Separation Science and Technology
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713708471

Salt Effect on Vapor-Liquid Equilibria: A Review of Correlations and Predictive Models

Anil Kumar[a]
[a] CHEMICAL ENGINEERING DIVISION, NATIONAL CHEMICAL LABORATORY, PUNE, INDIA

To cite this Article Kumar, Anil(1993) 'Salt Effect on Vapor-Liquid Equilibria: A Review of Correlations and Predictive Models', Separation Science and Technology, 28: 10, 1799 — 1818

To link to this Article: DOI: 10.1080/01496399308029242

URL: http://dx.doi.org/10.1080/01496399308029242

SEPARATION SCIENCE AND TECHNOLOGY, 28(10), pp. 1799–1818, 1993

REVIEW

Salt Effect on Vapor–Liquid Equilibria: A Review of Correlations and Predictive Models*

ANIL KUMAR
CHEMICAL ENGINEERING DIVISION
NATIONAL CHEMICAL LABORATORY
PUNE 411008, INDIA

ABSTRACT

The salt effect on vapor–liquid equilibria has been a subject of intense investigation from the points of view of both experimental data collection and modeling. In this review the available correlations and predictive models for estimating the salt effect are described. These models have been broadly classified into two categories depending upon whether the model is based on excess free energy or not. A comparative description of these models is presented with a view to judge their predictive capabilities.

INTRODUCTION

Addition of a salt to a binary solution of volatile solvent components can alter the composition of the vapor in equilibrium with the liquid. This alteration in composition is caused by the interaction of salt with the solvents. This phenomenon, popularly known as the "salt effect" on the vapor–liquid equilibria (VLE), has been the subject of investigation of both experimental data collection and modeling.

In terms of chemistry, there are several complexities in describing the salt interactions with the volatile solvent components. These complexities arise out of the selective effect due to a salt on the volatilities of the liquid components. In other words, a salt may induce the formation of association complexes or clusters of molecules of the more volatile solvent. Consequently, the structure of the liquid may be altered. This will cause a change in short-range interactions in solutions. These interactions are very difficult to take into account when attempting to understand the

---

* National Chemical Laboratory Communication 5643.

mechanism of the salt effect. Other factors, such as long-range electrostatic interactions between ions and association between cation and anion, may play significant roles. In the case of mixed solvents containing a salt, the physical picture is extremely complicated, and it is not surprising that valid physical theories are not yet available for such systems.

The application of this effect is of practical interest in such unit operations as the distillation of salt-containing liquids, liquid–liquid extraction for mixtures containing salts, salt precipitation from mixed solvents, etc. An important application of the salt effect on VLE is concerned with the possibility of using salts as the separating agents in extractive distillation processes. A very small amount of a salt can have a very pronounced effect on the relative volatility of the solvent species. Thus, azeotropes can be entirely eliminated by using a salt in a mixture of polar solvents. Extractive distillation using salts is therefore a potential alternative to the usual azeotropic or extractive distillation processes with a liquid as the separating agent. The use of salt in such processes can involve disadvantages such as insufficient solubility in nonaqueous solvents and corrosion of equipment. However, there are advantages to such processes: a smaller amount of separating agent is needed, the separating agent is free of overhead product, and less energy is required. Excellent reviews by Johnson and Furter (1), Furter and Cook (2), Furter (3, 4), and Ohe (5, 6) outline the basic principles and technical details regarding the above processes. Another good review was provided by Schmitt (7), but it is not readily available in libraries.

In this review we concentrate our discussion on various available correlations and predictive models which have been employed to describe this effect. The discussion presents the principles and applications of these models to several systems. Finally, the comparative performance of these models is presented to demonstrate their predictive capabilities.

CORRELATIONS AND PREDICTIVE MODELS

Various predictive tools have appeared in the past to describe the salt effect on VLE. With a view to streamline the scope of these tools, two categories can be broadly defined. Category I: The model equations are obtained without the excess free energy concept, i.e., approaches where the presence of salt is accounted for implicitly. Category II: The starting point of this model is excess free energy. Thus, Category I models are based on pseudocomplex formation, solvation, etc., while Category II models includes the use of Wilson, NRTL, UNIQUAC and UNIFAC, and their modified forms to describe this effect.

Category I

One of the developments in Category I pertains to the formation of a pseudobinary complex of the salt with a solvent in a mixture. Another development is concerned with the use of the concept of solvation, more particularly, preferential solvation. These correlations are discussed below.

Classic Work of Furter

Correlation of Furter and Extensions. The earliest model to account for the salt effect on VLE was put forward by Long and McDevit (8). In it, the ratio of the relative volatilities of a binary system without and with salt was related to the salt concentration. Furter (9) and Johnson and Furter (1) combined the effect of salt concentration on equilibrium vapor composition under the condition of a fixed ratio of two volatile components in the liquid phase. Their equation, derived from the difference in effects of the salt on the chemical potentials of the two volatile components, has the form

$$\ln(\alpha_s/\alpha) = kx_3 \qquad (1)$$

where α_s and α are the relative volatilities with and without salt and x_3 is the salt mole fraction. The parameter k should remain constant but it does not do so in practice; it varies strongly with the solvent composition. The constancy of k with changing salt concentration is estimated only when the ratio of volatile components in the liquid is held constant. Because the salt effect is a complex function of several interactions, k does not remain constant with changing composition.

Furter (3) and Johnson and Furter (1) described the model and its application to several systems. The article by Furter (3) discusses a further extension of the above relation to several systems under varying conditions. Other pertinent references to the above equation are from Furter and Cook (2), Meranada and Furter (10, 11) and by Jaques and Furter (12, 13). An excellent description is given in the monograph edited by Furter (14).

