodynamic and transport properties of aqueous solutions is important in engineering, designing new technological processes, developing theoretical models and also in research work. Accuracy in the design or performance of industrial equipment for handling operations or processes involving aqueous salt solutions requires accurate physical data on the solutions involved. For engineering utility, reliable solutions over wide range of concentration and temperature would be extremely valuable (Horvath, 1985). Volumetric properties of aqueous solutions, in conjunction with other thermodynamic properties provide useful information about water-solute interactions. Density and viscosity of aqueous solutions are required in both physical chemistry and chemical engineering calculations involving fluid flow, heat and mass transfer (Giro *et al.*, 2003).

Consequently, reliable and accurate data which can be applied to wide ranges of temperatures are required. The values of such quantities may sometimes be obtained from tables but it is usually found that even the most extensive tables do not contain all the data necessary for designing a technological process. The properties of fluid mixtures are required to understand the molecular interactions. It is usually found that the properties have only been studied for the pure components from which the liquid mixtures are constituted and some methods are required for estimating the properties of the mixtures from those of pure substances. Such predictions usually entail considerable difficulties. The most difficult case occurs when the properties of the compound or mixture in question have not been measured at all. In this case the only information available may be the structural formula of the given compound.

Although values of the necessary quantities can sometimes be estimated, it would clearly be preferable to perform the appropriate measurements and to determine the values of the properties under consideration experimentally. This is not practicable since the determination of the values of some physical properties requires the use of expensive special equipment. For this reason knowledge of the methods of computing the values of these physico-chemical quantities is of great importance for the technologist. It should theoretically be possible to compute the values of the necessary quantities from knowledge of the structure of the molecules and the character of the forces joining the atoms (Bretsznajder, 1971).

Alcohols are self-associated organic liquids and are widely used in the chemical industry. The main uses of alcohols are as solvents for fats, gums, resins, paints, lacquers and varnishes, in the making of dyes and for essential oils in perfumery. Aqueous solutions of alcohols have served as useful industrial solvent media for a variety of separation processes. It also has become popular in solar thermal systems. Alcohols and their binary mixtures are also used as solvents in chemistry and modern technology for homogeneous and heterogeneous extractive rectification (Naziev *et al*., 2004).

Urea is a bio-molecule, a nonelectrolyte and hydrophilic water structures breaker and is physiologically important compound. Aqueous urea and its derivatives are important solvents and have a wide range of applications. It causes protein and nucleic acid denaturation. Specific interactions of urea with a molecule or changes in the solvent structure may be responsible for the denaturation process (Islam and Waris, 2004). The physical effects of urea in aqueous solutions are of interest in diffusion and micelle formation (MacDonald and Guerrera, 1970).

Sodium chloride is present to a large extent in natural inorganic salt deposits. Sodium chloride is used in a plethora of applications, from manufacturing pulp and paper to setting dyes in textiles and fabric, to producing soaps and detergents. Sodium chloride is also the raw material used to produce chlorine which itself is required for the production of many modern materials including polyvinyl chloride and pesticides. Industrially, elemental chlorine is usually produced by the electrolysis of sodium chloride dissolved in water. Sodium metal is produced commercially through the electrolysis of liquid sodium chloride. The separation of sodium chloride has been a main objective in the inorganic industrial research long time ago (Taboada *et al*., 2005).

1.1 Literature Survey

Ling and Van Winkle (1958) determined densities and viscosities of 1-propanol + water, toluene + octane, 1-butanol + water, acetone + 1-butanol, benzene + 2-chloroethanol, carbon tetrachloride + 1-propanol, ethanol + 1,4-dioxane and methanol + 1,4-dioxane at temperatures 30, 55, 75 and 95 °C. It was found that the liquid viscosity for the same liquid composition was lower at higher temperature. The estimated precision in the liquid density determination was 0.05 %. Densities and refractive indices of 1-propanol, 2-propanol and methanol with water were measured at 20 and 25 °C by Chu and Thompson (1962). The density-composition curves for both 1-propanol and 2-propanol exhibit a steady decrease in density with increase in weight percent of alcohol. Densities and viscosities of binary aqueous solutions of 1-propanol have been studied and presented using power series equation by Mikhail and Kimel (1963) at 25, 30, 35, 40 and 50 °C. The maximum deviation of the calculated values as compared with the experimental values reported by Mikhail and Kimel (1963) was less than 0.15 % and 0.88 % for density and viscosity, respectively.

Viscosity studies of solutions of water in *n*-aliphatic alcohols were also reported at 15, 25, 35 and 45 °C (D’Aprano *et al*., 1979). The viscosity of most liquids as a function of temperature at constant pressure can be represented by Arrhenius equation. For most the systems, water decreases the viscosity of the dry alcohols, while for the lower members of the series literature data report an increase in viscosity on addition of water. Won *et al*. (1981) measured density, viscosity, surface tension, carbon dioxide solubility and diffusivity of methanol, ethanol, aqueous propanol and aqueous ethylene glycol solutions at 25 °C. The density and viscosity of aqueous propanol solutions agree well with the data of Mikhail and Kimel (1963).

