R & D NOTES

Vapor Liquid Equilibrium for Salt-Containing Systems: A Correlation of Vapor Pressure Depression and a Prediction of Multicomponent Systems

P. G. GLUGLA and S. M. SAX

Department of Chemical Engineering
University of Colorado
Boulder, CO 80309

A series of comprehensive reviews of extractive distillation with salts were written by Furter and Cook (1967) and Further (1977). These reviews document the effectiveness of extractive distillation with salts as a viable separation technique for many industrially important separations. The ethanol-water system is a typical example. Galan et al. (1975) showed that the ethanol-water azeotrope can be broken with the addition of either $CuCl_2$ or $NiCl_2$.

Extractive distillation with salts would be considered more often as a separation alternative if the fundamentals of the process were better understood. A screening technique must be developed if extractive distillation with salts is ever to become a popular separation technique. The obvious starting point is with a screening technique for vapor liquid equilibrium (VLE). A model that could predict the VLE of mixtures with salts would be invaluable to the process development engineer. Such a model could be used as a screening tool and could be used to support design calculations.

The objective of this effort was to use the UNIQUAC equation developed by Abrams and Prausnitz (1975) to produce a predictive correlation of vapor liquid equilibrium for systems containing salts. The strategy of this effort was to correlate binary data and to extend that correlation to multicomponent mixtures. The UNIQUAC equation is well suited to this objective because it does not require additional information to expand to ternary or higher forms. In this study, a binary is defined as one salt and one solvent. A ternary has one salt and two solvents. Note that this analysis is not limited to ternaries. Multicomponent systems are reached through a simple extension of the UNIQUAC equation.

Vapor pressure depression information, i.e., binary data, is the most commonly found VLE data involving salts. An excellent source of such data is the data compilation of Janz and Tomkins (1973). Vapor pressure depression information was used to determine the adjustable parameters in the binary UNIQUAC equation. These parameters and the ternary UNIQUAC equation were used to predict the VLE of a number of ternaries. The success or failure of these tests determined the effectiveness of the UNIQUAC equation as a predictive correlation for VLE of systems with salts.

GOVERNING EQUATIONS

Vapor pressure depression information was found in the literature in two forms. Janz and Tomkins (1973) supplied data in the form of vapor pressure vs. salt concentration. With this type of data, activity coefficients for the volatile component, γ'_i, were calculated assuming that the vapor was ideal as in Eq. 1:

$$P = \gamma'_i x'_i P_i^{V,\mathrm{sat}} \tag{1}$$

Many other authors, such as Skabichevskii (1969, 1970a,b,c), supplied activities of the volatile component vs. salt concentration. Activity coefficients were calculated from this data using Eq. 2.

$$a_i = \gamma'_i x'_i \tag{2}$$

Activity coefficients were used instead of osmotic coefficients since they are more widely known in engineering circles. Osmotic coefficients no longer have an advantage over activity coefficients because of the accuracy of modern computers.

For historical reasons the mole fraction was defined as follows (see Rousseau and Boone, 1978):

$$x'_i = \frac{N_i}{\sum_i N_i + \nu N_{\mathrm{salt}}} \tag{3}$$

The choice of this definition for mole fraction had little or no effect on the results of this study since ν was assumed to be constant and equal to 2. This condition is equivalent to assuming that the salts are full dissociated.

The multicomponent UNIQUAC equation as reported by

TABLE 1. UNIQUAC SIZE AND SURFACE CONSTANTS* USED IN THIS WORK

	r_i	q_i
Acetone	2.57	2.34
Ethanol	2.11	1.97
Isopentanol	4.13	3.59
Lithium bromide	1.06	1.16
Lithium chloride	0.84	1.01
Lithium nitrate	1.19	1.24
Lithium perchlorate	2.25	1.85
Methanol	1.43	1.43
Sodium bromide	1.24	1.39
Sodium chloride	1.01	1.23
Water	0.92	1.40

* The constants are dimensionless.

Abrams and Prausnitz (1975) and as applied here is as follows:

$$\ln \gamma'_i = \ln \frac{\Phi_i}{x'_i} + \left(\frac{Z}{2}\right) q_i \ln \frac{\vartheta_i}{\Phi_i} + l_i - \frac{\Phi_i}{x'_i} \sum_j x'_j l_j \tag{4}$$

$$-q_i \ln \left(\sum_j \vartheta_j \tau_{ji} \right) + q_i - q_i \sum_j \frac{\vartheta_j \tau_{ij}}{\sum_k \vartheta_k \tau_{kj}}$$

where

$$l_i = \left(\frac{Z}{2}\right)(r_i - q_i) - (r_i - 1) \tag{5}$$

and where the average area fraction, ϑ_i, and the average segment fraction, Φ_i, are defined as follows:

$$\vartheta_i = \frac{q_i x'_i}{\sum_j q_j x'_j} \text{ and } \Phi_i = \frac{r_i x'_i}{\sum_j r_j x'_j} \tag{6, 7}$$

