Salt Effect in Vapor-Liquid Equilibria:

Correlation of Alcohol-, Water-, Salt Systems

The isobaric data of Johnson and Furter for the systems methanol-water, ethanol-water, and 1-propanol water, each saturated with a variety of common inorganic salts, can be effectively correlated by means of the van Laar, the Wilson, or the Renon equations if pseudo-activity coefficients for the volatile components are computed using a modified reference fugacity for the liquid phase. This reference fugacity takes into account the lowring of the vapor pressure due to the dissolved salt. Furthermore, the activity coefficients are normalized as required by the above equations.

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SCOPE

The addition of a nonvolatile component such as a salt to alter the vapor-liquid equilibrium of a system containing two or more miscible liquids is a subject that has received increased attention in recent years. Despite the lack of an adequate mechanism to explain the salt effect, there is, nevertheless, an important need for characterizing such systems. Appropriate design of separation processes requires that means be available for correlating and extending vapor-liquid equilibrium data and determining their thermodynamic consistency. It was the purpose of this study, therefore, to develop a relatively convenient, empirical method whereby equilibrium data for such systems might be correlated by means of several well-accepted integrated forms of the Gibbs-Duhem equation.

CONCLUSIONS AND SIGNIFICANCE

Data for a number of alcohol-water systems saturated with various inorganic salts have been correlated by computing pseudo-activity coefficients for the volatile constituents. These coefficients were calculated using a reference fugacity corrected for the vapor pressure lowering due to the dissolved salt and by expressing the concentrations of the volatile components on a salt-free basis. Coefficients computed in this manner were readily correlated by means of the van Laar, Wilson, and Renon equations and exhibited the normalization required by these equations.

Although this procedure is not thermodynamically rigorous, it should be useful in evaluating other similar systems containing an added nonvolatile component and for comparing their behavior with the original salt-free systems.

DATA AND ANALYSIS

Literature pertaining to the salt effect in vapor-liquid equilibria and to extractive distillation employing salt as an added component was recently reviewed by Furter and Cook (1967). Moreover, Furter and his colleagues (1957, 1957a, 1960, 1966, 1971, 1972) have published extensive experimental data on a number of systems, notably those containing the lower alcohols, water, and some common salts. A fairly extensive bibliography on the subject has also been given by Ashcraft (1972).

The data used in this study were taken from Johnson and Furter (1960) who studied 18 alcohol-water-salt systems. These systems are listed in Table 1. The isobaric data contain equilibrium vapor and liquid compositions and temperatures, and include both salting-out and salting-in effects as shown in Figure 1 for two of the methanol-water-salt systems.

The equilibrium data of Johnson and Furter for salt-free systems (methanol-water, ethanol-water, and 1-propanol-water) were compared with data published in Perry (1963) and agreement between the two sets of data is extremely good. Because other data are not available for comparison with Furter's data on the salt systems, it was assumed that the data for the systems containing salt are as consistent as the data for the salt-free systems.

Activity coefficients were first computed for each volatile component from the standard equation for thermodynamic equilibrium

$$\phi_i\, y_i\, P = \gamma_i\, x_i\, f_i^{OL} \tag{1}$$

Following the procedures recommended by Prausnitz et al. (1967), computer subroutines were written to estimate values of the fugacity coefficient ϕ_i and of the standard state fugacity f_i^{OL}; these values were then used with the experimental data of Furter to calculate γ_i. Values of ϕ_i were found to be very close to 1, indicating that the vapor phase was essentially ideal. Reference fugacities were initially computed using the vapor pressure of the pure

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Table 1. Data Used in Study

Solvents	Salt	System number
methanol-water	sodium chloride	1
methanol-water	potassium chloride	2
methanol-water	ammonium chloride	3
methanol-water	sodium nitrate	4
methanol-water	lead nitrate	5
methanol-water	mercuric chloride	6
ethanol-water	sodium chloride	7
ethanol-water	potassium chloride	8
ethanol-water	ammonium chloride	9
ethanol-water	sodium nitrate	10
ethanol-water	lead nitrate	11
ethanol-water	mercuric chloride	12
1-propanol-water	sodium chloride	13
1-propanol-water	potassium chloride	14
1-propanol-water	ammonium chloride	15
1-propanol-water	sodium nitrate	16
1-propanol-water	lead nitrate	17
1-propanol-water	mercuric chloride	18

