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A Simple Model for Predicting the Effect of Electrolytes on the Vapor–Liquid Equilibrium Data of Solvent Mixtures*

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Abstract

A simple model based on a newly defined quantity, the inverse relative solubility coefficient for predicting the effect of an electrolyte on the vapor–liquid equilibrium (VLE) data, is proposed to give reliable predictions of vapor-phase composition, pressure, and temperature. The fundamental properties of the components are required to arrive at the predictions. The model excludes the use of any adjustable parameter.

INTRODUCTION

The conventional method for separating mixtures involving azeotropes is to shift the azeotropic composition by altering column pressure or by using extractive distillation by adding an alien component as a solvent to break the azeotrope. Unfortunately, an extra column for pressure adjustment or for solvent recovery is needed for both of these methods. Recent years have witnessed the emergence of an alternative extractive distillation in which an electrolyte rather than a liquid is employed as the extractive solvent. There are clear advantages to this technique: a solvent-free extract is produced at the top of the column, there is no need for an extra separation column, and there is less energy consumption than in conventional extractive distillation. Because of the complex interactions of the electrolyte with various solvent mixtures, the mechanism of this process is still poorly understood.

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The addition of an electrolyte to a solvent mixture usually changes the composition of the vapor in equilibrium with the liquid because of interactions between the ions and the solvent components. The available methods to account for this "salt effect" are summarized in excellent monographs by Furter (*1*) and Newman (*2*). Comprehensive reviews of extractive distillations with electrolytes were written by Furter and Cook (*3*) and Furter (*4*), where the effectiveness of extractive distillation with electrolytes as a viable separation technique for many industrially important separations was documented. More recent contribution in this area have been made by Schmitt and Vogelpohl (*5*), Glugla and Sax (*6*), Kikic et al. (*7*), and Lee et al. (*8*). Unfortunately, the use of a majority of these models requires multicomponent mixture data in addition to pure component information before a fuller appreciation of the model can be reached.

The present work proposes a new, simple, and accurate method for process development engineers to use in their design calculations for predicting the change in the vapor-phase composition, the total pressure, and the temperature data of electrolyte-containing solvent mixtures.

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MODEL

It is well known that when an electrolyte is dissolved in a solvent, it dissociates into a cation and an anion. The solubility of an electrolyte in any solvent depends on the dielectric constant D of the medium because D is the governing factor in determining the interionic forces in the solution. Thus, for example, NaCl is more soluble in water than in methanol because D for water is higher than for methanol at a given temperature. The inverse relationship between solubility and D has been discussed by Davies (*9*).

In our model we assume that a binary solvent mixture is comprised of a more volatile component, designated "1," and a less volatile component, designated "2." When an electrolyte is dissolved in a solvent mixture, the dielectric constant of the mixture should be the fundamental property governing the interaction of ions with each solvent. Thus, the vapor-phase composition of the more volatile solvent component is altered upon the addition of an electrolyte because the partial pressure of each solvent shifts from its original value as obtained on an electrolyte-free basis.

We assume that x_3 is the mole fraction of an electrolyte, x_1 denotes the mole fraction of the more volatile solvent, and x_2 the less volatile. The present simple model assumes that a "pseudo-complex" is formed between more volatile solvent 1 and an electrolyte, and hence the vapor-phase composition of solvent 1 is altered.

To account for this, we define a new term β, the inverse relative solubility coefficient, which varies with the solvent composition x_1 as

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

with limiting values of

$$\beta_{\text{lim},0} = \beta^{(0)} \qquad \text{if } x_1 = 0 \qquad (2)$$

and

$$\beta_{\text{lim},1} = \beta^{(0)} - \beta^{(1)} \qquad \text{if } x_1 = 1 \qquad (3)$$

Thus

$$\beta_{\text{lim},0}(D_r - 1) = \beta^{(1)} \qquad (4)$$

The most important relationship is the ratio $\beta_{\text{lim},0}/\beta_{\text{lim},1} = D_r$, which is equivalent to the ratio of dielectric constants of constituent solvents 1 and 2. Note that the β term indicates the solubility of an electrolyte in the solvent mixture in relative terms, not in absolute terms. The composition dependence of the dielectric constant in solvent mixtures is also linear (*10*, *11*).