The solvent structural parameters, q_i and r_i, were found using the van der Waal surface areas and volumes, A_{wk} and V_{wk}, given by Bondi (1968). The salt structural parameters were estimated using ionic radii from Waddington (1959). The q_i and r_i are related to areas and volumes as follows:

$$q_i = \frac{A_{wk}}{2.5 \times 10^9} \text{ and } r_i = \frac{V_{wk}}{15.17} \tag{8}$$

A_{wk} must be in units of cm^2/mol, and V_{wk} must be in units of cm^3/mol. q_i and r_i are dimensionless. Table 1 shows the surface and volume parameters used in this work. The lattice coordination number Z, was set equal to 10 as is common practice. τ_{ij} is related to the binary energy parameter as follows:

$$\tau_{ij} = \exp - \left(\frac{a_{ij}}{RT}\right) \tag{9}$$

TABLE 2. UNIQUAC BINARY PARAMETERS, a_{12} and a_{21}, AND STANDARD DEVIATIONS FOUND FROM THE BEST FIT OF VAPOR PRESSURE DEPRESSION DATA

System	Data Ref.	Data Temp. (K)	a_{12}, (J/mol)	a_{21}, (J/mol)	$SD \times 10^3$
Acetone-lithium bromide	Skabichevskii (1970a,c)	293.15	9,900	−2,957	2.0
Acetone-lithium nitrate	Skabichevskii (1970a)	293.15	11,400	−3,179	1.1
Acetone-lithium perchlorate	Skabichevskii (1970a,c)	293.15	7,578	−3,188	1.5
Ethanol-lithium chloride	Janz and Tomkins (1973)	288.15	9,924	−3,984	3.2
Isopentanol-lithium chloride	Skabichevskii (1969)	323.15	16,850	−5,069	11.2
Isopentanol-lithium nitrate	Skabichevskii (1970b)	323.15	12,240	−4,135	2.7
Isopentanol-lithium perchlorate	Skabichevskii (1970b)	323.15	11,620	−4,717	30.0
Methanol-lithium bromide	Skabichevskii (1969)	288.15	9,358	−4,453	1.1
Methanol-lithium chloride	Skabichevskii (1969)	288.15	11,280	−4,713	3.0
Methanol-lithium nitrate	Skabichevskii (1970b)	288.15	8,516	−4,042	1.3
Methanol-lithium perchlorate	Skabichevskii (1970b)	288.15	8,093	−3,975	4.9
Methanol-sodium bromide	Vlaslov and Antonov (1973)	298.15	9,303	−4,390	7.0
Methanol-sodium chloride	Vlaslov and Antonov (1973)	298.15	8,578	−3,908	0.2
Water-lithium chloride	Weast and Selby CRC (1966)	373.15	11,310	−5,869	0.2
Water-sodium bromide	Weast and Selby CRC (1966)	373.15	9,283	−5,090	0.04

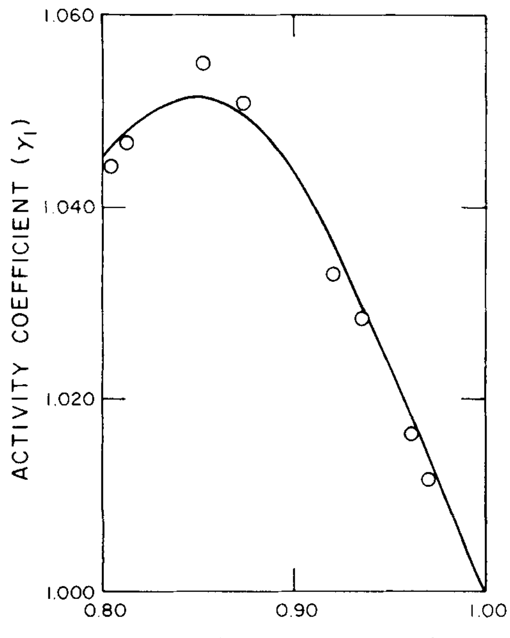

Figure 1. Comparison of experimental and correlated activity coefficients of acetone vs. acetone mole fraction for the acetone-lithium perchlorate binary at 293.15 K.

a_{ii} are equal to zero, and a_{ij} are generally nonzero. For a binary salt-solvent mixture, a_{12} and a_{21} are the only adjustable parameters. Also note that there are no ternary parameters in Eq. (4).

RESULTS AND DISCUSSION

Fifteen binary systems were correlated with the UNIQUAC equation. The binary parameters and the standard deviations of the experimental γ_i's from the predicted γ_i's are reported in Table 2. The UNIQUAC parameters were found by minimizing the standard deviation of the predicted γ_i's from the measured γ_i's with a common search technique. The maximum concentration that was examined in this portion of the study was 2 M. This limit was chosen because the salts were assumed to be totally dissociated.

By examining the standard deviations, one can see that acceptable fits were obtained with all systems. All of the experimental data sets contained a characteristic level of error. As a result, one would not expect to achieve exceedingly small standard deviations. It was found that the UNIQUAC equation can easily represent the data to within the inherent error in the data.