The Special Binary Approach. A special binary approach was proposed by Jaques and Furter (15, 16) in which two volatile solvents and a salt were treated as special binaries rather than as ternaries. In this pseudobinary technique, the presence of salt is recognized in adjustments made to the pure component vapor pressures from which the liquid-phase activity coefficients of two volatile components are calculated. In this approach, each of the two components of the binary is considered to be one of the volatile components individually saturated with the salt. The pure component vapor pressures used to calculate liquid-phase activity coefficient values for the volatile components are the vapor pressures of the volatile components, each saturated with the salt at the temperature in question, rather than of the volatile components alone. The activity coefficients of the volatile components are based on the standard states consisting of each volatile component saturated individually with the salt. Papers by Jaques and Furter (15) and by Jaques (16) give applications of the above approach, while Meranda and Furter (17) and Burns and Furter (18) discuss the range of its application. Extension of a special binary approach using the Wilson equation will be discussed later.

Vapor Pressure Depression Model of Lu

An empirical method was proposed by Lu (19) who utilized information on vapor pressure depression by the salt on each solvent and used the thus modified mole fractions along with salt-free activity coefficient for the prediction of the salt effect. The modified liquid-phase mole fraction of both the solvent components is given by

$$x_1' = x_1/(x_1 p_1^\circ/p_1 + x_2 p_2^\circ/p_2) \tag{2}$$

with an analogous expression for x_2. In the above expression, x_1 is the true mole fraction, and p_1° and p_2° are the vapor pressures of the pure solvents at the temperature of interest. The quantities p_1 and p_2 are the vapor pressures of solutions consisting of salt with liquids 1 and 2, respectively. These modified liquid-phase mole fractions are then employed in the standard equations correlating partial pressure with activity coefficients, and thus the vapor-phase compositions are computed.

This method, though very simple, is applicable to systems where very small deviations from ideality are obtained. Such systems include water–ethylene glycol–sodium sulfate with KCl and with KBr.

Preferential Solvation Models

Ohe Model. Gross and Halpern (20, 21) were the first to propose the concept of preferential solvation. They assumed that addition of a salt to a solvent mixture reduces the activity of one component. Their equations did not rigorously attempt to describe the salt effect on VLE, but they provided convincing evidence for this effect based on statistical interactions.

Ohe (22) later used preferential solvation to describe this effect on the methanol–ethyl acetate–$CaCl_2$ system. A typical example of preferential solvation is depicted in Fig. 1. According to Ohe, because $CaCl_2$ dissolves readily in methanol but only sparingly in ethyl acetate, it is of interest to

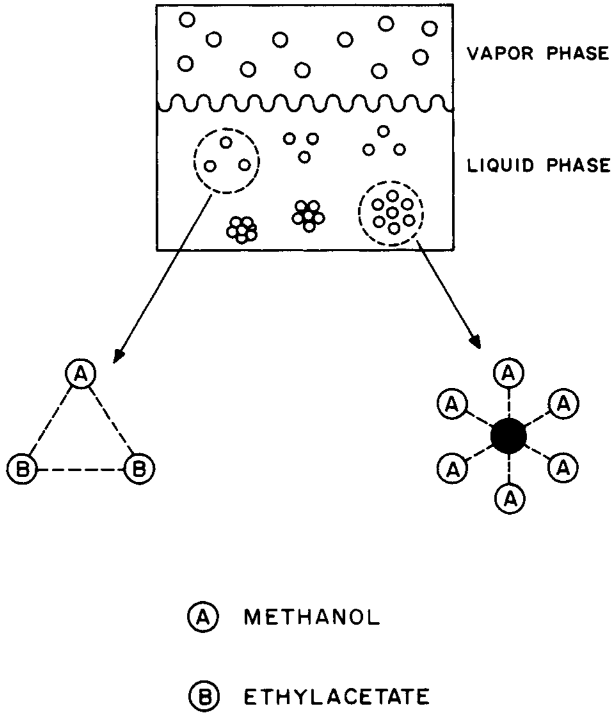

FIG. 1 A typical preferential solvation model for salt in mixed solvent system.

consider the interaction between methanol molecules and $CaCl_2$ only in methanol–ethyl acetate solutions. The free methanol molecules that are not clustered with ethyl acetate solutions increase linearly when the liquid-phase composition is above a certain value. Thus, the solubility of $CaCl_2$ is proportional to the increase in the number of methanol molecules. In this way, the dissolved $CaCl_2$ forms a preferential solvate with methanol, written $CaCl_2 \cdot 6CH_3OH$. Because the solvated methanol molecules cannot be evaporated, the composition of methanol participating in the VLE in the liquid phase is decreased. In order to proceed with the calculations, it is necessary to know the solvation number of each component. The salt effect can therefore be predicted by assuming that preferential solvation takes place over the entire range of liquid-phase composition. In essence, the preferential solvation number obtained is used to obtain the revised mole fraction, and equilibria is calculated. Ohe's work leads to the following conclusions.

(1) The preferential solvation number varies linearly with the liquid-phase composition of a solvent. (2) If the mixture is not saturated with salt, the preferential solvation number will increase with an increase in the mole fraction of solvent molecules forming the solvate. (3) The preferential solvation number is inversely proportional to the salt concentration.

In summary, the equilibrium composition of the vapor-phase composition is calculated by assuming that the solvated species cannot participate in the VLE. Therefore, the solvent that forms the preferential solvate is diminished in the vapor phase (salted in), while the other solvent is salted out. The inability of a single solvation number to represent VLE over the entire salt/solvent composition range is a major drawback of this method. A further objection to the assumption of solvation concerns systems where solvate formation may not be restricted to a single solvent in a liquid mixture. Ohe (22) examined the validity of his model by testing the experimental data for 14 systems under both isothermal and isobaric conditions. Unfortunately, the errors associated with his predictions are as large as 11% in the vapor-phase composition for systems like methanol–water–$CaCl_2$ and acetic acid–water–sodium acetate.