The value of the mole fraction which is being pseudo-complexed in the system can be related to β by

$$q_1 = 1 - \beta^{-1} \ln \gamma_1^* \qquad (5)$$

where γ_1^* indicates the activity coefficient of the more volatile solvent (designated as "1") in a solvent mixture of 1 and 2, and which is available in the literature. Also:

$$q_2 = 1 - q_1 \qquad (6)$$

Employing the above concept, the partial pressure of both solvents can be written as

$$P_1 = P\gamma_1 q_1 \qquad (7)$$

and

$$P_2 = P\gamma_2 q_2 \qquad (8)$$

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where γ_1 and γ_2 are the activity coefficients of solvents 1 and 2, respectively, in electrolyte–solvent 1 and electrolyte–solvent 2 systems. P is the total vapor pressure of the system when both the solvents and electrolyte are present.

Thus, the vapor-phase composition y_1 is

$$y_1 = P_1/(P_1 + P_2) \tag{9}$$

and

$$y_2 = 1 - y_1 \tag{10}$$

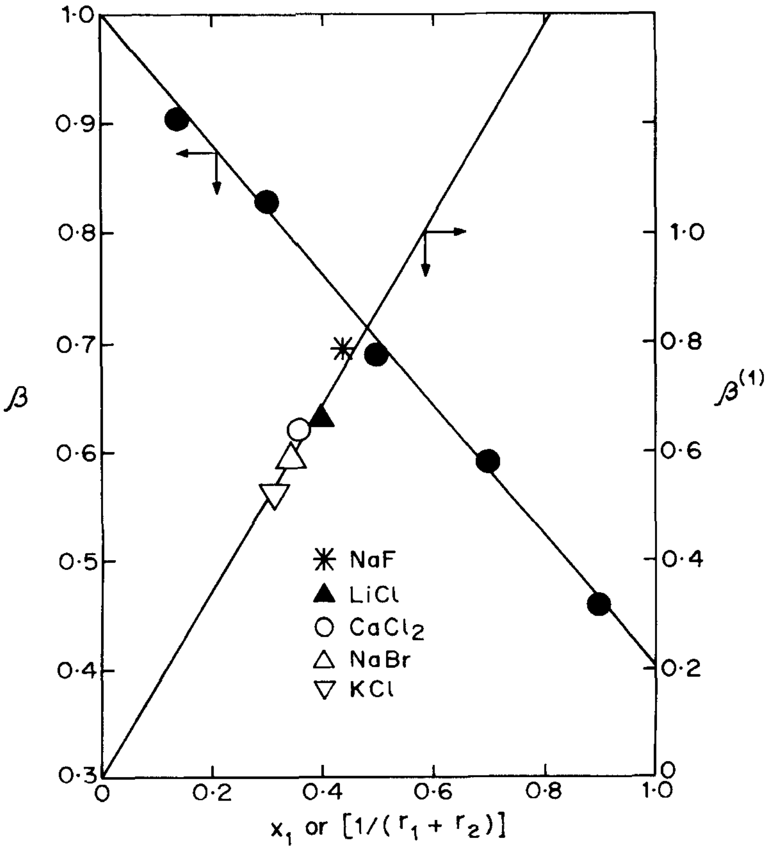

FIG. 1. Variation of the inverse relative solubility coefficient, β, with x_1 (electrolyte-free basis); relationship between $\beta^{(1)}$ and the inverse of the sum of crystal radii ($1/(r_c + r_a)$) for various electrolytes in the methanol–water system.

For the purpose of illustration, the functional form of β with x_1 for the case of methanol–water in the NaBr system is given in Fig. 1. This demonstrates the linear relationship. A good linear relationship was also observed in the other systems studied.

We now address our attention to evaluation of the $\beta^{(1)}$ term in Eq. (1). Based on our phenomenological observation for several systems we investigated, we propose that $\beta^{(1)}$ has the following form:

$$\beta^{(1)} = (M_1/M_2)(1/(r_c + r_a)) \tag{11}$$

where r_c and r_a refer to the crystallographic radii of cations and anions, respectively, and M_1 and M_2 are the molecular masses of solvents 1 and 2, respectively. Equation (11) is an important observation of the present investigation because it allows calculations for any electrolyte consisting of any ionic components. For the sake of illustration, this observation is demonstrated in Fig. 1 for various electrolytes in methanol–water systems. Note that accurate data on the VLE of our present interest are available for the methanol–water system with a number of electrolytes.

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RESULTS AND DISCUSSION

The experimental data tested against the present model are listed in Table 1. Both isobaric and isothermal data were examined. For calculating the solvent activity coefficients for binary solutions (electrolyte + solvent), the ion interaction model of Pitzer (*18*) was employed. The values of γ_1^* on an electrolyte-free basis were taken from Gmehling and Onken (*19*). The required dielectric constants for several solvents are listed elsewhere (*20*). The calculations are simple for isothermal conditions; for isobaric conditions the temperature is estimated and then corrected by using an iterative procedure with a simple computer program.