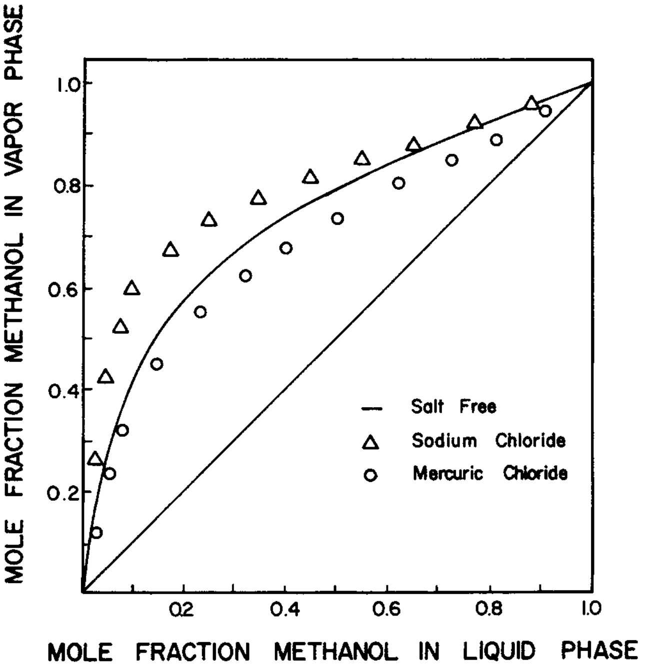

Fig. 1. Salt effects in methanol-water systems.

alcohol or water at the temperature of the system and included the Poynting correction factor.

$$f_i^{OL} = \phi_i^s P_i^s \exp \frac{-v_i^L P_i^s}{RT} \qquad (2)$$

Subsequently, the reference fugacity for water was modified to take into account the vapor pressure lowering due to the dissolved salt. Data on vapor pressure lowering of the alcohols was not available. In all cases, the mole fractions of the volatile components y_i and x_i in the vapor and liquid respectively, were computed on a salt-free basis.

Rigorous treatment would require, it should be noted, that values of x_i in Equation (1) should take into account the presence of the salt and its degree of dissociation in the liquid. Unfortunately, it is not possible at present to account for all the particles present in the liquid, that is, molecules of both volatile components, molecules of undissociated salt, ionic species, etc. The presence of salt is thus accounted for by modifying the reference fugacities for vapor pressure lowering as shown later.

CORRELATIONS

Three sets of equations were used to correlate the pseudo-activity coefficients as a function of concentration: the van Laar, the Wilson (1964), and the Renon (1968) equations. Although the Wilson equations are more complicated than those of van Laar they have been found to be superior to those of van Laar in correlating a wide variety of vapor-liquid systems. The equations of Renon are similar to those of Wilson but contain three parameters per binary system rather than two.

A computer program was written for each of the equations to determine the appropriate parameters which would provide the best fit of the experimental data. The parameters were found using a pattern search technique to minimize the absolute value of the difference between experimental and calculated values of the activity coefficients. The validity of the program was tested by comparing coefficients calculated in the program with those of Van Winkle (1958) for the 1-propanol-water system. The agreement was good. Also the values for the parameters in the Wilson equation for the salt-free methanol-water system compares favorably with published data in the literature. Table 2 shows the calculated values of mole fraction methanol in the vapor phase for several sets of Wilson parameters from the sources noted.

Although a knowledge of salt concentrations in the liquid phase is necessary (it is assumed, of course, there is no salt in the vapor phase), it is convenient to express concentrations of the volatile constituents in both the vapor and liquid phases on a salt-free basis. In this way it is easy to compare the degree to which the coefficients are modified by the presence of salt with those of the regular salt-free system. Solubility data used in this study are those given by Johnson and Furter.

DISCUSSION OF RESULTS

Experimental and calculated data and results have been tabulated* for the systems: methanol-, ethanol-, water each saturated with sodium chloride, potassium chloride, ammonium chloride, mercuric chloride, sodium nitrate, and lead nitrate, respectively. With the exception of mer-

Table 2. Comparison of Vapor Compositions for Methanol-Water

x_1	y_1	y_1'	y_1''	y_1'''	y_1''''
0.046	0.267	0.3606	0.3493	0.3501	0.360
0.094	0.402	0.4145	0.4035	0.4000	0.413
0.157	0.533	0.5257	0.5165	0.5035	0.524
0.217	0.602	0.5853	0.5784	0.5599	0.584
0.321	0.680	0.6671	0.6634	0.6414	0.668
0.425	0.745	0.7276	0.7259	0.7058	0.732
0.534	0.791	0.7776	0.7770	0.7615	0.785
0.632	0.829	0.8186	0.8185	0.8078	0.829
0.727	0.883	0.8530	0.8530	0.8467	0.866
0.817	0.920	0.8915	0.8915	0.8885	0.907
0.891	0.956	0.9193	0.9193	0.9182	0.936

y_1 = experimental, y_1' = van Winkle (1958), y_1'' = Prausnitz (1967), y_1''' = Prausnitz (1967), y_1'''' = this study.