Schmitt–Vogelpohl Model. Schmitt and Vogelpohl (23) recently used a "pseudobinary" approach to describe this effect. They assumed that the salt forms a pseudobinary complex with the more volatile component in preference over the less volatile solvent. The degree of complex formation was assumed to be proportional to the salt solubilities in the pure solvent components. Based on this hypothesis, a distribution coefficient k_Z, defined as the ratio of mole fraction of salt in pure components, is introduced. Thus, the composition of complex x_3^* in terms of mole fraction is given by

$$x_3^* = 0.5F - (0.25F^2 - k_Z x_3)^{0.5} \tag{3}$$

with

$$F = k_Z(x_1 + x_3) + x_2 + x_3 \tag{4}$$

where x_1 and x_2 refer to the mole fraction of Solvents 1 and 2, respectively, while x_3 is the mole fraction of salt. Since k_Z is calculated from the solubility of salt in the solvents, and x_1, x_2, and x_3 are known, it is possible to compute x_3^* and then substitute it to give the partial pressure of each solvent component p_i by the standard equation

$$p_i = P_i(12)\gamma_{(i3)}x_3^* \tag{5}$$

where $P_i(12)$ is the vapor pressure of the solvent mixture on a salt-free basis, and $\gamma_{(i3)}$ is the activity coefficient of the ith solvent with salt alone.

The merit of this approach lies in its sole use of binary experimental data with a good representation of ternary data. There were limitations when the model was applied to a low concentration of salt and a high concentration of water. However, it appears that a more accurate prediction is possible if the degree of dissociation as a function of salt concentration is explicitly considered in the model. The procedure of Schmitt and Vogelpohl (23) can be extended to multicomponent solvent mixtures, but no evidence for such an extension is presently available.

Modified Model of Schmitt and Vogelpohl. Lee et al. (24) recently modified the model of Schmitt and Vogelpohl (23) by incorporating the concept of preferential solvation. The need for such a modification arose because their model was not capable of estimating the salt effect in a very dilute salt concentration and a high water content. Lee et al. (24) suggested that formation of a complex depends on the solubility of a salt and that a salt will preferentially associate with the component in which it is more soluble. A distribution factor, different from the one used by Schmitt and Vogelpohl (23), then becomes

$$k_Z = x_3(13)/x_3(23) \tag{6}$$

where Component 2 is the preferential component. Thus, k_Z, the distribution factor, is related to both the concentration of the salt and the solubility. At saturated conditions, the k_Z of Lee et al. (24) is identical to that proposed by Schmitt and Vogelpohl (23). In order to simplify the calculational procedure, they further assumed that the saturated salt concentration is linear with the composition of the solvent mixture. It was shown by Lee et al. (24) that incorporation of the concept of preferential solvation in the model of Schmitt and Vogelpohl (23) improves the predictive capability. Unfortunately, the generality of this modified model has not been demonstrated since the solubilities of salts in different solvents are not available. Their modified model may be further improved by taking into account the degree of dissociation of salt in the solution as a function of salt concentration with varying composition of solvents.

Kumar Model. Another addition to the models assuming pseudocomplex formation has been due to Kumar (25), who used the dielectric constant data of pure solvents and their mixtures to account for such complex formation by using a new term, the inverse relative solubility coefficient β. The peculiarity of β can be traced to its linear dependence on solvent composition. It is also independent of a particularly rich or poor solvent composition. The mole fraction of a pseudocomplex is directly related to the activity coefficient of a more volatile component (γ_i) with which the salt is complexed.

The variation of β with x_1, the mole fraction of the more volatile solvent, is

$$\beta = \beta^{(0)} - \beta^{(1)}x_1 \tag{7}$$

where β yields the composition, q_1, of a pseudocomplexed species as

$$q_1 = 1 - \beta^{-1} \ln \gamma_1 \tag{8}$$

Another fascinating feature of the model is the a priori calculation of the parameters involved. While one parameter, $\beta^{(0)}$, is computed from knowledge of the dielectric constant, the other parameter, $\beta^{(1)}$, is estimated from the ionic radii of the salt. A study of different 23 systems under isobaric and isothermal conditions showed that vapor-phase composition, pressure, and temperature can be estimated to ±0.015, ±0.76 kPa, and ±0.30 K, respectively.

Comparative Performance of Models Classified under Category I

It is interesting to examine the comparative performance of a variety of correlations and models in predicting the vapor-phase composition (y) of the more volatile component, a quantity of potential application. The results are summarized in terms of percent deviations in Table 1. The experimental data sources are the same as those mentioned in the original articles dealing with the models. An examination of Table 1 indicates a

TABLE 1
Comparative Analysis of Predictive Capabilities of Models for Vapor-Phase Composition (y_1) Classified under Category I

Systems	Temperature or pressure	Special binary approach (15, 16)	Lu model (19)	Ohe model (22)	Schmitt–Vogelpohl model (23)	Lee model (24)	Kumar model (25)
Methanol–water:							
LiCl	60°C	4.3	10.2	11.2	25.7	4.3	2.8
$CaCl_2$	25°C	2.2	9.8	1.4	2.0	1.1	1.1
Isopropyl alcohol–water:							
LiCl	75°C	2.8	8.7	8.3	6.5	3.8	2.4
LiBr	75°C	3.3	11.3	9.8	10.9	3.3	2.2
$CaCl_2$	75°C	6.7	10.7	10.2	11.7	9.3	6.0
Methanol–water–$CaCl_2$	101.3 kPa	8.1	9.2	8.4	7.7	8.3	7.0
Methanol–ethyl acetate–$CaCl_2$	101.3 kPa	2.2	6.9	10.8	6.9	6.9	5.2
Ethanol–water–potassium acetate	101.3 kPa	5.3	7.2	12.1	10.4	6.2	4.4

very high percent deviation from the preferential model of Schmitt and Vogelpohl (23). The reason for such a poor prediction lies in the fact that the predicted values in water-rich regions are too far away from the experimental values. The definition of k_Z originally given by Schmitt and Vogelpohl (23), which was revised by Lee et al. (24), is the main reason for such a large deviation. The recent models by Lee et al. (24) and by Kumar (25) perform better than the other models discussed above.

