Vapor-Liquid Equilibrium for Salt Containing Systems: Correlation of Binary Solvent Data and Prediction of Behavior in Multicomponent Solvents

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When salts or electrolytes are encountered in the design of separation equipment, the effects of these electrolytes on the vapor-liquid equilibrium behavior of nonelectrolytes are often neglected. This is the case because there has not been a method for the correlation of data for salt containing systems which can be used for varying salt and solvent compositions. Boone, Rousseau, and Schoenborn (1976) proposed a method for correlating data from binary solvent-salt systems which are not restricted in this manner. This work proposes an extension that correlates phase equilibrium behavior using the Prausnitz UNIQUAC equation, which can be used for systems having regions of immiscibility. In addition, the model used for binary solvent systems is extended to multisolvent salt systems, and it is shown that vapor-liquid equilibrium data for these systems can be predicted from data on binary solvent-salt systems.

SCOPE

A description of the vapor-liquid equilibrium properties of solvent-salt systems would aid in the design, analysis, and optimization of a separation process in which a salt is a component. The salt may, in fact, be added to aid the separation, as is done in the addition of magnesium nitrate for the extractive distillation of nitric acid. Alternatively, the salt may be present as a reactant, product, or catalyst from a reactor ahead of the separation process.

Boone, Rousseau, and Schoenborn (1976) recommended a procedure to correlate vapor-liquid equilibrium behavior of binary solvent-salt systems. With suitable pseudobinary definitions, equilibrium data were successfully correlated using vapor pressure lowering data, salt free infinite dilution activity coefficients, and a single, system dependent parameter. This procedure has an important advantage over previous correlation procedures because it can correlate equilibrium data for various salt and solvent compositions; previous correlations are limited to salt saturated systems or systems with constant ratios of volatile components. The liquid solution model of Boone et al. is generalized so that it can be used to correlate equilibrium data for systems having regions of liquid-liquid immiscibility and predict the behavior of multicomponent solvent-salt systems from binary solvent-salt data.

CONCLUSIONS AND SIGNIFICANCE

The correlation procedure developed by Boone, Rousseau, and Schoenborn (1976) for modeling salt-binary solvent systems has been extended to include the more versatile UNIQUAC equation. The use of this equation makes it possible to model systems which exhibit regions which approach immiscibility. The model was shown to fit vapor-liquid equilibrium data taken on seven salt-binary solvent combinations; one of these combinations, lithium chloride-propanol-water, did approach immiscibility.

The binary solvent solution model was modified and used to predict the vapor-liquid equilibrium behavior of

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salt-ternary solvent systems. Equilibrium data for two systems of this type were obtained and used to test the predictions. The accuracy of the predictions was acceptable but not within the limits of Holmes and Van Winkle (1970).

Because of the additions and modifications to the model of Boone et al., a wider range of systems can now be correlated. Furthermore, the model lends itself to the prediction of vapor-liquid equilibrium properties for multisolvent solutions.

When an electrolyte or salt is added to a solvent, it is usually found that the solubility of a nonelectrolyte in the salt solution is different from its solubility in the pure solvent. The addition of an electrolyte can cause miscible solvents to form immiscible mixtures; for example, when potassium carbonate is added to ethanol-water mixtures, the liquid can separate into two phases. In cases where the effect is not sufficiently strong for phase separation, there usually remain strong effects on the vapor-liquid equilibria of the system. When a salt is added to a two-solvent system, the equilibrium vapor phase is usually enriched in one of the components, and the equilibrium vapor phase composition of the other is reduced. The component which has an increased vapor composition is said to be salted out, while the other component is salted in.

In this study, a simple model of a liquid phase that contains nonvolatile salts is presented and used to correlate and predict vapor-liquid equilibrium behavior. The model is based on empirical observations and, because of its success in describing difficult systems, shows promise for use in the design or analysis of separation processes that have nonvolatile salts in the streams being separated.

LIQUID MODEL

Rousseau, Ashcraft, and Schoenborn (1972) and Jacques and Furter (1972) have shown that vapor-liquid equilibrium data for salt saturated systems can be correlated using the Wilson equation and other integrated forms of the Gibbs-Duhem equation. For these correlations to work, it was necessary to treat the binary solvent-salt systems as pseudobinary mixtures. This involved expressing the compositions on a salt free basis and adjusting the vapor pressure of the solvents to include the vapor pressure lowering caused by the salt.

Elements of the solution model used in this study were defined by Boone, Rousseau, and Schoenborn (1976). In the model, the ternary mixture of solvent 1-solvent 2 and salt was treated as a binary solution by defining the mixture of component 2 and salt as a pseudocomponent. The ratio of component 2 and salt was held constant in the pseudocomponent structure. Based on this model, component 1 was chosen to be the salted out solvent and was relabeled component 1*; component 2 was the salted in solvent, and the salt-component 2 mixture was labeled component 2*. These definitions allowed treatment of the system as a binary consisting of components 1* and 2*. Activity coefficients were correlated by the Wilson equation from equilibrium data on this system:

$$\ln \gamma_{i^*} = 1 - \ln \left(\sum_{j^*} x_{j^*} \Lambda_{i^*j^*} \right) - \sum_{k^*} \left(x_{k^*} \Lambda_{k^*i^*} \Big/ \sum_{j^*} x_{j^*} \Lambda_{k^*j^*} \right) \tag{1}$$

where

$$\Lambda_{i^*j^*} = (v_{j^*}{}^L / v_{i^*}{}^L) \exp \{-(\lambda_{i^*j^*} - \lambda_{i^*i^*})/RT\} \tag{1a}$$

An obvious disadvantage of the above procedure is that each salt to solvent 2 ratio corresponds to a different pseudobinary system and, therefore, different Wilson parameters. This problem was resolved by Boone, Rousseau, and Schoenborn (1976) by a determination of the effect of salt molality on infinite dilution activity coefficients of the pseudobinary components. The technique of Shreiber and Eckert (1971) was then used to estimate the Wilson parameters from the infinite dilution activity coefficients. The following discussion shows how this was done and the utility of the technique.

