R & D NOTES

Vapor–Liquid Equilibria—Isopropanol–Water System Saturated with Potassium and Calcium Nitrate

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INTRODUCTION

Research interests in the experimental determination of the effect of dissolved salt on the vapor–liquid equilibria of solvent systems and the correlation of such data have been well sustained over the last few decades because of the importance of salt distillation in the separation of close boiling and azeotropic mixtures, and the lack of general applicability of existing correlation methods for such data. Review articles have been published on the chemistry (Long and McDevit, 1952), the correlation methods (Furter, 1975; Jaques, 1983), the thermodynamic consistency test (Jaques and Furter, 1972; Jaques, 1974), and the economic and technical aspects of salt distillation (Cook and Furter, 1968; Furter, 1968, 1972). In this study, the vapor–liquid equilibria of the isopropanol–water system saturated with potassium and calcium nitrate were experimentally determined. The experimental data were correlated by a recently proposed modified Wilson equation (Tan, 1984), as shown in Eq. 1, for the excess free energy of mixing function.

$$\frac{\Delta G_S^E}{RT} = -[X_1 \ln(A_{31}X_1 + A_{12}X_2) + X_2 \ln(A_{32}X_2 + A_{21}X_1)] \quad (1)$$

The corresponding expressions for the activity coefficients of the two solvent components are given by Eqs. 2 and 3.

$$\ln\gamma_{S1} = -\ln(A_{31}X_1 + A_{12}X_2) + X_2\left[\frac{A_{12}}{A_{31}X_1 + A_{12}X_2} - \frac{A_{21}}{A_{32}X_2 + A_{21}X_1}\right] \quad (2)$$

$$\ln\gamma_{S2} = -\ln(A_{32}X_2 + A_{21}X_1) - X_1\left[\frac{A_{12}}{A_{31}X_1 + A_{12}X_2} - \frac{A_{21}}{A_{32}X_2 + A_{21}X_1}\right] \quad (3)$$

For the equation to be valid over the entire composition range, all four interaction parameters should be positive. In the absence of dissolved salt, $A_{31} = A_{32} = 1$ thereby reverting the equation to its original form.

EXPERIMENTAL

The vapor–liquid equilibria data were obtained with an Othmer still at 760 ± 3 mm Hg (101 + 0.4 kPa). The construction of the still and the experimental setup and procedure have been described in detail by Tan (1984). BDH AR grade isopropanol, distilled-deionized water and MERCK AR grade potassium or calcium nitrate were used to make up the solutions. Salt saturation at the solution bubble point was ensured by the presence of excess undissolved salt in the boiling solution. The compositions of the equilibrium phases were analyzed by density measurements at 30 ± 1°C using 5 mL pyknometers. For the analysis of the liquid phase, the condensate obtained by distilling the solution to dryness was used, which gave an accuracy to within ± 0.003 mole fraction of alcohol.

RESULTS AND DISCUSSION

Vapor-Liquid Equilibria Data

As shown in Figure 1, the data on the isopropanol–water system at 760 ± 3 mm Hg (101 ± 0.4 kPa) obtained with the present experimental setup and procedure compared very well with those reported by Hirata et al. (1975).

The vapor–liquid equilibria for the systems saturated with potassium and calcium nitrate were also shown in Figure 1. A

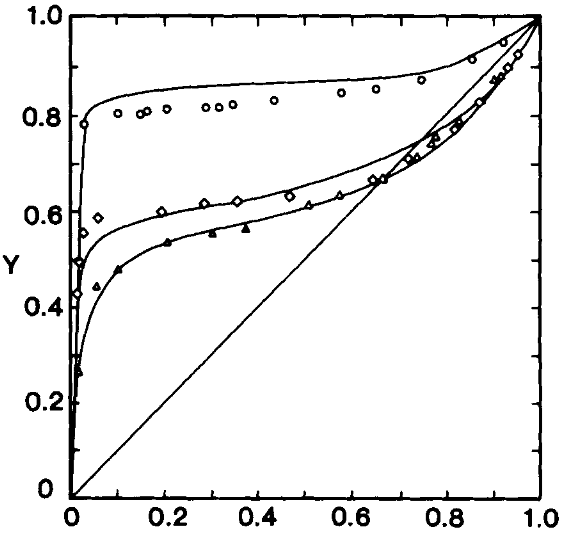

Figure 1. Vapor-liquid composition plot. (○ = calcium nitrate, ◇ = potassium nitrate, △ = no dissolved salt; — = predicted curves).