Limitations of Models Classified under Category I

A severe complication associated with these models is that the reference fugacity for the pseudocomponents must be calculated as a function of salt concentration. Therefore, changes in the salt concentration necessitate a redefinition of the pseudocomponent reference states.

Another drawback of these models is their inability to represent liquid–liquid equilibria in electrolyte-containing mixed systems. The two liquid phases must necessarily have different salt concentrations, and therefore, according to the pseudobinary approach, the two phases have to be made of totally different pseudocomponents, prohibiting the expression for a liquid–liquid phase equilibrium relationship.

Category II

Although the methods mentioned above under Category I are useful for many purposes, they have a common drawback; they are not based on expressions for the excess free energy function which explicitly takes the presence of electrolyte into account. Such expressions are, however, the most convenient starting points for a thermodynamic description of phase equilibria in an electrolyte-containing mixed solvent systems.

In the past two decades there has been an upsurge in the application of local composition models to the estimation of VLE. To understand the basic concept of local composition, an article by Hu et al. (26) should be referred to, where the local composition concept is critically examined on a molecular basis. The models based on local composition appear more realistic because the calculated excess Helmholtz energy and the local compositions receive support from the results of Monte Carlo simulation and perturbation theory. Local composition models such as Wilson (27), nonrandom two liquid (i.e., NRTL) (28), UNIQUAC (29), and UNIFAC (30) were primarily developed for nonelectrolyte solutions with a postulation of local compositions in the immediate neighborhood of any species. These local compositions are different from system compositions, and they reflect the local solvent–solvent short-range interactions that contribute to the excess free energy. However, these models can be applied to electrolyte-containing systems with an appropriate addition for long-range interaction forces. There have been several modifications, and these pertinent modifications will be discussed as and when they appear in the following text. In general, the excess free energy, g^E, of an electrolyte-containing mixture can be expressed as the sum of two contributions:

$$g^E = g^E_{l\text{-}r} + g^E_{s\text{-}r} \tag{9}$$

where $g^E_{l\text{-}r}$ and $g^E_{s\text{-}r}$ indicate contributions to excess free energy from long- and short-range interactions, respectively. In all the models presented so far, $g^E_{l\text{-}r}$ has been described by some or other form of the Debye–Huckel term (31). It is the second term ($g^E_{s\text{-}r}$) which is described by any local composition model or its modified forms.

Margules Equation-Based Models

Schuberth Model. Margules equation was used by Schuberth (32, 33) and Schuberth and Nhu (34) for calculating g^E. Under isothermal conditions, one ternary and six binary parameters are required for calculating salt effect on a binary solvent mixture. Good results were obtained for y and total pressure data for a binary solvent system, i.e., methanol–water with KNO_3, NaBr, and NaH_2PO_4. Unfortunately, this method has not been used rigorously.

Hala Method. Another model in which the Margules equation has been used is from Hala (35). He combined the 3-suffix Margules equation with an empirical term which takes the electrostatic interactions between the ions into account. Only one ternary parameter had to be fitted to experimental results in his model. Binary and ternary data for methanol–water–LiCl at 60°C were correlated using one ternary and six binary parameters.

Models Based on Wilson Equation

Model of Boone et al. Boone et al. (36) employed the concept of the pseudobinary approach advanced by Jaques and Furter (15), and they calculated the activity coefficients by the Wilson equation. From an appropriate definition of a pseudobinary system, infinite dilution activity coefficients for the salt-containing system were estimated from a knowledge of vapor pressure lowering, salt-free infinite dilution activity coefficients, and a single system-dependent constant. For this study, a different pseudobinary approach was adopted. Solvent 1, which was salted out, was designated component 1*, while the mixture of solvent 2 and the salt in a constant mole ratio was designated component 2*. Defining the system in this manner means that it can be treated as a binary, and equilibrium relationships governing the behavior of systems can then be

$$\gamma_i^* x_i^* f_i^\circ = \phi_i^* y_i^* P \tag{10}$$

where ϕ_i is the fugacity coefficient of component i, superscript * denotes a component in the pseudobinary mixture, and

$$x_1^* = n_1/(n_1 + n_2 + n_3) \tag{11}$$

and

$$x_2^* = (n_2 + n_3)/(n_1 + n_2 + n_3) \tag{12}$$

Since the salt is nonvolatile,

$$y_i^* = y_i \tag{13}$$

Choosing the reference state of each component in the pseudobinary solution to be the pure component, the reference state fugacities are

$$f_1^\circ = P_1^S \tag{14}$$

$$f_{2*}^\circ = P_{2*}^S = P_2^S - \Delta P_2^S \tag{15}$$

where f denotes the fugacity coefficient, superscript ° is the reference state, P_i^S is the vapor pressure of solvent i determined at the normal boiling point, and Δ denotes lowering.

Parameters for the Wilson equation are determined from infinite dilution activity coefficients. Boone et al. (36) claimed a good degree of success on five salt systems in methanol–water solvents.

Revised Hala Method. Hala (37) later replaced the Margules expression by the Wilson equation. With this modified model he could accurately predict the y values for the methanol–water system with LiCl. Unfortunately, his equations have not been used for other systems. This method has a serious limitation in the sense that on increasing the concentration of solvent 2, the salt concentration decreases, approaching zero for pure solvent 2. The part of the concentration range rich in solvent 2 is therefore not properly described. Another problem associated with the use of the Wilson equation is its poor quality fit in systems approaching immiscibility.

NRTL-Based Models

Bekerman and Tassios Model. Bekerman and Tassios (38) applied the NRTL equation where they estimated the binary interaction parameters from binary data. It was observed that when the binary interaction parameters were used to predict the thermodynamics of ternary systems, the NRTL parameters were highly sensitive. The optimum value of NRTL parameters could not be ascertained throughout the composition; hence, the method yielded less reliable estimates for ternary systems. The form of the NRTL equation used by them was the standard expression as given by Renon and Prausnitz (28).