The beginning equation was the usual expression relating vapor and liquid phase fugacities:

$$y_{i^*} P = \gamma_{i^*} x_{i^*} P_{i^*}{}^s \tag{2}$$

Conditions were restricted to low pressure, and the reference state was the ideal solution in the sense of Raoult's law.

The salt effect S_1 was defined in terms of the equation

$$S_1 = f_1 / f_{1'} \tag{3a}$$

where

$$x_1 / x_2 = x_{1'} / x_{2'} \tag{3b}$$

The superscript (′) denotes the salt free system, whereas no superscript refers to the component mole fraction in the ternary mixture. Under limiting conditions, the salt effect is related to salt concentration by the Setschenow equation

$$S_1 = \exp (k_s C_e) \tag{4}$$

Recognizing that component 1 is identical to component 1*, Boone et al. (1976) showed that Equations (3) and (4) may be combined to give

$$\frac{\gamma_{1^*}{}^\infty}{\gamma_{1'}{}^\infty} = \frac{1}{x_2{}^\infty} \frac{P_1{}^s(2)}{P_{1s}(2^*)} \exp (k_s C_e) \tag{5}$$

where $P_1{}^s(i)$ is the vapor pressure of component 1 at the boiling point of component i. It was also shown that

$$\frac{\gamma_{2^*}}{\gamma_{2'}} = \frac{x_{2'} y_{2^*} P_{2'}{}^s}{x_{2^*} y_{2'} P_{2^*}{}^s} \tag{6}$$

which at infinite dilution becomes

$$\frac{\gamma_{2^*}{}^\infty}{\gamma_{2'}{}^\infty} = \frac{P_2{}^s(1)}{P_{2^*}{}^s(1)} = \frac{P_2{}^s(1)}{P_2{}^s(1) - \Delta P_2{}^s} \tag{7}$$

Boone, Rousseau, and Schoenborn (1976) showed how Equations (5) and (7) could be used to estimate the effect of varying salt concentrations on the infinite dilution activity coefficients and the associated Wilson parameters. The data necessary to make these estimations include vapor pressures of solvents 1 and 2, vapor pressure lowering of solvent 2, infinite dilution activity coefficients or vapor-liquid equilibrium data for salt free solutions of solvents 1 and 2, and a single salt parameter, k_s. Compositions used in the calculations were determined as follows:

$$x_{1*} = x_1 \tag{8}$$

$$x_{2*} = x_2 + x_3 \tag{9}$$

$$C_e = 1\,000\, x_3/x_2M_2 \tag{10}$$

It was shown that this approach could be used to correlate vapor-liquid equilibrium data for methanol-water solutions of five different salts, four that caused salting out of methanol and one that caused salting in.

This study proposes two extensions of the above procedure. The first extension is to systems that approach immiscibility. Since the Wilson equation does not fit such systems, the UNIQUAC equation of Abrams and Prausnitz (1975) will be used:

$$\ln\gamma_i = \ln(\phi_i/x_i) + (z/2)q_i\ln(\theta_i/\phi_i) + l_i - (\phi_i/x_i)\sum_j x_j l_j - q_i\ln\left(\sum_j \theta_j\tau_{ji}\right) + q_i - q_i\sum_j\left(\theta_j\tau_{ij}\Big/\sum_k \theta_k\tau_{kj}\right) \tag{11}$$

where

$$l_i = z(r_i - q_i)/2 - (r_i - 1) \tag{11a}$$

$$\phi_i = r_i x_i \Big/ \sum_j r_j x_j \tag{11b}$$

$$\theta_i = q_i x_i \Big/ \sum_j q_j x_j \tag{11c}$$

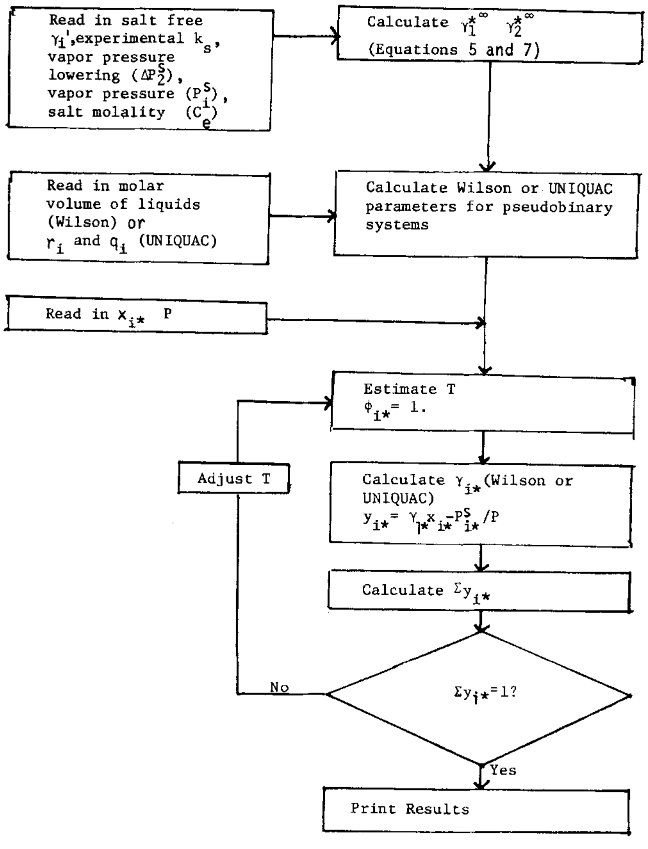

Fig. 1. Block diagram for vapor-liquid equilibrium calculations.

$$\tau_{ij} = \exp\{-(u_{ji} - u_{ii})/RT\} \tag{11d}$$

This equation has been used successfully to correlate both liquid-liquid and vapor-liquid equilibrium data.