Densities and refractive indices of pure alcohols from methanol to 1-decanol at various temperatures were presented by Ortega (1982). The data are discussed and correlated versus temperature through an empirical relationship. The empirical equation of Eykman is used to check the accuracy of experimental densities and refractive indices. Dizechi and Marschall (1982) measured kinematic viscosities and densities of eight binary and four ternary liquids mixtures of polar components at various temperatures and the data were correlated with McAllister's equation and modified form of the McAllister's equation. Mean percentage deviations and standard percentage errors for viscosity were found generally to be smaller than 1 %. Sakurai (1988) measured the densities of 2-propanol with water over the entire mole fraction range and from 5 to 45 °C at 5 °C intervals. The densities of 2-propanol generally decrease with temperature and composition of alcohol. The apparent molar volumes of water in 2-propanol increases with temperature.

Kinematic viscosities of eight binary, five ternary and one quaternary liquid mixtures are reported for a wide range of temperatures and composition. The data were correlated with the McAllister equation and also with two modified versions of the McAllister equation (Soliman and Marschall, 1990). Liew *et al*. (1993) determined the viscosities of long chain *n*-alcohols from 15 to 80 °C. Plot of the logarithm of viscosity versus reciprocal absolute temperature were almost linear. The energies of activation were found to increase with chain length. The viscosities and densities of 1-propanol + 1-butanol, 1-propanol + 1-pentanol, 1-butanol + 1-pentanol, 1-butanol + 1-nonanol, 1-butanol + 1-decanol, 1-pentanol + 1-octanol, 1-heptanol + 1-octanol and 1-decanol + 1-undecanol were measured over the entire composition range at 35 and 40 °C and at atmospheric pressure. The viscosity data were correlated by the McAllister equation with an average absolute error (AAD) 0.2 % (Shan and Asfour, 1998).

Hynčica *et al*. (2004) measured the density for dilute aqueous solutions of methanol, ethanol, 1-propanol and 2-propanol in a wide interval of temperature and pressure. Herráez and Belda (2006) measured refractive index and density of binary mixtures of monoalcohols with water at 25 °C and atmospheric pressure. The excess molar volumes are negative in all these systems. Tôrres *et al.* (2007) determined the volumetric properties of binary mixtures of acetonitrile and alcohols at different temperatures and atmospheric pressure. The experimental results were fitted with the Redlich-Kister type equation.

Romanklw and Chou (1983) determined the densities of aqueous sodium chloride, potassium chloride, magnesium chloride and calcium chloride in the concentration range 0.5 to 6.1 m by using oscillating tube-type densitometer. The data were represented by using least-squares polynomial regression analysis. Statistical evaluation of the experimental data indicates that uncertainties in the concentration of the solutions during weighing are the major source of error in the density measurement. Afzal *et al*. (1989) determined viscosities of aqueous solutions of the chlorides of potassium, sodium, calcium, magnesium, strontium, barium, cobalt, nickel, chromium and copper in the wide range of concentrations and from 20 to 50 °C at 5 °C intervals. The ion-solvent interaction terms were evaluated in the concentrations range of 0.1 to 5.0 M. The data were represented by a newly suggested empirical equation. The viscosity coefficients estimated were found to be comparable with literature values.

Zhang and Han (1996) determined the viscosity and density of water + sodium chloride + potassium chloride solutions at 25 °C. A 3.5th term in molarity was added to the extended Jones-Dole equation to produce a new equation. This extended Jones-Dole type equation can represent well the viscosities of the systems studied to saturated concentrations. The viscosity and density of water + sodium chloride + calcium chloride solutions and water + potassium chloride + calcium chloride solutions were measured over the entire concentration range at 25 °C. The extended Jones-Dole equation represents well for these systems up to high concentration (Zhang *et al.*, 1997).

Herskovits and Kelly (1973) determined the relative viscosity and the viscosity B and C coefficients of alcohols, urea and amide solutions. The most significant finding of their study was that viscosity increments of most of those solutes were in the ranges predicted by the Einstein and Simha equations for rigid spherical or ellipsoidal particles. Viscosities for solutions of some α-amino acids in 5 mol kg^{-1} aqueous urea have been determined from 5 to 35 °C at 10 °C intervals. The viscosity B-coefficients for the amino acids in the aqueous urea solution have been calculated (Wang *et al.*, 2000). Islam and Waris (2004) investigated the solute-solvent and ion-solvent interactions in leucine + aqueous urea, sodium chloride + aqueous urea and potassium chloride + aqueous urea systems. Pal and Kumar (2004) measured the viscosities and densitites of L-glycine, L-alanine and L-valine in aqueous urea solutions ranging from 5 to 25 % urea by mass. The viscosity data have been analysed by Jones-Dole equation. The values of the B-coefficients for all amino acids in aqueous urea are positive indicating that the ion-solvent interactions are strong.