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[*] Data has been deposited as Document No. 01861 with the National Auxiliary Publications Service (NAPS), c/o CCM Information Corp., 866 Third Ave., New York 10022 and may be obtained for $2.00 for microfiche or $5.00 for photocopies.

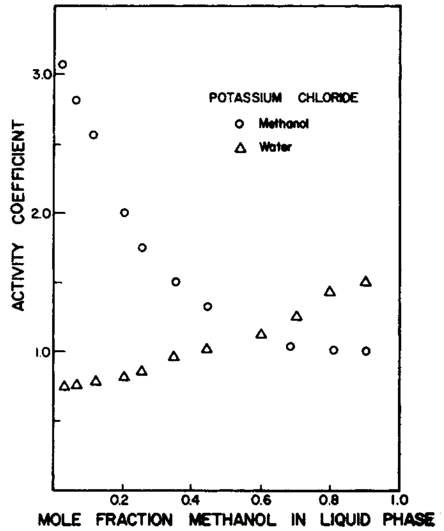

Fig. 2. Activity coefficients: Methanol-water-potassium chloride.

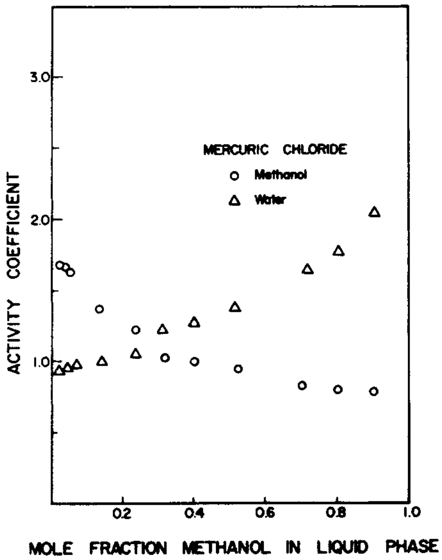

Fig. 3. Activity coefficients: Methanol-water-mercuric chloride.

curic chloride, all these compounds cause salting-out of the alcohol. Typical of the results computed without correcting the reference fugacity for the vapor-pressure lowering are those shown in Figure 2 for methanol and water saturated with potassium chloride. As shown in Figure 3, mercuric chloride is unique among the salts examined because it depresses the activity of both water and alcohol but has a greater effect on the alcohol presumably because of its greater solubility in the latter.

Because the equations of Wilson, Renon, and van Laar are valid only for normalized activity coefficients, they cannot be used to correlate the activity coefficients as calculated by Equation (1) where the saturated vapor pressure of the pure component is used as the reference fugacity.

One of the effects of a salt is to lower the vapor pressure of the liquid in which it is soluble. For water, the vapor pressure lowering is almost a linear function of salt concentration as shown in Figure 4. This figure is based on data from The Handbook of Chemistry and Physics (1966). Unfortunately, data on the vapor pressure lowering of the alcohols and water by mercuric chloride are not available. Thus, if the reference fugacity is taken to be the saturated vapor pressure of the pure liquid component minus the vapor pressure lowering due to the salt, f_i^{OL} in Equation (1) can be replaced by $P_i^s - \Delta P_i$ where P_i^s is the saturated vapor pressure of the pure liquid and ΔP_i is the vapor pressure lowering due to the salt.

Since the salts listed, except mercuric chloride, have negligible solubility in the alcohols, the reference fugacity for the alcohols can be taken as