The second extension is to systems that contain more than two solvents. The objective is to show that phase equilibrium data for systems containing two solvents and a salt can be used to predict the equilibrium behavior of multisolvent systems.

Both of these extensions are described in subsequent sections and are tested against experimental data.

EXPERIMENTAL EQUIPMENT AND PROCEDURE

Vapor-liquid equilibrium data for alcohol-water salt mixtures were obtained using an improved Othmer recirculation still as modified by Johnson and Furter (1960). The alcohol was component 1, water was component 2, and salt was component 3. Each set of experiments was conducted so that the salt to water ratio was held constant while the alcohol to water ratio was varied. References to salt molality mean moles of salt per 1 000 g water.

Seven binary solvent systems were used to test the UNIQUAC equation. The data for five of these systems were presented by Boone, Rousseau, and Schoenborn (1976), while new data on ethanol-water-lithium chloride and 1-propanol-water-lithium chloride were obtained in this study. Equilibrium data for two ternary solvent-salt systems were also obtained: methanol-1-propanol-water-lithium chloride and ethanol-1-propanol-water-lithium chloride.

Table 1. Values of the Salt Parameter

System	k_s
Methanol-water-$HgCl_2$	0.050
Methanol-water-KCl	0.280
Methanol-water-NaF	0.195
Methanol-water-NaBr	0.120
Methanol-water-LiCl	0.075
Methanol-water-LiCl	0.124
Ethanol-water-LiCl	0.124
1-propanol-water-LiCl	0.245

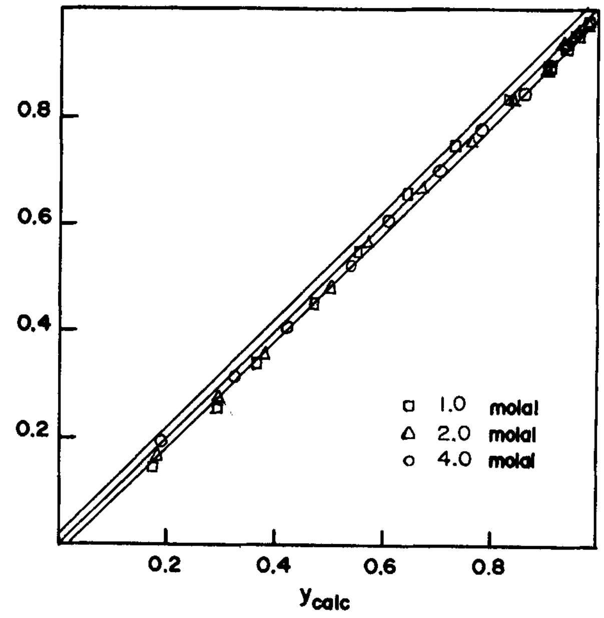

Fig. 2. Comparisons of experimental with calculated methanol vapor phase compositions using optimum UNIQUAC parameters: methanol-water-sodium bromide.

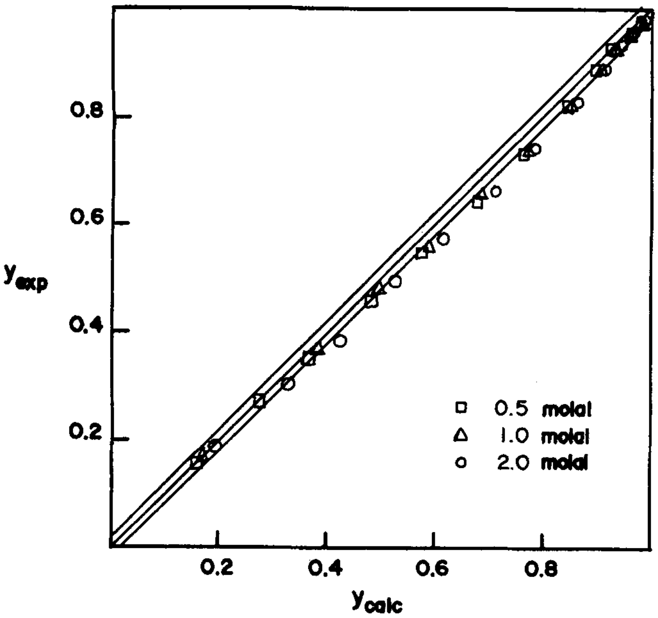

Fig. 3. Comparisons of experimental with calculated methanol vapor phase compositions using optimum UNIQUAC parameters: methanol-water-potassium chloride.

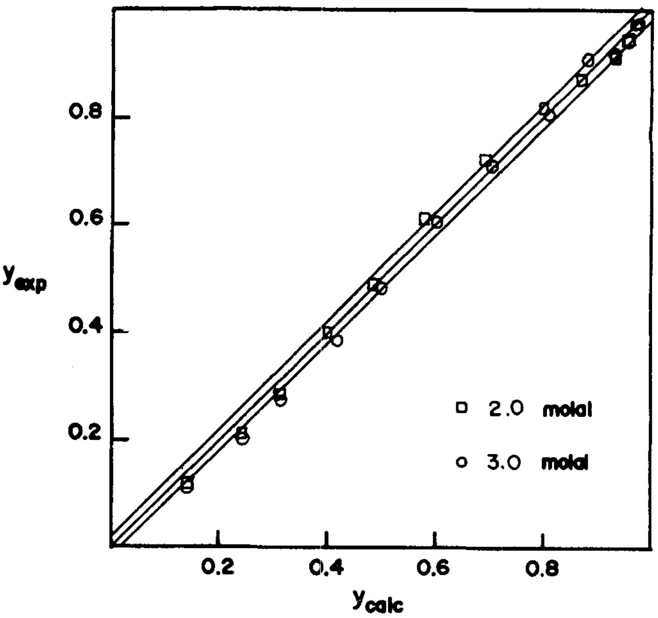

Fig. 4. Comparisons of experimental with calculated methanol vapor phase compositions using optimum UNIQUAC parameters: methanol-water-mercuric chloride.