1.2 Density

The density of a substance, ρ is the ratio of its mass to its volume. Both mass and volume are extensive quantities. They specify how much of the substances are physically present in the mixture. The dimensions of density are $M\ L^{-3}$. Density is an intensive quantity relating to the nature of the substance. The property varies not only with molecular weight but also with molecular interaction and structure. The density of fluids is an important element for research and industrial field. Density is used to solve variety of problems such as quality control in the production of industrial liquids or concentration determination in the food and beverages industries, as in measuring sugar and alcohols concentration. Specific applications for density include chemical spill models for substances such as oil or toxic gases. In addition, density is often required for the estimation of other chemical properties; such as molar refraction and viscosity (Nelken, 1990).

The density is useful in conversion of concentration unit and in the investigation of interactions in solutions. The density data are used to calculate the apparent molar volumes and partial molar volume at infinite dilution. Apparent molar volumes and partial molar volumes give a direct measure of displacement of water by solute and thus reflect the compatibility of the solute with water. Studies of the apparent molar volumes and partial molar volumes of electrolyte solutions are used to examine the ion-ion, ion-solvent, and solvent-solvent structural interactions.

Density is a function of temperature for pure liquid. It can be expressed as:

$$\rho = kT + m' \qquad (1.1)$$

where ρ is the density, k and m' are constants and T the temperature. More complicated relations may have to be used at wider temperature ranges. Density is a function of compositions at a given temperature and pressure. For nonideal solutions, empirical calibration will give the relationship between density and composition. The information of density is important in identification, analysis and characterization of many substances in liquid, solid or gaseous state (Ortega, 1982). As density is one of the design data, accurate fundamental values are needed in plant design to avoid serious effect on plant performance and economics, ranging in severity from insignificant to critical. Effects of data uncertainties on data-sensitive process design problems are fairly large.

There are currently large amounts of aqueous solutions or combination of different solutes that involve water and being used in many types of industrial processes. Therefore, the need to obtain the densities of these multicomponent aqueous solutions is paramount during, before and after each process in order to make analyses or implement improvements. There are many techniques used to perform direct measurements of fluid densities. Some of these measurement techniques are by utilizing pycnometers, sinker method (hydrometer), dilatometers, magnetic float densitometer and vibrating tube flow densitometer (Teng and Mather, 1996). A pycnometer is basically a simple device that is normally made of glass with various types of sizes. Densities under constant pressure and temperature are obtained through a simple calculation of mass per volume. The pycnometer has a fixed volume and allows the weight of the liquid to be measured.

A vibrating tube flow densitometer is a more complex instrument but it provides higher accuracy of the required data. Figure 1.1 shows a general sketch of a vibrating tube flow densitometer. It works mainly by measuring the natural vibrating frequency of a tube loaded with the liquid under study. When a tube is filled with a certain solution, it will vibrate at a different frequency from that of a tube with a solution of a different concentration or an empty tube. Although these measurement techniques for densities of aqueous solutions are easily available and provide adequate accuracy, however, direct measurement is very time consuming and not economical for industrial processes that requires a vast amount of data. Therefore, many density prediction methods are studied nowadays.

1.3 Densities of Pure Liquids

For most pure liquids at constant pressure, the change in density with temperature can be summarized accurately by the following equations (Teng and Mather, 1996):

$$\rho = A + BT \tag{1.2}$$

$$\rho = A' + B'T + C'T^2 \tag{1.3}$$

where the values A, B, A', B' and C' are parameters of equation and T is the temperature. The term B is negative, and either B' or C' is negative because the density of fluids decreases with increase in temperature.