Rastogi Model. For such a model (39), g^E is represented as a combination of the extended Debye–Huckel equation and the NRTL equation. Unfortunately, this model was examined in methanol–water with 6 mol·kg^{-1} and in ethanol–water with 1 mol·kg^{-1}. Exhaustive testing is lacking for this model.

Chen Model. One of the most used treatments of electrolyte solutions is from Chen et al. (40) and from Chen and Evans (41), who developed a local composition model for the excess free energy of aqueous electrolyte solutions with a good degree of success in fitting their thermodynamic properties. In this connection, two fundamental postulates regarding the liquid lattice structure of electrolyte systems should be recalled: 1) the local composition of cations or anions around a central cation or anion is zero and 2) the distribution of cations or anions around a central molecule is such that the net local ionic charge is zero.

The concept was further extended by Mock et al. (42) for mixed solvent systems. This extended model does not contain any term from Debye–Huckel for long-range interaction forces because they found that such a term had very little effect on the phase equilibrium behavior of water. Thus, in the model of Mock et al. (42) the local interaction contribution term of the electrolyte NRTL model is used to describe the salt effect on VLE.

The local interaction contribution of their model is expressed as

$$\begin{aligned} g^{ex}/RT &= \sum_m X_m\Big(\sum_j X_j G_{j,m}\Gamma_{jm}\Big/\sum_k X_k G_{km}\Big) \\ &+ \sum_c X_c \sum_{a'} \Big(X_{a'}\Big/\sum_{a''} X_{a''}\Big)\Big(\sum_j X_j G_{jc,a'c}\Gamma_{jc,a'c}\Big/\sum_k X_k G_{kc,a'c}\Big) \\ &+ \sum_a X_a \sum_{c'} \Big(X_{c'}\Big/\sum_{c''} X_{c''}\Big)\Big(\sum_j X_j G_{ja,c'a}\Gamma_{jc,c'a}\Big/\sum_k X_k G_{ka,c'a}\Big) \end{aligned} \tag{16}$$

with

$$X_j = x_j C_j \; (C_j = Z_j \text{ for ions and } C_j = \text{unity of molecules}) \tag{17}$$

and

$$\begin{aligned} G_{ji} &= \exp(-\alpha_{ji}\Gamma_{ji}) \\ G_{ji,ki} &= \exp(-\alpha_{ji,ki}\Gamma_{ji,ki}) \end{aligned} \tag{18}$$

In the above expressions, a, a', and a'' are the anions; c, c', and c'' are the cations; ijk are the species; m denotes the molecular solvent; and X and x denote the effective and true liquid-phase mole fractions, respectively. The relevant expression for the solvent activity coefficient is derived from Eq. (16).

In order to proceed with the calculations, it is necessary to estimate the binary adjustable parameters for each solvent–solvent, solvent–salt, and salt–salt pairs in the system. For example, 9 binary adjustable parameters for 3 pairs must be estimated in the case of a 2 solvent + 1 salt system. Mock et al. (42) examined 47 single solvent and 33 mixed solvent electrolyte systems. The model has been reported to yield VLE predictions to $\Delta T = 0.1$ K, $\Delta y = 0.01$, and $\Delta P = 1$ kPa.

UNIQUAC-Based Models

Model of Rousseau and Boone. The correlation procedure developed by Boone et al. (36) for modeling the salt effect was further extended by Rousseau and Boone (43) by including the UNIQUAC equation. In fact, as noted above, Boone et al. (36) employed the Wilson equation which, unfortunately, does not fit the data accurately. To achieve correlation, it was necessary to treat the binary solvent–salt systems as pseudobinary mixtures. The procedure outlined by the authors could be used with any correlating equation (Wilson, Van Laar, Margules, etc.). However, the precision of fit varies with the system, the equation used, and the procedure used to evaluate the correlation parameters. The UNIQUAC equation is superior to the Wilson equation in fitting the experimental data. The UNIQUAC equation for the activity coefficient of any species i as used by the authors is

$$\ln \gamma_i = \ln(\phi_i/x_i) + (Z/2)q_i \ln(\Theta_i/\phi_i) + l_i - (\phi_i/x_i) \sum_j x_i l_j - q_i \ln\Big(\sum_j \Theta_j \Gamma_{ji}\Big) + q_i - q_i \sum_j \Big(\Theta_j \Gamma_{ij} \Big/ \sum_k \Theta_k \Gamma_{kj}\Big) \quad (19)$$

where

$$l_i = [Z(r_i - q_i)/2] - (r_i - 1) \quad (20)$$

$$\phi_i = r_i x_i \Big/ \sum_j r_j x_j \quad (21)$$

$$\Theta_i = q_i x_i \Big/ \sum_j q_j x_j \quad (22)$$

$$\Gamma_{ij} = \exp\{-(u_{ji} - u_{ii})/RT\} \quad (23)$$

In the above equations, Z is the lattice coordination number, r and q are the volume and area parameters of the pure components, the u's are UNIQUAC interaction parameters, and x_i is the liquid-phase mole fraction.

The average deviation based on the calculation of 7 systems was 0.5 K and 0.011 in the temperature and vapor-phase composition, respectively.

Glugla and Sax Model. Glugla and Sax (44) applied the UNIQUAC equation developed by Abrams and Prausnitz (29) to produce a predictive correlation of VLE for systems containing salts. The strategy of their effort was to correlate binary data and to extend that correlation to calculate for multicomponent solutions. The authors noted that routine application of the UNIQUAC equation to such systems was successful as long as the maximum salt concentration was less than 2 M and for the fully ionized salts. The form of the equation used by Glugla and Sax was the same as Eq. (19). Although they analyzed 15 binary data sets, their analysis on ternary systems was limited to only 3 systems. The standard deviations calculated based on these 3 systems, i.e., methanol–water–LiCl, –NaBr, and acetone–methanol–LiCl were 0.02, 0.03, and 0.2, respectively, for vapor-phase composition. It should be noted that these authors observed serious predictive problems for the acetone–methanol–LiCl system.