Temperatures were measured with Fisher thermometers calibrated against boiling points of pure liquids. Pressure was maintained at 760 ± 1 mm Hg. Equilibrium compositions were determined with a Perkin Elmer vapor fractometer using a type W column and a thermal conductivity detector. Liquid samples were distilled to remove the salt before analysis. Composition and temperature measurements were accurate to ± 0.005 mole fraction and 0.1°C, respectively.

CORRELATING EQUATIONS

The procedure outlined above could be used with any correlating equation such as the Wilson, Van Laar, Margules, etc. However, precision of the fit varies with the system, the equation, and the procedure used to evaluate the correlation's parameters. For example, vapor-liquid equilibrium behavior of the salt free 1-propanol-water system correlated well using the Wilson equation and parameters determined from infinite dilution activity coefficients; however, using the infinite dilution activity coefficients to estimate parameters for the UNIQUAC equation led to a correlation that incorrectly predicted an immiscible region.

Values of infinite dilution activity coefficients were obtained by determining UNIQUAC and Wilson parameters that gave the best fits to the complete set of salt free vapor-liquid equilibrium data. Optimum fit was taken to mean minimization of the objective function:

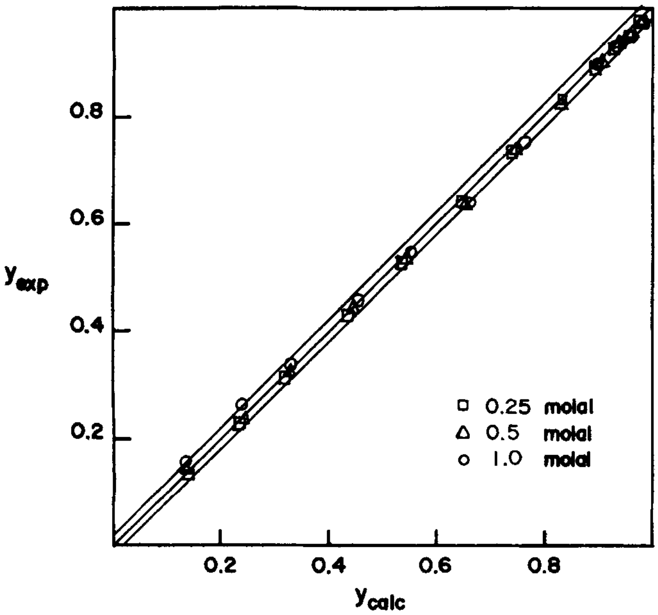

Fig. 5. Comparisons of experimental with calculated methanol vapor phase compositions using optimum UNIQUAC parameters: methanol-water-sodium fluoride.

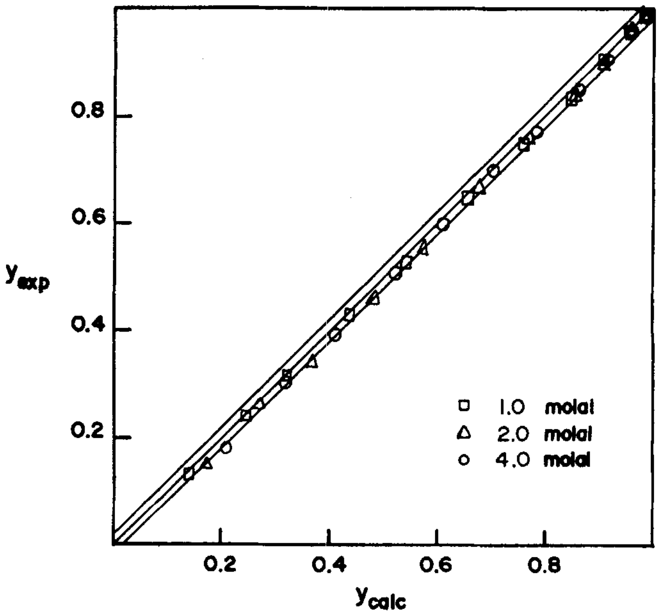

Fig. 6. Comparisons of experimental with calculated methanol vapor phase compositions using optimum UNIQUAC parameters: methanol-water-lithium chloride.

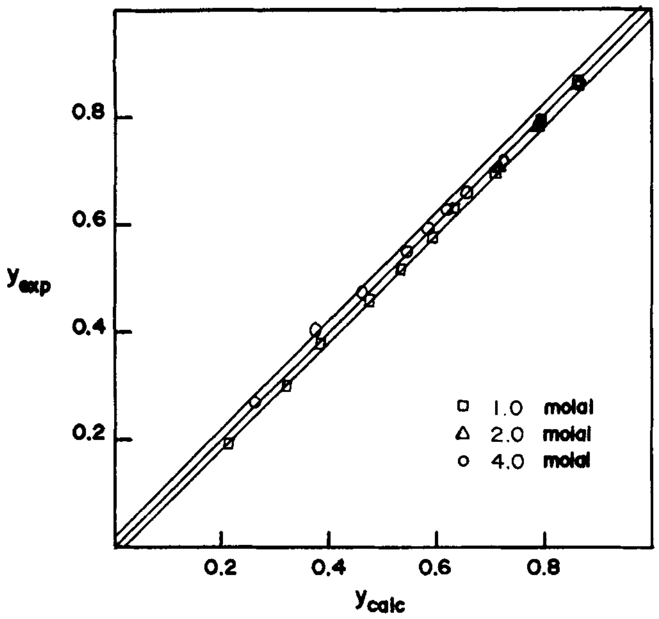

Fig. 7. Comparisons of experimental with calculated ethanol vapor phase compositions using optimum UNIQUAC parameters: ethanol-water-lithium chloride.

$$Q = \Sigma(1 - \gamma_{1'}^{\text{calc}}/\gamma_{1'}^{\text{exp}})^2 + \Sigma(1 - \gamma_{2'}^{\text{calc}}/\gamma_{2'}^{\text{exp}})^2 \quad (12)$$

Then, because infinite dilution activity coefficients for the salt free systems are needed to predict the effect of salt on vapor-liquid equilibrium behavior, they were calculated using the optimum parameters in the appropriate correlation. If one wished instead to determine infinite dilution activity coefficients experimentally, numerous procedures exist for doing so (Kobayashi, Chappelear, and Deans, 1967). The application of the principles described in this model are not restricted to a particular method of evaluating these quantities.