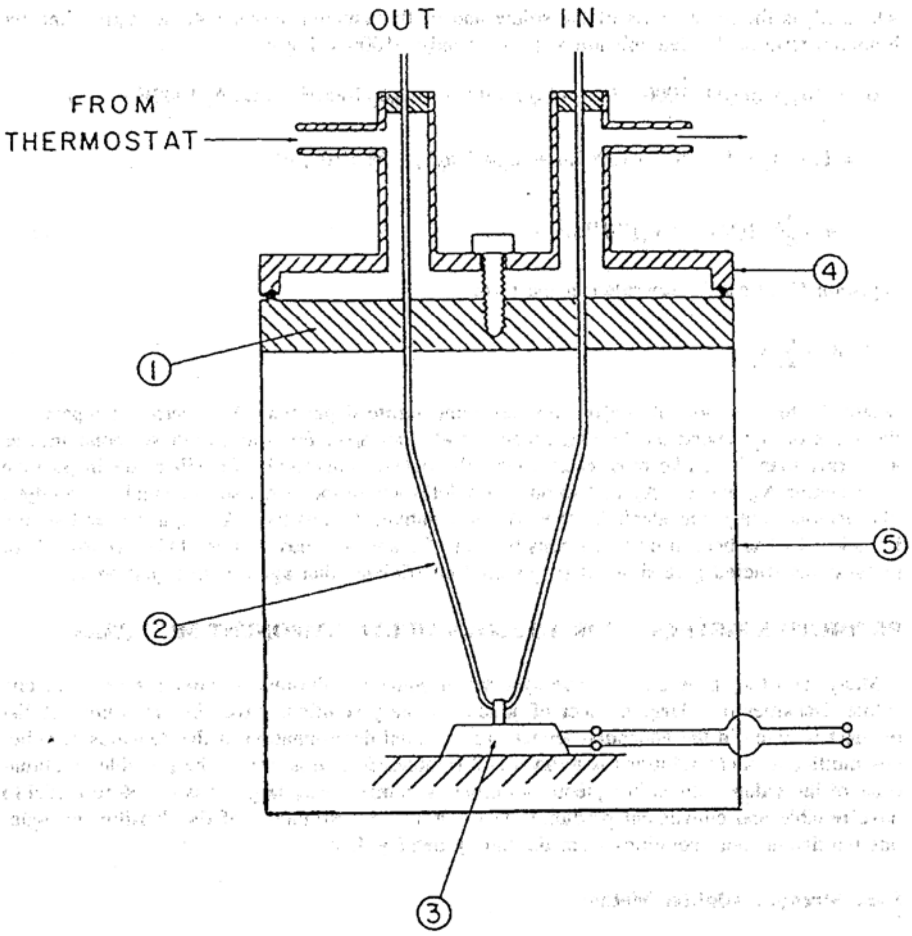

Figure 1.1 A general sketch of a vibrating tube flow densitometer (1, anchoring plate; 2, vibrating tube; 3, magnetic pickup; 4, thermoregulated jacket; 5, thermoregulated vessel) (Teng and Mather, 1996).

1.4 Densities of Aqueous Solutions

For aqueous binary solutions at constant pressure, the density can be expressed as (Xu *et al*., 1992):

$$\rho = \Sigma\, ø_i\rho_i + ø_2\,(1 - ø_2)\,(1 + \Sigma\, b_iø^i_2)\,(\Sigma\, e_iT^i) \qquad (1.4)$$

where ρ_i is density of the pure component i, $ø_{i,}$ $ø_2$, volume fractions of component i and the solute, and b_i, e_i are polynomial coefficients. In order to obtain a good polynomial fit, Equation (1.4) needs a large number of data points over the temperature and concentration ranges. Densities of most aqueous binary solutions at constant temperature and pressure with increase of its molalities show different behaviors.

Figure 1.2 displays some of the general behaviors of densities of aqueous binary solutions with the increase of their molalities. Densities of soluble solutes with limited solubility are illustrated on Curve I. According to Perry *et al*. (1997), this category belongs to almost all inorganic soluble salts. Curve II represents substances such as acetic acids and sulfuric acids that pass through the maximum point of concentration as they near their pure solute. Densities of aqueous solutions that increase with concentration from dilute solutions to pure solutes are illustrated in Curve III. In Curve IV, the density of the solution initially increases until a maximum value and then begins to decrease until it is no longer higher than the density of pure water but lower. According to Shindo and Kusano (1979), the solute 2-methoxyethanol displays this type of behavior. For Curve V, it represents a solute that has an increase in density in the dilute region but then gradually its density decreases with concentration. Touhara *et al*. (1982) explained that methyethanolamine displays such behaviors. Through

Curve VI, it can be seen that the densities of the aqueous solution decrease with increase concentration. Solute such as acetone (Kurtz *et al.*, 1965) and some alcohols (Herráez and Belda, 2006) give such behaviors.