Model of Sander et al. Sander et al. (45) proposed a method wherein they combined the Debye–Huckel term with a modified UNIQUAC equation with concentration-dependent parameters. The model parameters are ion specific, and no ternary parameters were required. Although a detailed framework of the model and equations is given in their paper, the useful working equations are summarized below.

The Debye–Huckel term accounting for long-range interactions is given by

$$\ln \gamma_m^{\mathrm{DH}} = M_m 2\mathrm{A}/b^3[1 + bI^{0.5} - 1/1 + bI^{0.5} - 2\ln(1 + bI^{0.5})] \quad (24)$$

where $\mathrm{A} = 1.327757 \times 10^5\, d_m^{0.5}/(DT)^{1.5}$

$b = 6.35969 d_m^{0.5}/(DT)^{0.5}$

and I, the ionic strength, is defined as $= 0.5\sum m_i z_i$; z_i is the ionic charge and m is the molecular solvent.

The Gibbs energy in the UNIQUAC model consists of residual and combinatorial components. Although the combinatorial part remains unchanged (29, 46), the residual term becomes

$$\ln \gamma_m^{\mathrm{R}} = q_m\{1 - \ln(\sum_k \Theta_k\psi_{kn}) - \sum_l (\Theta_l\psi_{nl}/\sum_k \Theta_k\psi_{kl})\}$$
$$- (2q_n/T) \sum_i\sum_m \Theta_i^2\Theta_m \sum_{j\neq i} \delta_{ij,m}\Theta_j(\psi_{mi}/\sum_k \Theta_k\psi_{ki} + \psi_{im}/\sum_k \Theta_k\psi_{km}) \tag{25}$$

The ψ values in this equation are calculated with the concentration-dependent a values described by Eqs. (26)–(29). In Eq. (25), q_n and Θ are the UNIQUAC surface area parameter and surface area fraction, respectively. The ψ terms are concerned with the residual term accounting for interactions between the molecules, and they are defined as

$$\psi_{kl} = \exp(-a_{kl}/T) \tag{26}$$

where

$$a_{kl} = u_{kl} - u_{ll} \tag{27}$$

with u being the interaction energy parameters.

In the case of mixed solvent systems, the concentration-dependent interaction parameters between ion i and solvent m are u_{im} and u_{mi}. The following equations are used:

$$a_{im} = a_{im}^{*} + \Theta_i \sum_{j\neq i} \delta_{ij,m}\Theta_j \tag{28}$$

$$a_{mi} = a_{mi}^{*} + \Theta_i \sum_{j\neq i} \delta_{ij,m}\Theta_j \tag{29}$$

where the superscript * indicates the reference interaction parameters and δ is a parameter; summation is over all the ions except i. Both a_{im} and a_{mi} have the same concentration dependence.

Finally, the activity coefficient of solvent m is now given by

$$\ln \gamma_m = \ln \gamma_m^{\mathrm{DH}} + \ln \gamma_m^{\mathrm{C}} + \ln \gamma_m^{\mathrm{R}} \tag{30}$$

where $\ln \gamma_m$ indicates contribution due to combinatorial part.

With regard to the estimation of parameters, Sander et al. (45) reported the data base for 46 binary single salt/single solvent data sets and 54 ternary single salt/binary solvent data sets with a total of 524 binary and 941 ternary data points. Seventy percent of the binary data sets have water as one of the solvents. The maximum salt concentration for 1:1 is 10 and 6.5 mol·kg^{-1}.

Now let us look at the predictive capability of this model. Sander et al. noted large deviations in the activity coefficients owing to the deficiency of the model and also due to inconsistent data sets. However, the vapor-phase composition can be estimated to 0.012. For the data sets at 760 mmHg, the mean absolute deviation was 20–40 mmHg. The regression for 54 ternary data sets was presented by Sander et al.

Modified Model of Sander et al. Macedo et al. (47) later modified the model of Sander et al. (45) by altering the Debye–Huckel term to ensure a more correct representation of the long-range interaction forces. The modification involved the division of Eq. (24) by the density of the solvent mixture. This improved the predictive capability and range of application of the model of Sander et al. (45).

UNIFAC-Based Models

Model of Kikic et al. Kikic et al. (48) modified the original model of Sander et al. (45) where the Debye–Huckel term was combined with a modified UNIQUAC term with concentration-dependent parameters. There were some problems (49) with respect to the form of the Debye–Huckel term used by Sander et al. (45), but they were subsequently solved by Macedo et al. (47). However, Kikic et al. (48) attempted to use a theoretically more consistent Debye–Huckel term in accordance with the McMillan solution theory as described by Cardoso and O'Connell (49). To account for short-range interaction forces, Kikic et al. (48) adopted a UNIFAC concentration-independent model (5) rather than the UNIQUAC term. Hence, their model consisted of a modified Debye–Huckel term as proposed by Macedo et al. (47) with UNIFAC concentration-independent terms.

The UNIFAC portion of the model is the same as discussed elsewhere (30). Calculations were presented for 9 cations, 6 anions, and 5 solvent groups. The model is capable of representing VLE for solvent–water–salt mixtures with an expected average accuracy of around 9% for the total pressure and of around 4% for the vapor-phase composition. In view of the fact that the model is a predictive group contribution method, it has a much broader range of applicability than the Sander et al. (45) model.