The salt parameter k_s was determined for the seven binary systems by rearranging Equation (5):

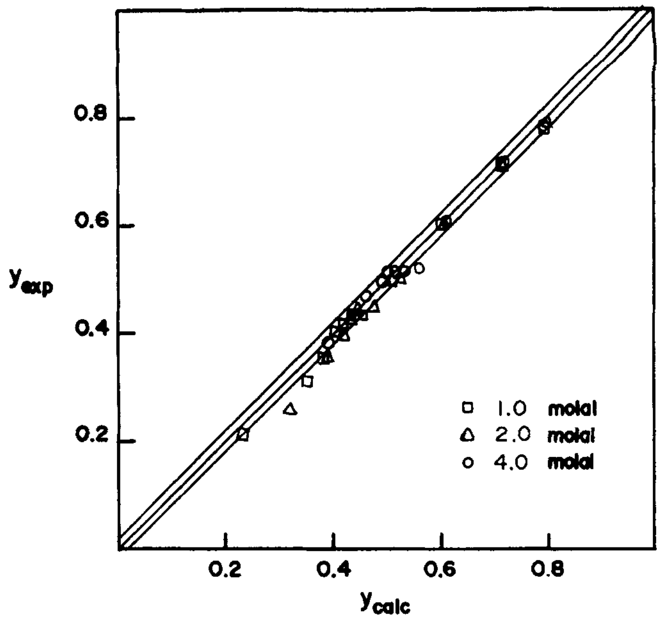

Fig. 8. Comparisons of experimental with calculated 1-propanol vapor phase compositions using optimum UNIQUAC parameters: 1-propanol-water-lithium chloride.

$$k_s C_e = \ln \{x_2^{\infty} [P_1^s(2^*)/P_1^s(2)] (\gamma_{1*}^{\infty}/\gamma_{1'}^{\infty})\} \quad (13)$$

If the Setschenow equation is valid, plots of C_e vs. the right-hand side of Equation (13) are linear with a slope of k_s and pass through the origin. Equilibrium data were determined at three salt molalities for each of the seven systems. The values of k_s shown in Table 1 were determined from a linear least-squares fit through the origin for each of these systems using graphically determined infinite dilution activity coefficients for each salt concentration.

With the information determined from these data, equilibrium vapor compositions and temperatures can be calculated for any liquid composition. A flow diagram out-

TABLE 2. DEVIATIONS OF CALCULATED AND EXPERIMENTAL DATA USING OPTIMUM INFINITE DILUTION ACTIVITY COEFFICIENTS

		Wilson				UNIQUAC			
		ΔT°C		$\Delta Y_1 (\times 10^3)$		ΔT°C		$\Delta Y_1^* (\times 10^3)$	
	C_e	avg	max	avg	max	avg	max	avg	max
MeOH-H_2O-NaBr	1.00	0.6	1.0	6	15	0.6	1.5	10	31
	2.00	0.4	0.8	8	23	0.5	0.9	9	26
	4.00	0.7	1.4	11	18	0.7	1.9	6	20
MeOH-H_2O-KCl	0.50	0.6	1.2	16	41	0.3	0.6	10	33
	1.00	0.8	1.4	19	51	0.5	1.2	14	28
	2.00	0.4	0.9	27	64	0.3	0.7	22	41
MeOH-H_2O-$HgCl_2$	2.00	0.6	1.7	12	38	0.7	1.7	18	40
	3.00	1.1	1.7	11	19	0.7	1.7	18	37
MeOH-H_2O-NaF	0.25	0.5	0.9	5	9	0.5	0.9	4	8
	0.50	0.2	0.4	10	23	0.3	0.7	4	8
	1.00	0.3	0.6	14	37	0.4	1.0	7	22
MeOH-H_2O-LiCl	1.00	0.6	0.9	9	21	0.4	1.1	3	10
	2.00	0.6	1.0	9	19	0.5	1.0	9	25
	4.00	0.7	1.4	5	13	0.7	1.6	8	30
EtOH-H_2O-LiCl	1.00	0.5	0.8	9	24	0.3	0.6	8	15
	2.00	0.5	1.4	9	24	0.4	0.9	6	13
	4.00	0.4	0.9	14	39	0.4	0.8	11	29
PrOH-H_2O-LiCl	1.00	1.0	2.5	21	38	0.8	2.3	14	45
	2.00	1.3	2.3	25	53	0.9	2.5	19	66
	4.00	1.5	2.9	41	81	0.7	1.0	16	60
Overall		0.7	1.3	14	33	0.5	1.2	11	29

lining these calculations is shown in Figure 1. Basically, the procedure is as follows. Calculate $\gamma_{1'}{}^{\infty}$ and $\gamma_{2'}{}^{\infty}$ using optimum salt free UNIQUAC or Wilson parameters. Use these values and the salt parameter in Equations (5) and (7) to estimate infinite dilution activity coefficients for the liquid composition determined from Equations (8), (9), and (10). Use the infinite dilution activity coefficient for the salt containing system to estimate values of UNIQUAC or Wilson parameters. With these parameters, bubble point calculations may be performed to give the desired vapor composition and temperature.