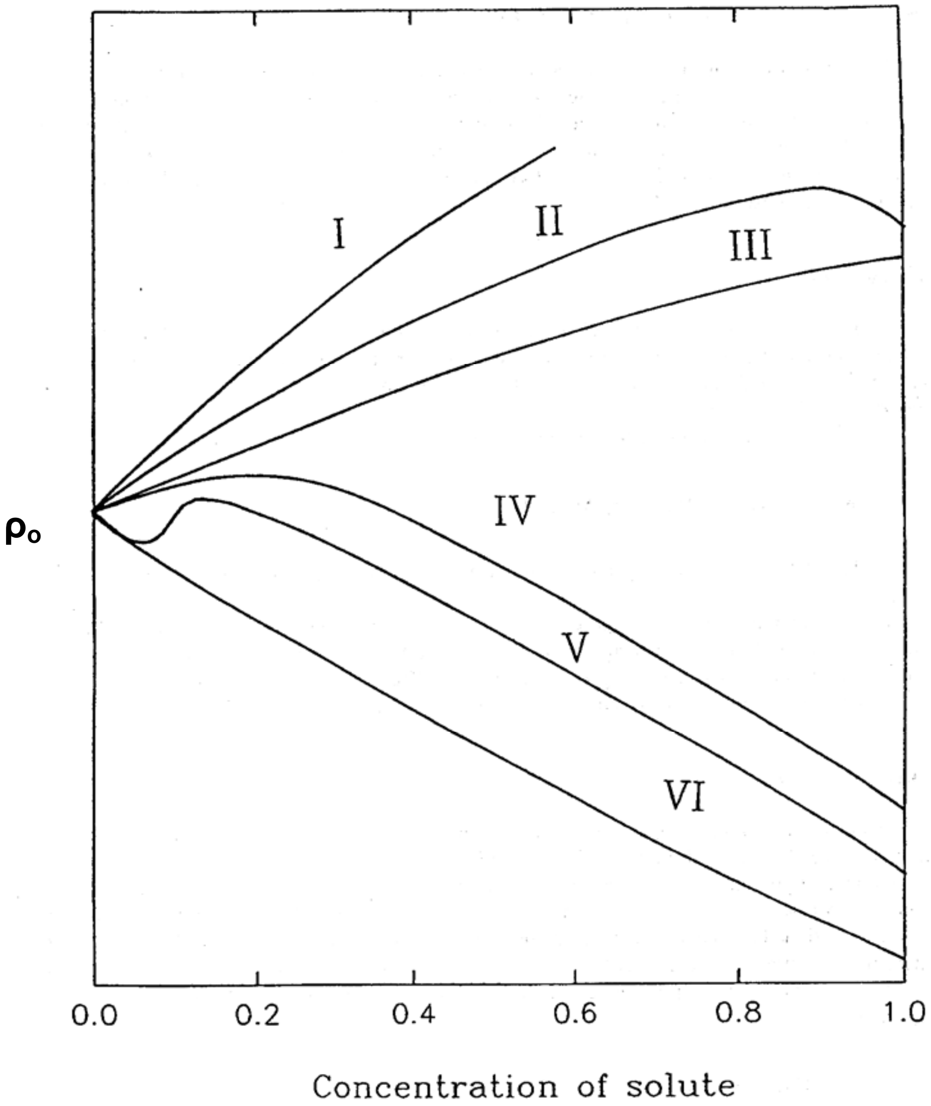

Figure 1.2 Some general behaviors of densities of aqueous solutions with the increase of their molalities (Teng and Mather, 1996).

1.5 Representation of Densities Data for Aqueous Binary Solutions

There are various equations representing density as a function of concentration that had been proposed (Horvath, 1985). Of the various proposed equations, many researchers have used the following equation to represent the density data of aqueous binary solutions:

$$1000\ (\rho - \rho_o) = a_1m + a_2m^{3/2} + a_3m^2 + a_4m^{5/2} \qquad (1.5)$$

where a_1 to a_4 are temperature dependent parameters, m is the molality, ρ, the density of the solution and ρ_o as the density of water.

Teng and Lenzi (1975) and Teng and Mather (1996) had proposed another form for representing the density data. Density is considered to be related to the apparent molal volume, Φ_v by equation (1.6a):

$$\begin{aligned}\rho &= (1000/m + M_2) / (\Phi_v + 1000/m\rho_o)\\ &= (\rho_o + m\rho_oM_2/1000) / (1 + m\rho_o\Phi_v/1000) \qquad (1.6a)\end{aligned}$$

with M_2 as the molar mass of the solute and Φ_v the apparent molal volume. By expanding the binomial term in the denominator with $-1< m\rho_o\Phi_v/1000 <1$ gives rise to:

$$\begin{aligned}\rho &= \{\rho_o + m\rho_oM_2/1000\}\ \{1 - m\rho_o\Phi_v/1000 + (m\rho_o\Phi_v/1000)^2 -\\ &\quad (m\rho_o\Phi_v/1000)^3 + \ldots\}\\ &= \rho_o + \rho_o\{(M_2 - \rho_o\Phi_v)/1000\}\ m + \rho_o^2\Phi_v\{(\rho_o\Phi_v - M_2) / 10^6\}\ m^2 +\\ &\quad \rho_o^3\Phi_v^2\{(M_2 - \rho_o\Phi_v)/10^9\}\ m^3 + ,,, \qquad (1.6b)\end{aligned}$$

Equation (1.6b) can be simplified in the form of:

$$\rho = \rho_o + \Sigma\ a_jm^j \qquad (1.7)$$

where a_j is the polynomial coefficient that is dependent on temperature and m^j is the molality of the solute. If Equation (1.7) is to be compared with Equation (1.6b), then it shows that:

$$a_1 = \rho_o\{(M_2 - \rho_o\Phi_v) / 10^3\}$$

$$a_2 = \rho_o^2\Phi_v\{(\rho_o\Phi_v - M_2) / 10^6\}$$

$$a_3 = \rho_o^3\Phi_v^2\{(M_2 - \rho_o\Phi_v) / 10^9\}$$

At a certain temperature, the signs of a_j depend on the magnitudes of M_2 and $\rho_o\Phi_v$. For solutes whose molar masses are larger than $\rho_o\Phi_v$, like most electrolytes, the density polynomial fit will result in positive a_1, negative a_2, positive a_3 and so on. Equation (1.7) has been used to fit density of many aqueous systems (Teng and Lenzi, 1975).