Most data sets exhibited a maximum in the activity coefficient vs. concentration curve. A typical data set and its UNIQUAC representation arc are shown in Figure 1. In all cases the UNIQUAC equation was able to match the maximum.

The quality of the UNIQUAC representation of the data was extremely insensitive to a_{12}. Setting a_{12} equal to 8,400 J/mol caused at most a 5% increase in the minimum standard deviations of the systems studied. In situations where the quantity of data is limiting, a viable way to proceed is to reduce the correlation to a one parameter model by setting a_{12} equal to 8400 J/mol.

The isopentanol systems seem to produce the poorest results. This might be due to the fact that isopentanol cannot conform to the cell theory assumption implicit in the UNIQUAC equation. Isopentanol is the most complex solvent in this study. It might not be possible for the isopentanol systems to maintain constant coordination throughout salt concentration range. A concentration-dependent lattice coordination number might be needed to treat solvents with complex structure.

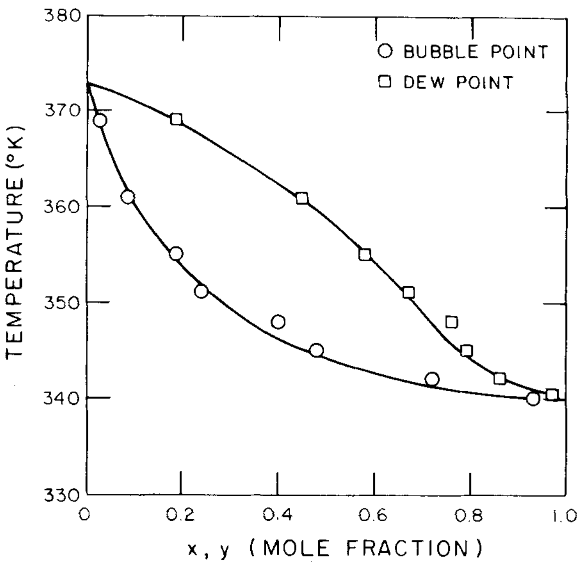

Figure 2. Comparison of experimental and predicted bubble point and dew point temperatures vs. the salt-free methanol mole fractions for the methanol-water-lithium chloride ternary at 1 atm. Salt concentration was one molar.

Three ternaries were examined: methanol-water-LiCl, methanol-water-NaBr, and acetone-methanol-LiCl. The energy parameters listed in Table 2 were used to generate the VLE behavior of these selected ternaries. The computations were compared to experimental data. The data for the methanol-water-LiCl and the methanol-water-NaBr systems are from Ramalho et al. (1961), and the data for the acetone-methanol-LiCl system are from Ohe et al. (1969). The standard deviations of the predicted vapor phase mole fractions from the experimental vapor phase mole fractions were 0.02, 0.03, and 0.2, respectively. The bubble point and dew point curves for the methanol-water-LiCl ternary are shown in Figure 2.

The prediction of the behavior of the first two ternaries was very encouraging. However, the results for the acetone-methanol-LiCl ternary were unacceptable at least for design purposes. The source of the problem was that the two molar maximum concentration assumption was badly violated by the experimental data. However, the acetone-rich end of the binary is below the two molar limit. If we restrict our interest to the regions of the curve that satisfies the two molar limit, the standard deviation is 0.05. An azeotrope exists with this area of interest at 0.91 mol fraction of acetone (salt-free). The UNIQUAC prediction of the azeotrope occurred at 0.90 mol fraction of acetone (salt-free).

CONCLUSIONS

The routine application of the UNIQUAC equation to salt-containing systems was successful as a predictive correlation of VLE as long as the maximum salt concentration was less than 2 M and the salt was fully dissociated. This UNIQUAC analysis can predict the effect of salt concentration as well as the effect of solvent concentration on the VLE of mixtures with salts. If necessary, the analysis can be reduced to require one adjustable parameter per binary by fixing a_{12} to a value of 8,400 J/mol. This simplification typically produces a 5% increase in error.

NOTATION

A_{wk} = van der Waals area, cm^2/mol
a_i = activity of the ith component
a_{ij} = binary energy parameter
l_i = see Eq. 5
N_i = number of moles of the ith component
P = system pressure
$P_i^{V,sat}$ = vapor pressure of the ith component when pure and at the temperature of the experiment
q_i = pure component area parameter
R = gas constant
r_i = pure component volume parameter
T = temperature
V_{wk} = van der Waals volume, cm^3/mol
x'_i = special mole fraction of the ith component as defined in Eq. 3
Z = lattice coordination number, set equal to 10

Greek Letters

Φ_i = segment fraction of the ith component
ν = degree of dissociation
γ'_i special activity coefficient of the ith component as defined in Eqs. 1 and 2.
ϑ_i = area fraction of the ith component
τ_{ij} = see Eq. 9

Superscripts and Subscripts

$'$ = special mole fraction and associated activity coefficient as defined in Eqs. 1 through 3
i = ith component
j = jth component
wk = van der Waals

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