Dahl and Macedo Model. Very recently, Dahl and Macedo (50) used the modified Huron–Vidal second-order model (MHV2) to describe the salt effect on VLE. The MHV2 is a group contribution equation (51) which combines the Soave–Redlich–Kwong (SRK) equation of state (52) with a model for the excess Gibbs energy g^E, i.e., the modified UNIFAC model (53). In fact, they had earlier investigated the applicability of the MHV2 model (54) alone for the calculation of VLE for a mixed solvent–salt system by using salt–solvent interaction parameters estimated from VLE data. In the approach of Dahl and Macedo (50), the salt is assumed to be a single component and not dissociated into ions, and therefore the number of parameters is significantly reduced. Only short-range interactions are taken into account, and the symmetric reference state is used for all species. Therefore, standard thermodynamic calculations can be performed by assuming the presence of salt in all the equilibrium phases. It should be noted that the long-range Debye–Huckel term is not used in this model, and thus the model does not have the correct limiting value in accordance with the Debye–Huckel term. The typical MHV2 mixing rule for C components used by them is

$$q_1\left(\alpha_{\text{mix}} - \sum_{i=1}^{C} z_i\alpha_{ii}\right) + q_2\left(\alpha^2_{\text{mix}} - \sum_{i=1}^{C} Z_i\alpha^2_{ii}\right) = g^E/RT + \sum_{i=1}^{C} Z_i \ln(b/b_{ii}) \tag{31}$$

where $\alpha_{\text{mix}} = a_{\text{mix}}/bRT$ and $\alpha_{ii} = a_{ii}/b_{ii}RT$. The terms a_{ii} and b_{ii} refer to the pure component values as outlined by Soave (52). q_1 and q_2 are -0.478 and -0.0047, respectively, and z_i is the phase composition. The fugacity coefficient is given by

$$\ln \phi_i = \ln[RT/P(v - b)] + (1/v - b + \alpha/V + b)b_{ii} - \ln(v + b/v)(\partial(n\alpha)/\partial n_i)_{Tnj} \tag{32}$$

where $n\alpha$ is computed from the above mixing rule, i.e., Eq. (31).

These authors have reported molecular R_v and Q_v values and the main group definition for 16 salt along with values of the modified UNIFAC interaction parameters.

Dahl and Macedo (50) tabulated the results of their models and attempted to compare them with some contemporary models. An examination of their work indicates that excellent predictions of the salt effect on VLE can be obtained with a limited number of parameters.

Comparative Performance of Models Classified under Category II

In order to demonstrate the ability of the models to predict the vapor-phase composition of systems involving salt, a comparative tabulation is given in Table 2. Fresh calculations were performed for several models, and thus some numerical differences appear compared to the original papers (we used somewhat different input values). An examination of Table 2 suggests that the recent model of Dahl and Mecado (50) based on UNIFAC yields the most accurate prediction of the salt effect on VLE. The most attractive feature of this model is with respect to its concentration-independent parameters. Therefore, the number of parameters used to de-

TABLE 2
Comparative Analysis of Predictive Capabilities of Models for Vapor Phase Composition (y_1) Classified under Category II

Models	Systems[a] 1	2	3	4	5	6
	Margules Equation-Based Model					
Hala (35)	13.7	14.8	10.3	22.1	24.1	11.9
	Wilson Equation-Based Model					
Boone et al. (36)	13.5	13.1	10.1	16.1	14.2	11.2
	NRTL-Based Model					
Bekerman and Tassios (38)	5.7	4.9	6.9	11.2	10.2	8.9
Mock et al. (42)	3.1	2.9	2.2	1.9	2.7	6.3
	UNIQUAC-Based Models					
Rousseau and Boone (43)	8.2	4.9	7.2	10.3	10.8	7.7
Glugla and Sax (44)	14.9	14.2	9.2	18.2	12.1	13.1
Sander et al. (45)	2.9	2.4	7.9	1.3	4.9	3.8
Macedo et al. (47)	2.9	0.8	1.2	0.8	2.0	1.8
	UNIFAC-Based Models					
Kikic et al. (48)	2.5	2.4	7.6	1.3	4.4	3.0
Dahl and Macedo (50)	1.9	0.6	1.7	0.9	1.9	2.1

[a] Systems: 1 = methanol–water–NaBr; 2 = ethanol–water–NaCl; 3 = methanol–water–$CaCl_2$; 4 = 2-propanol–water–$CaCl_2$; 5 = 1-propanol–water–KCl; 6 = acetone–water–KCl.

scribe the mixture is less than 30% the number of parameters used for the UNIQUAC model of Macedo et al. (47). With this background, the model of Dahl and Macedo (50) yields a good performance. However, one restriction of the UNIQUAC and UNIFAC models compared to MHV2 is that the interaction parameters between an ion (such as Cl^-) and a solvent should be valid for all sets containing this ion. In this model, different parameters are used for NaCl, KCl, $CaCl_2$, etc., and thus more flexibility is gained for application purposes. In general, this model is superior to several other models discussed above.

CONCLUSIONS

It is apparent from the above study that a substantial number of investigations have been made on correlating and predicting the salt effect on VLE. The models which are based on excess free energy are more realistic because pertinent interactions in the solutions are taken into account.

Both categories of the models are used frequently, although the models described under Category II are more versatile to use for practical problems and can be extended to the study of liquid–liquid equilibrium, an aspect excluded in the present review. If one examines the second category of models, one notes that we still lack accurate expressions for estimating liquid-phase nonideality. The reason for this lies in the fact that the electrostatic contribution in mixed solvents is not properly accounted for. How the standard Gibbs function varies with solvent composition is not accurately known. Application of these models was restricted to a single salt with two solvents; their validity for multi-ions with multisolvent systems remains a challenge.