1.6 Predictive Methods for Aqueous Multicomponent Mixtures

In industry, aqueous solutions usually contain more than one solute of various combinations. Direct experimental determination of the densities of aqueous multicomponent solutions is tedious and troublesome. In addition, the possible combinations of individual solutes in aqueous solutions are tremendously large. It is therefore useful to have reliable and convenient predictive methods for the estimation of the densities of aqueous multicomponent solutions from the binary data (Teng and Mather, 1996). There exist some techniques or methods for the prediction of aqueous multicomponent mixtures. These methods are mainly equations that can be used to calculate the value of densities of the required aqueous multicomponent mixtures.

A simple constant ionic strength method (Teng and Mather, 1996) assumes that the density of a mixed solution at a given ionic strength is additive in the densities of the individual binary solutions at the same ionic strength, I:

$$\rho = \Sigma\, y_i \rho_{iI} \qquad \text{(constant I)} \tag{1.8}$$

where y_i is the molality fraction of solute i in the mixed solution and ρ_{iI} is the density of the binary solution of solute i with the same ionic strength as that of the mixed solution. Although it is a simple method, extrapolation from the density-concentration relation may be needed for mixed solution of ionic strength beyond the solubility of that particular solute. This occurs when the mixed solution involves a solute of low solubility. Since this method involves ionic strength, it can only be used to system containing electrolytes.

Young and Smith Mixing Rule (1954) proposed that the apparent molal volume of an aqueous mixed electrolyte solution is an additive function of the apparent molal volume of each electrolyte in a binary solution at the same ionic strength as that of the mixed solution:

$$\Phi_v = \Sigma\, y_i \Phi_{vI} \qquad \text{(constant I)} \tag{1.9}$$

with y_i is the molality fraction of solute i in the mixed solution, Φ_{vI} as the apparent molal volume of the solute i that has the same ionic strength as that of the mixed solution.

The densities of binary aqueous solutions can be expressed as a function of concentration by means of the logarithmic equation:

$$\rho = \rho_o - \text{In}\,\{1 - B(p')\,p'\} \tag{1.10}$$

where p’ is the weight fraction of solute, B(p’) is a “density function”, expressed either by a linear equation, B(p’) = B(0) + βp’ or by an equation of a function represented by a discontinuous line consisting of linear segments. The constant B(0) and β depend on the nature of the solute and are determined empirically. This method can only be applied to solute that has high solubility in water.

Teng and Lenzi (1975) had proposed a method to predict the densities of multicomponent aqueous solutions from binary data, which is based on solutions of the same density (isopycnotic). It assumes a linear relation between the solute molalities of binary and multicomponent aqueous solutions at the same density, ρ. It can be expressed generally as:

$$\Sigma\, m_i / m_{oi} = 1 \qquad \text{(constant } \rho\text{)} \qquad (1.11)$$

where m_{oi} is molality of binary solute i having the same density as the mixed solution, m_i, molality of solute i in mixed solution. It states that when two or more aqueous solutions of the same density are mixed, the resultant solution will have nearly the same density. The short-range solute-solute interactions and hydration cross-effects or their mutual cancellation are assumed to be negligible. This method can be applied to systems involving electrolyte-electrolyte, electrolyte-nonelectrolyte, nonelectrolyte-nonelectrolyte and polyelectrolytes. However, a limitation of the method is that the muticomponent density must be within the density region of the binaries.

An equation for the apparent molal volume of an electrolyte Mv_MXv_X had been derived by Pitzer *et al*. (1978):

$$\Phi_v = V°_2 + v\,|Z_M Z_X|\,(A_v / 3b)\ln(1 + bI^{1/2}) - 2v_M v_X RT\,(mB^v_{mx} + m^2 C^v_{mx}) \qquad (1.12)$$

where $B^v_{mx} = (\partial\beta^{(0)} / \partial P)_T + (\partial B^{(1)} / \partial P)_T\,(2/\alpha^2 I)\,\{1 - (1 + \alpha I^{1/2})\exp(-\alpha I^{1/2})\}$ (1.13)

$$C^v_{mx} = (v_M v_X)^{1/2}\,(\partial C^\Phi / \partial P)_T / 2 \qquad (1.14)$$

A_v is the Debye-Hückel coefficient, $b = 1.2$, $\alpha = 2.0$. Least-squares regression enables values of $\partial\beta^{(0)} / \partial P$, $\partial B^{(1)} / \partial P$ and $\partial C^\Phi / \partial P$ to be generated for an electrolyte with enough value of Φ_v and m. Unfortunately, the interaction among ions with like-charges is not taken into account in equation (1.12). Equation (1.12) needs to be used to calculate the four Φ_v for the possible cation-anion combinations of a ternary solution of mixed-type electrolytes that does not have common ions.