Use of the present model to predict VLE data for electrolyte-containing systems yields excellent results. The listed root-mean-square deviations (rmsd) for vapor-phase composition for solvent 1, pressure, and temperature values proves the predictive capability of our model. In Fig. 2, the performance of the model is demonstrated in terms of experimental (*15*) and predicted y_1 against electrolyte-free x_1 for the ethanol–water–$CuCl_2$ system at 101.13 kPa. The observed and predicted y_1 for methanol–water–NaBr at 298.15 K, isopropanol–water–LiCl at 358 K, and ethanol–water–LiCl at 298.15 K are plotted in Fig. 3 for ready comparison. It is interesting to note that the present model is applicable to the entire range of solvent compositions. On the contrary, the model of Schmitt and Vogelpohl (*5*) failed to describe the VLE at higher concentrations of water. The reason

TABLE 1
Summary of Prediction of VLE Data for Several Electrolyte-Containing Systems

Solvents	Electrolyte	Δy_1	rmsd ΔP (kPa)	rmsd ΔT (K)	Source of data
Methanol–water	NaBr	0.004	0.14	—	*1, 2*
	LiCl	0.006	0.10	—	*1*
	KCl	0.004	0.09	—	*1*
	NaF	0.005	—	0.20	*1*
	$CaCl_2$	0.007	—	0.17	*12*
Ethanol–water	LiCl	0.003	0.09	—	*1*
	NaCl	0.005	—	0.06	*1*
	KCl	0.009	—	0.08	*1*
	KI	0.007	—	0.04	*13*
	KI	0.029	—	0.19	*14*
	NH_4Br	0.011	—	0.09	*13*
	NH_4Cl	0.020	—	0.12	*1*
	NaBr	0.042	—	0.40	*14*
	NaI	0.066	—	1.92	*14*
	$CaCl_2$	0.032	—	0.18	*14*
	$CuCl_2$	0.010	—	0.28	*15*
1,4-Dioxane–water	$NaClO_3$	0.015	0.19	—	*16*
	$LiClO_3$	0.007	0.07	—	*16*
Isopropanol–water	$CaCl_2$	0.014	0.50	—	*17*
	LiBr	0.013	0.70	—	*17*
	LiCl	0.008	0.49	—	*17*
Propanol–isopropanol	$CaCl_2$	0.012	—	0.15	*12*
Average rmsd		0.015	0.26	0.30	

for the success of our model lies in the fact that our primary quantity β is a linear function in both water-rich and water-poor regions.

An examination of Table 1 shows that the predicted results are accurate throughout except for the system involving ethanol–water with KI/NaBr/NaI. The accuracy of these data sets published by Meranada and Furter (*14*) was later questioned by Jaques and Furter (*21*). In general, the average rmsd for vapor-phase composition (y_1), pressure (P), and temperature (T) for the array of data investigated in the present study are 0.015, 0.26 kPa, and 0.30 K, respectively.

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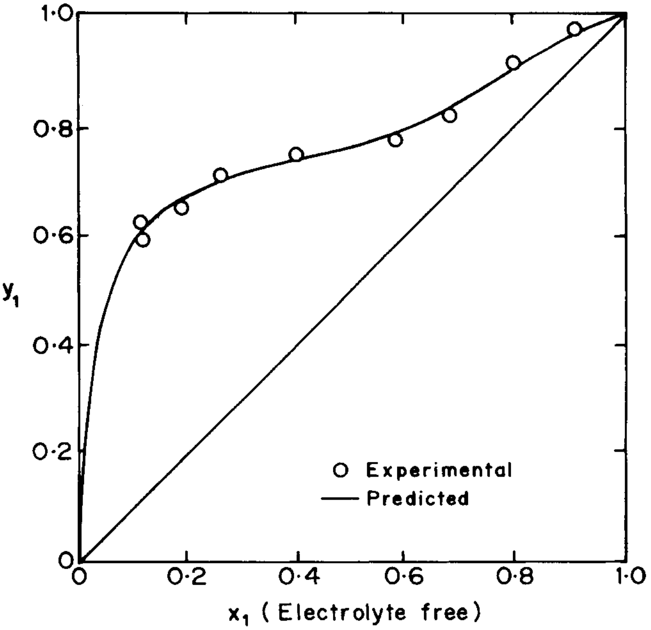

FIG. 2. Experimental and predicted vapor composition (y_1) of the ethanol–water–$CuCl_2$ system at 101.13 kPa.