$$f_1^{OL} = P_1^s \tag{3}$$

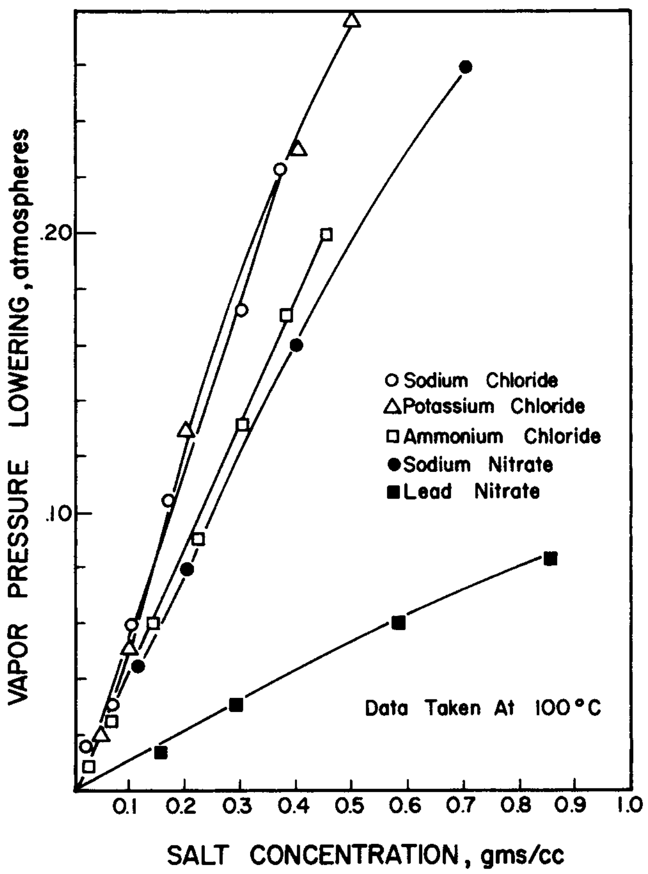

Fig. 4. Vapor pressure lowering.

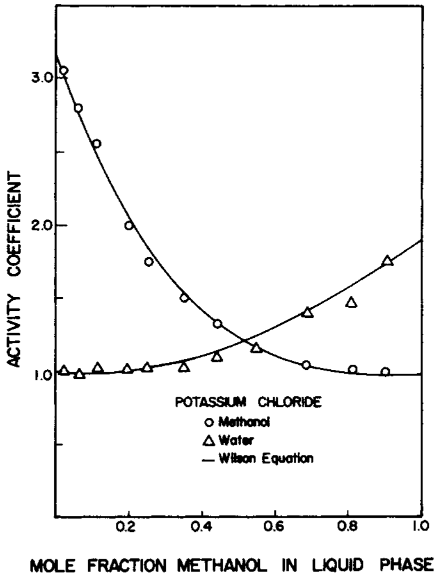

Fig. 5. Normalized activity coefficients: methanol-water-potassium chloride.

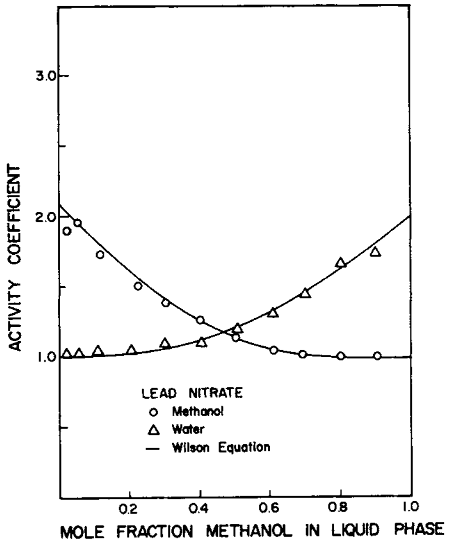

Fig. 6. Normalized activity coefficients: methanol-water-lead nitrate.

TABLE 3. PARAMETERS FOR VAN LAAR, WILSON, AND RENON EQUATIONS

System	A	B	λ_{12}-λ_{22}	λ_{12}-λ_{22}	g_{12}-g_{11}	g_{12}-g_{22}	α
1	1.23	0.81	255.0	676.6	401.9	729.0	0.90
2	1.30	0.83	311.0	675.5	429.6	732.8	0.87
3	1.21	0.67	365.0	561.0	157.7	754.0	0.70
4	1.23	1.01	264.5	712.0	351.0	638.3	0.50
5	0.93	0.61	390.0	446.0	285.6	460.1	1.10
7	3.02	0.97	1355.0	1100.0	527.2	1821.6	0.52
8	2.81	0.98	1100.5	1161.0	651.8	1648.4	0.58
9	2.43	1.04	994.5	999.0	715.6	1402.8	0.60
10	3.21	1.10	1390.0	1341.0	675.6	1903.8	0.50
11	2.18	0.98	799.5	955.0	228.2	1278.7	0.31
13	3.45	1.18	1438.0	1388.5	338.5	2228.1	0.30
14	3.55	1.14	1555.0	1508.5	933.7	2148.1	0.50
15	3.66	1.10	1410.0	1705.0	1650.8	2189.3	0.51
16	3.56	0.72	1304.0	1244.0	823.8	2277.5	0.61
17	3.23	1.16	1701.6	1501.3	716.1	1973.2	0.50