Comparisons of smoothed experimental data and calculated results are shown in Figures 2 to 8. The 45 deg line represents perfect agreement, while the other two lines show the boundaries of good agreement, which was taken as 0.02 mole fraction units. In addition, Table 2 lists the average deviations in bubble point temperature and vapor compositions when calculated as

$$\Delta T = | T_{\text{calc}} - T_{\text{exp}} | \tag{14a}$$

$$\Delta y_1 = | y_{1\text{ cal}} - y_{1\text{ exp}} | \tag{14b}$$

The overall average deviations in temperature and mole fraction were, respectively, 0.5°C and 0.011 mole fraction units. As indicated by Holmes and Van Winkle (1970), these deviations indicate good agreement between calculated and experimental values.

It was particularly difficult to fit the 1-propanol-water-lithium chloride systems. Additions of lithium chloride to 1-propanol-water mixtures tend to encourage phase separation. Figure 9 shows equilibrium data for mixtures of 1-propanol in 4.0 molal aqueous lithium chloride solutions. Also shown on the figure are plots of smoothed salt free data and UNIQUAC and Wilson correlations for the 4.0 molal systems. The system is obviously approaching an unstable condition, where the addition of a small amount of lithium chloride would cause the formation of a second liquid phase. As had been expected, the Wilson equation does a rather poor job of fitting the data.

The Wilson and UNIQUAC equations require specific volume and area data on each of the system components. Since data on the pseudocomponents were not available, pure solvent values were used; the results indicate this to be a satisfactory approximation. Furthermore, when a set of experimental water-methanol-lithium chloride values was determined and used in the Wilson equation, no improvement in data fit was observed.

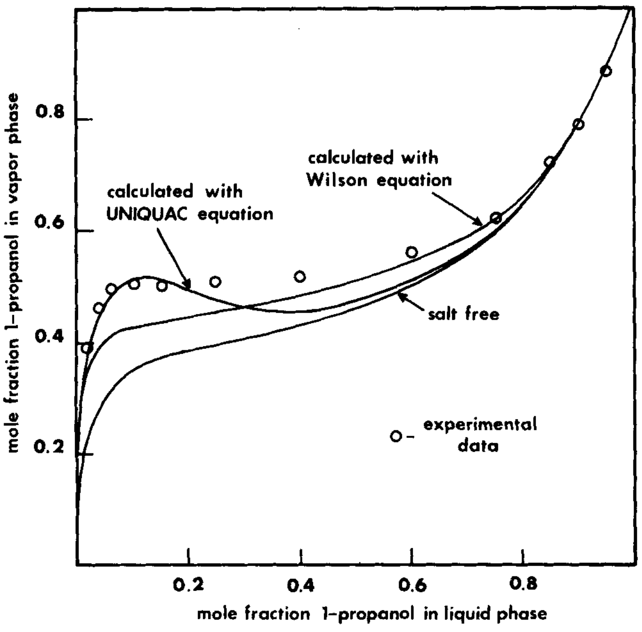

Fig. 9. Vapor-liquid equilibrium diagram for 1-propanol-water-4.0. molal lithium chloride.

TERNARY SOLVENT-SALT SYSTEMS

An important advantage of the Wilson and UNIQUAC equations is that parameters estimated from binary equilibrium data can be used to predict the behavior of multicomponent systems. An hypothesis of this study was that a system of three solvents and a salt can be treated as a pseudoternary system in a manner analogous to the pseudobinary system. Consider, for example, the case of mixtures of methanol-1-propanol-water-lithium chloride. Both methanol and 1-propanol are salted out, while water is salted in. Using the rules established for binary solvent mixtures, solutions of water and salt in a constant molal ratio would be designated as a single pseudocomponent. Compositions of pseudoternary mixtures are then determined as

$$x_{1*} = x_1 \tag{15a}$$

$$x_{2*} = x_2 \tag{15b}$$

$$x_{3*} = x_3 + x_4 \tag{15c}$$

where 1 = methanol, 2 = propanol, 3 = water, and 4 = lithium chloride.

In cases where more than one component is salted in, the component with the greatest degree of salting in would be treated with the salt as a single pseudocomponent.

To predict the equilibrium behavior of a pseudoternary system defined by Equation (15), Wilson or UNIQUAC parameters are required for the following pseudobinary pairs:

Table 3. Vapor-Liquid Equilibrium Data for Methanol-1-Propanol-Water-Lithium Chloride at 760 mm Hg

C_e (molal)	T°C	X_1	Y_1	X_2	Y_2	X_3	Y_3
1.0	81.9	0.164	0.407	0.098	0.208	0.738	0.385
2.0	82.6	0.168	0.424	0.101	0.224	0.731	0.352
4.0	78.0	0.377	0.618	0.221	0.165	0.403	0.217
4.0	76.2	0.455	0.702	0.269	0.147	0.276	0.152
4.0	70.6	0.711	0.896	0.066	0.034	0.223	0.070
4.0	85.5	0.089	0.222	0.197	0.356	0.714	0.422
4.0	86.1	0.073	0.267	0.042	0.281	0.885	0.452
4.0	82.5	0.155	0.410	0.099	0.203	0.746	0.387

Table 4. Vapor-Liquid Equilibrium Data for Ethanol-1-Propanol-Water-Lithium Chloride at 760 mm Hg

C_e (molal)	T°C	X_1	Y_1	X_2	Y_2	X_3	Y_3
1.0	86.6	0.200	0.385	0.157	0.191	0.644	0.424
2.0	84.1	0.199	0.387	0.159	0.202	0.642	0.411
4.0	87.9	0.041	0.252	0.031	0.262	0.929	0.486
4.0	86.0	0.072	0.350	0.053	0.259	0.875	0.391
4.0	84.0	0.144	0.388	0.112	0.223	0.744	0.389
4.0	79.4	0.761	0.825	0.075	0.054	0.165	0.120
4.0	80.6	0.563	0.709	0.106	0.081	0.331	0.211
4.0	82.7	0.337	0.556	0.141	0.146	0.522	0.298
4.0	89.0	0.091	0.144	0.614	0.508	0.296	0.346
4.0	87.3	0.125	0.219	0.416	0.387	0.459	0.394
4.0	85.5	0.185	0.338	0.257	0.279	0.559	0.382