REFERENCES

1. A. J. Johnson and W. F. Furter, *Can. J. Chem. Eng.*, *38*, 78 (1960).
2. W. F. Furter and R. A. Cook, *Int. J. Heat Mass Transfer*, *10*, 23 (1967).
3. W. F. Furter, *Adv. Chem. Ser.*, *155*, 26 (1976).
4. W. F. Furter, *Can. J. Chem. Eng.*, *55*, 229 (1977).
5. S. Ohe, K. Yokoyama, and S. Nakamura, *I. H. E. Eng. Rev.*, *2*, 11 (1969).
6. S. Ohe, *Chem. Econ. Eng. Rev.*, *5*, 54 (1970).
7. D. Schmitt, "Der Einfluss von Salzen auf das Damf-Flussigkeitsgeichgewicht Binarer Stoffgemische und die Rektifikation Azeotroper Gemische bei Zugabe von Salzen," Ph.D. Thesis, Universitat Karlsruhe, 1975.
8. F. A. Long and W. F. McDevit, *Chem. Rev.*, *51*, 119 (1952).
9. W. F. Furter, Ph.D. Thesis, University of Toronto, 1958.
10. D. Meranada and W. F. Furter, *Can. J. Chem. Eng.*, *44*, 298 (1966).
11. D. Meranada and W. F. Furter, *AIChE J.*, *17*, 38 (1971).
12. D. Jaques and W. F. Furter, *Can. J. Chem. Eng.*, *50*, 502 (1972).
13. D. Jaques and W. F. Furter, *Ind. Eng. Chem., Fundam.*, *13*, 238 (1974).
14. W. F. Furter (Ed.), *Thermodynamic Behavior of Electrolytes in Mixed Solvents* (Adv. Chem. Ser.), 1976, p. 155.
15. D. Jaques and W. F. Furter, *AIChE J.*, *18*, 343 (1972).
16. D. Jaques, *Ibid.*, *20*, 189 (1974).
17. D. Meranada and W. F. Furter, *Ibid.*, *18*, 111 (1972).
18. J. A. Burns and W. F. Furter, *Adv. Chem. Ser.*, *177*, 11 (1979).
19. B. C-Y. Lu, *Ind. Eng. Chem.*, *52*, 871 (1960).
20. P. Gross and O. Halpern, *J. Chem. Phys.*, *2*, 184 (1934).
21. P. Gross and O. Halpern, *Ibid.*, *2*, 188 (1934).
22. S. Ohe, *Adv. Chem. Ser.*, *155*, 53 (1976).
23. D. Schmitt and A. Vogelpohl, *Fluid Phase Equil.*, *9*, 167 (1982).
24. L-S. Lee, Y-Z. Tsao, and B. L. M. Yang, *Can. J. Chem. Eng.*, *69*, 788 (1991).
25. A. Kumar, *Sep. Sci. Technol.*, *28*, 1203 (1993).
26. Y. Hu, E. G. Azevedo, and J. M. Prausnitz, *Fluid Phase Equil.*, *13*, 35 (1983).
27. G. M. Wilson, *J. Am. Chem. Soc.*, *86*, 127 (1964).
28. H. Renon and J. M. Prausnitz, *AIChE J.*, *14*, 135 (1968).
29. D. S. Abrams and J. M. Prausnitz, *Ibid.*, *21*, 116 (1975).

30. A. Fredenslund, J. Gmehling, and P. Rasmussen, *Vapor Liquid Equilibria Using UNIFAC*, Elsevier, Amsterdam, 1977.
31. R. A. Robinson and R. H. Stokes, *Electrolyte Solutions*, 2nd ed. (rev.), Butterworths, London, 1965.
32. H. Schuberth, *Z. Phys. Chem. (Leipzig)*, *255*, 165 (1974).
33. H. Schuberth, *Ibid.*, *258*, 1162 (1977).
34. H. Schuberth and N. V. Nhu, *Ibid.*, *258*, 106 (1977).
35. E. Hala, *Inst. Chem. Eng.*, *Symp. Ser.*, *32*, 3:8 (1969).
36. J. E. Boone, W. Rousseau, and E. M. Schoenborn, *Adv. Chem. Ser.*, *155*, 36 (1976).
37. E. Hala, Paper presented at the 3rd International Conference on Phase Equilibria and Fluid Properties for Chemical Process Design, Callaway Gardens, Georgia, 1983.
38. E. Bekerman and D. Tassios, *Adv. Chem. Ser.*, *155*, 3 (1976).
39. A. K. Rastogi, Dr.Eng.Sci. Thesis, New Jersey Institute of Technology, 1981.
40. C-C. Chen, H. I. Britt, J. F. Boston, and L. B. Evans, *AIChE J.*, *28*, 588 (1982).
41. C-C. Chen and L. B. Evans, *Ibid.*, *32*, 1655 (1986).
42. B. Mock, L. B. Evans, and C-C. Chen, *Ibid.*, *32*, 1655 (1986).
43. R. W. Rousseau and J. E. Boone, *Ibid.*, *24*, 718 (1978).
44. P. G. Glugla and S. M. Sax, *Ibid.*, *31*, 1911 (1985).
45. B. Sander, A. Fredenslund, and P. Rasmussen, *Chem. Eng. Sci.*, *41*, 1171 (1986).
46. G. Maurer and J. M. Prausnitz, *Fluid Phase Equil.*, *2*, 91 (1978).
47. E. A. Macedo, P. Skovberg, and P. Rasmussen, *Chem. Eng. Sci.*, *45*, 875 (1990).
48. I. Kikic, M. Fermeglia, and P. Rasmussen, *Ibid.*, *46*, 2775 (1991).
49. M. Cardoso and J. P. O'Connell, *Fluid Phase Equil.*, *33*, 315 (1987).
50. S. Dahl and E. A. Macedo, *Ind. Eng. Chem. Res.*, *31*, 1195 (1992).
51. M. L. Michelsen, *Fluid Phase Equil.*, *60*, 213 (1990).
52. G. Soave, *Chem. Eng. Sci.*, *27*, 1197 (1972).
53. B. L. Larsen, P. Rasmussen, and A. Fredenslund, *Ind. Eng. Chem. Res.*, *26*, 2274 (1987).
54. S. Dahl and M. L. Michelsen, *AIChE J.*, *36*, 1829 (1990).

Received by editor October 23, 1992