Söhnel *et al.*, (1984) proposed that the density of a binary solution can be described by the equation:

$$\rho = \rho_o + \alpha' c - \beta' c^{3/2} \qquad (1.15)$$

where c is the molar concentration (molarity) of the solute, α' and β' are parameters of equation. For an aqueous ternary solution:

$$\rho = \rho_o + \Sigma\,\alpha_i' c_i - (\Sigma\,\beta_i'^{3/2} c_i)^{3/2} \qquad (1.16)$$

Densities of several aqueous ternary solutions from 15 to 100 °C had been predicted using the above equation. The error was especially large for systems of high solute concentration due to the equation not taking into account the short-range interactions that are important in concentrated solutions.

Patwardhan and Kumar (1986, 1993) developed a unified model for the prediction of thermodynamic properties of aqueous mixed-electrolyte solutions.

$$\rho = \Sigma\, \Sigma\, \psi_{ij} / \Sigma\, \Sigma\, (\psi_{ij} / \rho°_{ij}) \qquad (1.17)$$

where $\psi_{ij} = (1000y_{ij} + m_{ij}M_{ij})$

$y_{ij} = (ISF)_i\,(CF)_j + (ISF)_j\,(CF)_i$

(CF) = charge fraction, m_iz_i / CH

(CH) = total charge, $\Sigma\, m_iz_i$

(ISF) = ionic strength fraction, $m_iz_i^{\,2} / 2I$.

Like Pitzer equation, for a solution of two electrolytes that contain four different ions - two cations, two anions, it requires the density information of four different electrolytes that involve all the four ions at the ionic strength of the mixed solution. The limitation of the method lies in the solubility of the electrolytes involved.

An empirical approach was proposed by Hu (2000) in order to obtain the density values of multicomponent aqueous solutions that conform to the isopiestic linear relations, which means having the same water activity. This particular approach is used to estimate the densities of multicomponent systems from binary densities data at the same water activity. Equation (1.18) displays the empirical approach:

$$\rho = \Sigma_i\, (m_i / m_i°)\, \rho_i° \qquad (1.18)$$

where m_i is molality of solute i in the aqueous multicomponent solution, $m_i°$, molality of solute i in the aqueous binary solution with the same water activity as the aqueous multicomponent solution, ρ, density of the aqueous multicomponent solution, $\rho_i°$, density of the aqueous binary solution with the molality of $m_i°$.

Pereira *et al*. (2001) have proposed an equation relating relative density to solvent density. The equation includes the effects of composition and the temperature. It is also a predictive model, based on the characteristics parameters for each solute.

$$\rho_{rel} = 1 + d_1 w + d_2 w + (T - T_{ref}) \tag{1.19}$$

where ρ_{rel} is relative density, d_1,d_2 are parameters, w is mass fraction of solute and T the temperature.

1.7 Comparison of the Predictive Methods

These density predictive methods require density values of the aqueous binary solutions of the solutes involved. Good representation of the density of binary solutions as a function of compositions is important. Most methods use simple polynomial representation. Pitzer's equation requires obtaining parameters for the apparent molal volumes of the binary solutions from non-linear least-squares regression. The simple constant ionic strength method and isopycnotic equation are linear in apparent molar volume, while isopycnotic equation is linear in molality ratio. The others are additive and explicit in density. The simple ionic strength additive method gives generally higher errors (Teng and Lenzi, 1975). The Young and Smith Mixing Rule have been shown to give good density prediction for electrolyte mixtures. The Patwardhan and Kumar method is an additive method but is not a simple one, especially when it involves solutes of different types of ions. Pitzer's equation has been tested for some aqueous ternary systems with a common ion (Kumar and Atkinson, 1983; Kumar, 1985). It gives excellent predictions of the density, especially when the binary mixing terms are included. All of these methods are only applicable to aqueous electrolyte solutions. For nonelectrolyte solutions, ionic strength is undefined. The method that can be applied to aqueous systems other than electrolytes is the isopycnotic method but the aqueous binary solution of the solutes involved must have common density. From the methods obtained, it was found that there is no convenient predictive method for density of ternary systems especially for solutions without common density.