TABLE 5. PARAMETERS FROM EXPERIMENTAL DATA

System	C_e	λ_{12}-λ_{11}	λ_{12}-λ_{22}	u_{12}-u_{22}	u_{12}-u_{22}
MeOH-H_2O-NaBr	0	205	480	40	40
	1.00	351	465	−199	392
	2.00	347	495	−162	366
	4.00	378	551	−151	420
MeOH-H_2O-KCl	0	205	480	40	40
	0.50	512	413	−324	636
	1.00	570	412	−341	701
H_2O-MeOH-$HgCl_2$	0	205	480	40	40
	2.00	643	57	391	−205
	3.00	790	−68	574	−219
MeOH-H_2O-NaF	0	205	480	40	40
	0.25	250	470	−61	161
	0.50	322	459	−192	359
	1.00	379	455	−241	462
MeOH-H_2O-LiCl	0	205	480	40	40
	1.00	230	504	50	50
	2.00	251	525	−19	161
	4.00	285	581	−36	246
EtOH-H_2O LiCl	0	382	955	140	140
	1.00	500	965	60	258
	2.00	553	991	58	295
	4.00	673	1 044	40	400
PrOH-H_2O LiCl	0	1 016	1 285	200	200
	1.00	1 144	1 306	149	309
	2.00	1 313	1 326	113	404
	4.00	1 606	1 403	61	600

A: $1^* - 2^*$ (methanol-1-propanol)
B: $2^* - 3^*$ (1-propanol-water-salt)
C: $1^* - 3^*$ (methanol-water-salt)

Note that pseudobinary system A is in fact a real binary system, and, therefore, parameters determined from salt free solutions of methanol and 1-propanol may be used to describe its equilibrium behavior. The parameters for binary sets B and C vary with the salt to water ratio and must be estimated either from the salt parameter and vapor pressure lowering data, as previously described, or from experimental equilibrium data at the appropriate salt concentration.

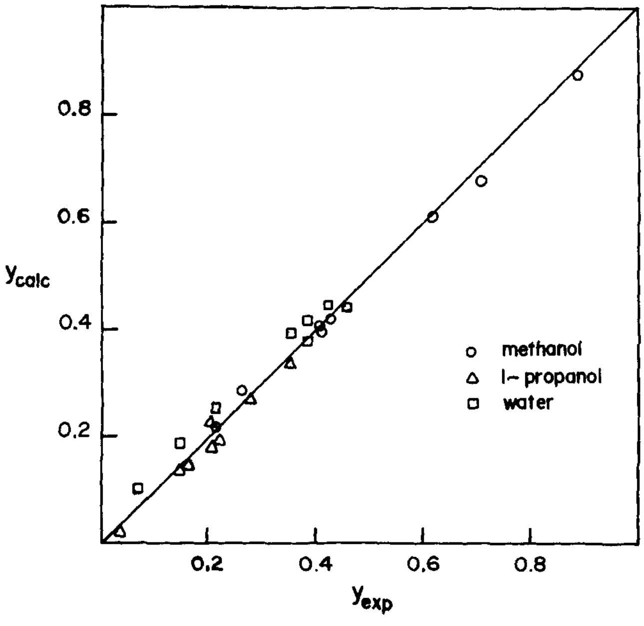

Fig. 11. Comparison of experimental with predicted vapor phase compositions using the Wilson equations: methanol-1-propanol-water-lithium chloride.

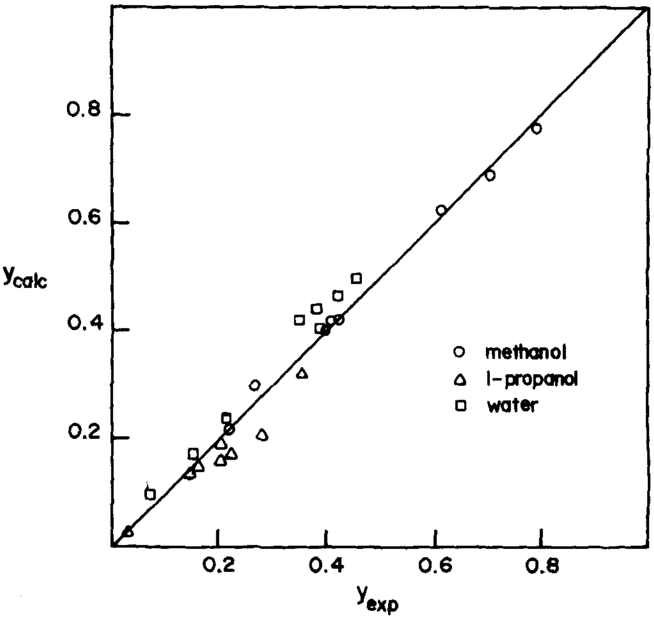

Fig. 10. Comparison of experimental with predicted vapor phase compositions using the Wilson equations: methanol-1-propanol-water-lithium chloride.

To test the hypothesis, experimental vapor-liquid equilibrium data were obtained for two ternary solvent-salt systems: methanol-1-propanol-water-lithium chloride and ethanol-1-propanol-water-lithium chloride. These data are given in Tables 3 and 4.