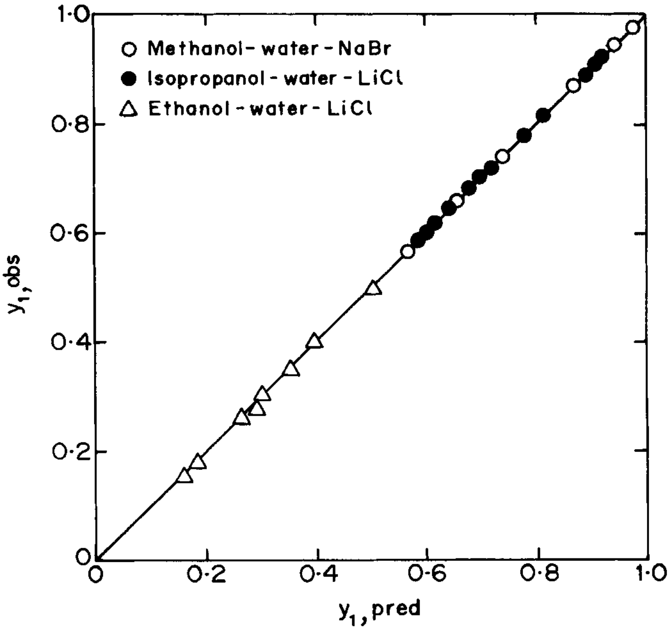

FIG. 3. The observed against the predicted y_1 for the methanol–water–NaBr, isopropanol–water–LiCl, and ethanol–water–LiCl systems.

CONCLUSIONS

The present model emerges as a simple but powerful tool for predicting the effect of electrolytes on the VLE of solvent mixtures under both isothermal and isobaric conditions. The novelty of the present work lies in the fact that no adjustable parameters are needed, and the model is capable of predicting the required properties at all concentrations with good accuracy by using the molecular and ionic properties of the components. The model can be successfully employed for any relevant practical applications.

REFERENCES

1. W. F. Furter (Ed.), *Thermodynamic Behavior of Electrolytes in Mixed Solvents* (Advances in Chemical Series, ACS Symposium Series 155), 1976, Chaps. 1–7.
2. S. A. Newman (Ed.), *Thermodynamics of Aqueous Systems with Industrial Applications* (ACS Symposium Series 133), 1980.
3. W. F. Furter and R. A. Cook, *Int. J. Heat Mass Transfer, 10,* 23 (1967).
4. W. F. Furter, *Can. J. Chem. Eng., 55,* 229 (1977).
5. D. Schmitt and A. Vogelpohl, *Fluid Phase Equil., 9,* 167 (1982).
6. P. G. Glugla and S. M. Sax, *AIChE J., 31,* 1911 (1985).
7. I. Kikic, M. Fermeglia, and P. Rasmussen, *Chem. Eng. Sci., 46,* 2775 (1991).
8. L.-S. Lee, Y.-Z. Tsao, and B. L. M. Yang, *Can. J. Chem. Eng., 69,* 788 (1991).
9. C. W. Davies, *Ion Association,* Butterworths, London, 1962.
10. G. Akerlof, *J. Am. Chem. Soc., 54,* 4125 (1932); *58,* 1241 (1936).
11. H. S. Harned and B. B. Owen, *Physical Chemistry of Electrolyte Solutions,* 3rd ed., Reinhold, New York, 1958.
12. Y. Nishi, *J. Chem. Eng. Jpn., 8,* 175 (1975).
13. J. A. Burns and W. F. Furter, *Adv. Chem. Ser., 177,* 11 (1979).
14. D. Meranada and W. F. Furter, *AIChE J., 18,* 111 (1972).
15. M. A. Galan, M. D. Labrador, and J. R. Alvarez, *Adv. Chem. Ser., 155,* 85 (1976).
16. A. N. Campbell and B. G. Oliver, *Can. J. Chem., 47,* 2671 (1969).
17. E. Sada, T. Morisue, and K. Miyahara, *J. Chem. Eng. Jpn., 8,* 196 (1975).
18. K. S. Pitzer, *J. Phys. Chem., 77,* 268 (1973).
19. J. Gmehling and U. Onken, *Chem. Data Ser. Aqueous-Org. Systems, 1,* 150 (1977).
20. A. A. Maryott and E. R. Smith, *Tables of Dielectric Constants of Pure Liquids,* NBS Circular 514, 1951.
21. D. Jaques and W. F. Furter, *AIChE J., 18,* 343 (1972).

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