without serious error. Since the salts are more soluble in water, however, the reference fugacity for the latter component may be redefined as

$$f_2^{OL} = P_2^s - \Delta P_2 \tag{4}$$

Pseudo-activity coefficients for 15 alcohol-water-salt systems were recalculated using Equations (2) and (3) for the reference fugacities of the alcohol and water, respectively. In general, the use of the modified reference fugacity resulted in normalized pseudo-activity coefficients as shown in Figures 5 and 6 for the methanol-water systems. That is,

$$\gamma_i \rightarrow 1 \quad \text{as} \quad x_i \rightarrow 1$$

The fact that some data points still show activity coefficients slightly less than 1.0 may be the result of inaccurate experimental data or of inaccurate values of the vapor pressure lowering due to the salt.

Values for the parameters in the Wilson, Renon, and van Laar equations were computed for the fifteen systems using the revised coefficients. These parameters are listed in Table 3. Although the Renon equations contain three parameters, they were not significantly better than the Wilson equations. The solid lines shown in Figures 5 and 6 consequently represent the latter equations.

The salts used in this study can be ranked in the following order based on their ability to lower the pseudo-activity coefficient of water: sodium nitrate (greatest lowering), ammonium chloride, potassium and sodium chloride, lead nitrate, mercuric chloride. This ordering of the salts also happens to be the ordering of the salts arranged according to their decreasing solubility in water. For inorganic salts, then, the greater the solubility of the salt in water, the greater will be the depression of the pseudo-activity coefficient of water.

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NOTATION

A, B = parameters in van Laar equation
$g_{ij} - g_{ii}$ = parameters in Renon equation (evaluated via pattern search)
P = total pressure
P_i^s = saturation (vapor) pressure of pure component i
ΔP_i = vapor pressure lowering of component i
R = gas constant
T = absolute temperature
f_i^{OL} = standard state fugacity for component i
v_i = molar volume of component i
x, y = mole fraction of volatile components, salt-free basis, in liquid and vapor

Greek Letters

α = parameter in Renon equation (evaluated via pattern search)
γ_1 = activity coefficient, alcohol
γ_2 = activity coefficient, water
γ_2' = activity coefficient, water, based on modified reference fugacity
γ_2'' = calculated activity coefficient (Wilson equation)
γ_2''' = calculated activity coefficient (Renon equation)
γ_2'''' = calculated activity coefficient (van Laar equation)
$\lambda_{ij} - \lambda_{ii}$ = parameters in Wilson equation (evaluated via pattern search)
ϕ_i = fugacity coefficient, component i

Subscripts

1 = alcohol
2 = water
3 = salt

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Investigation of the Thermodynamic Behavior of the System, Acetone-Carbontetrachloride, by the Equilibrium Sedimentation Technique

The *equilibrium sedimentation technique* for the direct determination of the chemical potential composition derivatives of a liquid mixture is applied to the binary system acetone-carbontetrachloride. Equilibrium concentration profiles obtained in an ultracentrifuge are used with the Wilson equation to quantitatively determine the composition variation of the activity coefficients over the entire range of composition. Results agree well with previous data and indicate the technique to be accurate and reliable.

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SCOPE

The *phenomenon of sedimentation equilibrium*, although well understood (Fujita, 1962), has only recently been proposed (Cullinan, 1968) as a basis for a practical experimental technique for the determination of liquid solution thermodynamic properties. The objective of this paper is the experimental determination of the composition variation of the activity coefficients of the binary liquid system acetone-carbontetrachloride at 20°C. over the entire range of composition.

The technique involves the measurement of equilibrium composition profiles established in an ultracentrifuge. From these profiles the variation of solution activity with composition is calculated from the governing thermodynamic condition of uniformity of total chemical-mechanical potential.

CONCLUSIONS AND SIGNIFICANCE

Comparison of the results with the best existing data indicates that the equilibrium sedimentation technique is a reliable and accurate method for the determination of liquid solution activity coefficients. The method offers several distinct advantages over conventional vapor-liquid equilibrium techniques. First, the method permits the characterization of the entire composition range with a small number of experiments. Second, the method gives a direct measure of the composition variation of solution activity. Finally, the equilibrium sedimentation technique is directly applicable to the determination of the composition variation of the activity coefficients of multicomponent liquid systems.

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