Pseudobinary Wilson and UNIQUAC parameters listed in Table 5 were used to estimate equilibrium temperatures and vapor compositions for specified liquid mixtures. (It should be noted that although Wilson and UNIQUAC parameters for each salt to water ratio were used in these calculations, conditions at other ratios could be estimated using the procedure outlined earlier.) Comparisons of experimental and predicted equilibrium temperatures and vapor compositions for these ternary mixtures are shown in Figures 10 to 13. Using the Wilson equation, the average deviation in vapor composition for the methanol-1-propanol-water-lithium chloride system was 0.027, while

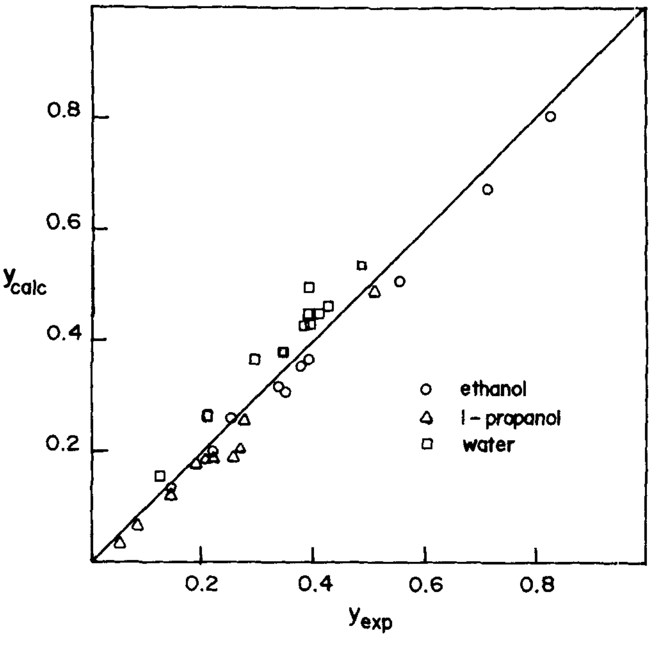

Fig. 12. Comparison of experimental with predicted vapor phase compositions using the Wilson equations: ethanol-1-propanol-water-lithium chloride.

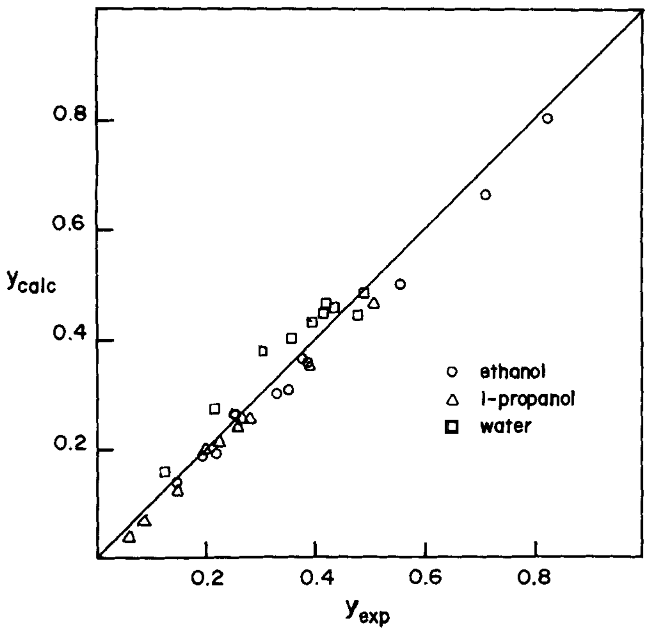

Fig. 13. Comparison of experimental with predicted vapor phase compositions using the UNIQUAC equations: ethanol-1-propanol-water-lithium chloride.

the average deviation for the UNIQUAC equation was 0.020. The fit for the ethanol-1-propanol-water-lithium chloride system was not as accurate; vapor compositions of ethanol and 1-propanol were consistently underestimated by an average of 0.026 mole fraction units, and, therefore, the water composition was off an average of about 0.05 mole fraction units. Temperature predictions had an average deviation of 0.7°C using the Wilson equation and 0.6°C using the UNIQUAC equation.

While the above results are not within the rule of thumb agreement of 0.020 mole fraction units, they can still be considered good. Holmes and Van Winkle (1970) found the equilibrium behavior of methanol-ethanol-water systems to be among the most difficult to predict from binary data. Using the Wilson equation, they found an average deviation of 0.022 mole fraction units in the vapor phase composition; a maximum deviation of 0.084 mole fraction unit was noted. Thus, the systems tested probably correspond to worst cases, and, in general, better agreement can be expected for other ternary solvent systems.

CONCLUSIONS

The use of the pseudocomponent model makes it possible to correlate vapor-liquid equilibrium data at varying salt concentrations using the Wilson or UNIQUAC equations. The UNIQUAC equation is superior to the Wilson equation in fitting data for systems approaching immiscibility. The work in this paper shows that vapor-liquid equilibrium behavior for salt-ternary solvent mixtures can be predicted from data on pseudobinary systems using the Wilson or UNIQUAC equations.

These two major extensions to previously developed models should be useful in designing or modeling separation processes operating on streams containing nonvolatile salts.

NOTATION

C_e = salt concentration
f_i = fugacity of component i
k_s = salt parameter
l_i = defined by Equation (11*a*)
M = molecular weight
P = pressure
P_i^s = vapor pressure of i at the system temperature
$P_i^s(j)$ = vapor pressure of i at the boiling point of j
ΔP_i^s = vapor pressure lowering of i due to addition of salt
Q = error defined by Equation (12)
q_i = pure component area parameter for component i
R = gas constant
r_i = pure component volume parameter for component i
S_i = salt effect on component i
T = temperature
u_{ji}-u_{ii} = UNIQUAC interaction parameter
v_i^L = specific liquid volume of component i
x_i = liquid mole fraction of component i
x_i^∞ = mole fraction of solvent i in salt mixture without other solvents
y_i = vapor mole fraction of component i
z = lattice coordination number, a constant set equal to 10, Abrams and Prausnitz (1975).

Greek Letters

γ_i = activity coefficient of component i
ϕ_i = defined by Equation (11*b*)
θ_i = defined by Equation (11*c*)
τ_{ij} = defined by Equation (11*d*)
Λ_{ij} = defined by Equation (1*a*)
λ_{ij}-λ_{ii} = Wilson interaction parameter

Superscripts

$'$ = value of variable in salt free mixture of solvents
* = value of variable in pseudobinary or pseudoternary mixtures
∞ = infinite dilution

Subscripts

i = component i
j = component j
k = component k

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