1.8 Viscosity

Viscosity is a measure of the internal fluid friction, which tends to oppose any dynamic change in the fluid motion (Poling *et al*., 2001). Viscosity is the property of a fluid-liquid or gas that mainly characterizes its flow behavior. The concept of viscosity embraces the idea of the internal friction between the molecules of the fluid for, whenever any part of a fluid is caused to move, neighboring parts tend to be carried along too. This resistance to the development of velocity differences within a fluid is the essential feature of viscosity and it forms the basic of the quantitative assessment of viscosity (Dinsdale and Moore, 1962).

Viscosity varies with temperature. In general, the viscosity of a simple liquid decreases with increasing temperature and vice versa. As temperature increases, the average speed of the molecules in a liquid increases and the amount of time they spend "in contact" with their nearest neighbors decreases. Thus, as temperature increases, the average intermolecular forces decrease.

Viscosity is normally independent of pressure, but liquids under extreme pressure often experience an increase in viscosity.

The measurement of viscosity is of considerable importance in both industrial production and fundamental science. Viscosity is the quantity that determines the forces to be overcome when fluids are used in pipelines or bearing, and it controls the flow of liquid in such processes. In other applications the measurement of viscosity affords a convenient means of checking the constancy of a product. Viscosity measurement has also proved to be a valuable tool for the physical chemist since the viscosity coefficient is profoundly influenced by the size, shape and arrangement of the molecules.

For laminar flow of a Newtonian fluid, the dynamic viscosity, η can be defined simply as the force per unit area required to maintain unit difference in velocity between two parallel layers of the fluid which are unit distance apart (Stokes and Mills, 1965). It may be written as:

$$\eta = \tau / (\partial u / \partial y) \tag{1.20}$$

where η is the absolute viscosity, τ is the force per unit area or shear stress and $\partial u/\partial y$ is the velocity gradient normal to the planes of flow. Because η appears as a proportionality factor between the shear stress and velocity gradient, it is usually termed the coefficient of viscosity. The dimensions of absolute viscosity are $M\ L^{-1}\ T^{-1}$. The kinematic viscosity is a measure of the resistive flow of a fluid under the influence of gravity. It is defined as the ratio of absolute viscosity to density and can be expressed as:

$$\nu = \eta / \rho \tag{1.21}$$

where ν is the kinematic viscosity. The dimensions in this case are $L^2 T^{-1}$. The unit of kinematic viscosity is the stoke, with the units square centimeters per second. In the SI system of units, viscosities are expressed in Pa s and kinematic viscosities in either $m^2 s^{-1}$ or $cm^2 s^{-1}$. Relative viscosity is the ratio of the viscosity of a solution to that of the pure solvent under the same conditions. The relative viscosity of solutions is given by

$$\eta_{rel} = \eta / \eta° \tag{1.22}$$

The specific viscosity is the ratio of the difference between the solution and solvent viscosities to the solvent viscosity. The specific viscosity has the form:

$$\begin{aligned}\eta_{sp} &= (\eta - \eta°) / \eta° \\ &= \eta_{rel} - 1 \qquad (1.23)\end{aligned}$$

1.9 Viscosity of Water

According to Franks (1972), the primary reference liquid for viscosity measurements is water. Therefore, viscosity of water at different temperatures must be very accurate at atmospheric pressure.

1.10 Viscosities of Pure Liquids

The viscosity of a liquid is a measure of the forces that work against movement or flow when a shearing stress is applied (Grain, 1990). The molecules in a liquid are held together much more strongly than in a gas. Viscosity is a measure of the force needed to overcome the mutual attraction of the molecules so that they can be displaced relative to each other. The more strongly the molecules are held together, the smaller the flow for a given shearing stress. With increasing temperature, the random kinetic energy of the molecules helps to overcome the molecular forces and reduces the viscosity.

Newton deduced that the viscosity produces retarding forces proportional to the velocity gradient (*du/dx*) and to the area (A_L) of contact between moving sheets of liquid (James and Prichard, 1974). Thus the retarding force is shown as:

$$F \propto A_L\, du/dx = \eta\, A_L\, du/dx \qquad (1.24)$$

where η is the coefficient of viscosity or dynamic viscosity. This equation is not valid for the non-Newtonian liquids.

The viscosity of a liquid always decreases with temperature and many empirical equations representing the dependence have been proposed. The viscosity of liquids depends on factors such as molecular size and intermolecular forces. The best known equation for representing the viscosity-temperature relation is due to Andrade-Guzman Equation as shown below:

$$\eta = A''\exp^{B''/T} \qquad (1.25)$$

with η is the viscosity, T is temperature in Kelvin, and A'' and B'' are constants. This equation is successful for simple liquids but associated liquids, oils, fused salts, and some liquid metals are known to show serious deviations (Misra and Varshni, 1961). Equation (1.25) can be modified to Arrhenius type equation in the form of:

$$\eta = A''\exp^{E(vis)/RT} \qquad (1.26)$$