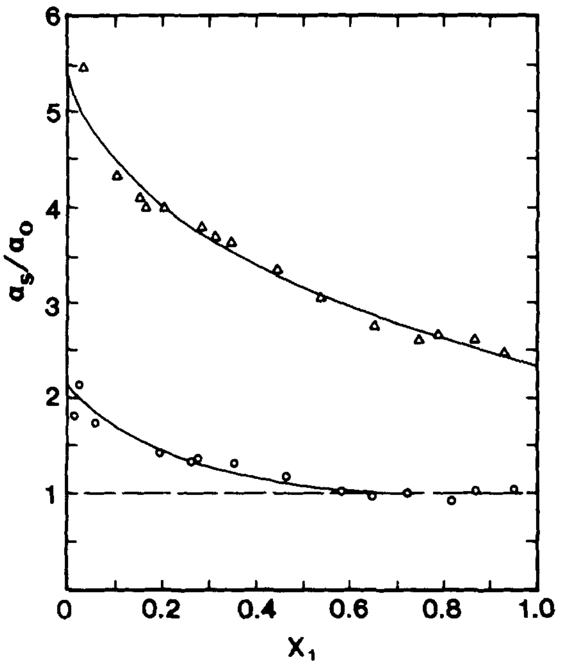

Figure 2. Relative volatility enhancement factor—liquid composition plot. (△ = calcium nitrate, O = potassium nitrate).

large increase in the relative volatility, to the extent that the azeotrope was completely eliminated, was observed in the system saturated with calcium nitrate. However, saturation with potassium nitrate showed only moderate effect on the relative volatility of the water-rich mixtures and almost negligible effect on the alcohol-rich mixtures. The azeotropic composition was shifted only slightly toward the alcohol end. Figure 2 shows the enhancement in the relative volatility of the system due to the presence of the dissolved salts for various liquid compositions. Potassium nitrate was also reported to have moderate effect on the ethanol-water system by Tursi and Thompson (1951) and by Jaques and Furter (1972). The significant difference in the effect of the two nitrate salts may be attributed to the difference in their solubilities in the two solvent components. Calcium nitrate is about 1.5 times more soluble in water than potassium nitrate. In isopropanol, calcium nitrate is soluble to the extent of 14 g/100 g alcohol while potassium nitrate is barely soluble. Since the relative solubilities of the salt in the two solvents are not significantly different for the two nitrates, it may therefore be inferred that the salt effect on the vapor–liquid equilibria depends more significantly on the actual solubility rather than on the relative solubility of the salt in the two solvents. However, salt-solvent interactions are very complex, and such factors as differences in the ionic dissociation (Bekerman and Tassios, 1975), and ionic size and solvation parameters (Ohe, 1975) may be significant.

Thermodynamic Consistency Test

For the thermodynamic consistency test, the activity coefficients were calculated based on the saturation vapor pressure of the pure component saturated with the salt. The saturation vapor pressure-temperature relationship for water and isopropanol saturated with the nitrate salts was experimentally determined and given in the form of Eqs. 4 and 5, as suggested by Jaques and Furter (1972).

For water $$\log P^o_{S2} = m \log P^o_{02} - c \qquad (4)$$

For alcohol $$P^o_{S1} = \epsilon P^o_{01} \qquad (5)$$

For potassium nitrate, $m = 0.858$ and $c = -0.220$; for calcium nitrate, $m = 0.9915$, $c = 0.6696$ and $\epsilon = 0.9696$. These compared favorably with those reported by Jaques and Furter (1972). No data were reported for isopropanol saturated with potassium nitrate, for which $\epsilon = 0.9858$ was obtained in this study. The vapor–liquid equilibria for the potassium nitrate-saturated sys-

TABLE 1. EXPERIMENTAL AND PREDICTED RESULTS

		Isopropanol-Water Saturated with Potassium Nitrate ($A_{12} = 0.05123$, $A_{21} = 0.76122$, $A_{31} = 0.9980$, $A_{32} = 1.2329$)																
X		0.952	0.930	0.867	0.814	0.719	0.643	0.580	0.467	0.357	0.288	0.262	0.194	0.058	0.024	0.019	*Mean*	σ
	Expt*	0.927	0.895	0.828	0.768	0.710	0.658	0.637	0.632	0.629	0.619	0.606	0.605	0.392	0.564	0.497		
Y	Pred**	0.927	0.900	0.835	0.793	0.736	0.703	0.680	0.648	0.624	0.611	0.606	0.594	0.541	0.459	0.429		
	Pred/Expt	1.000	1.006	1.009	1.033	1.037	1.068	1.068	1.025	0.992	0.987	1.000	0.982	0.914	0.814	0.863	0.987	0.071
	Pred-Expt																0.005	0.041
	Expt	82.3	81.9	81.2	80.7	80.5	80.4	80.6	80.6	80.9	81.1	81.2	81.6	82.3	84.3	91.3		
T, °C	Pred	81.4	81.2	80.7	80.6	80.5	80.7	80.9	81.4	81.9	82.3	82.5	83.0	85.5	89.5	90.8		
	Pred/Expt	0.989	0.991	0.994	0.998	1.001	1.003	1.004	1.010	1.013	1.016	1.016	1.017	1.039	1.061	0.995	1.010	0.019
	Pred-Expt																0.8	1.6
		Isopropanol-Water Saturated with Calcium Nitrate ($A_{12} = 0.05123$, $A_{21} = 0.76122$, $A_{31} = 1.0153$, $A_{32} = 3.8754$)																
X		0.918	0.859	0.788	0.743	0.650	0.575	0.435	0.347	0.315	0.284	0.201	0.167	0.152	0.103	0.031		
	Expt	0.949	0.921	0.892	0.872	0.848	0.841	0.824	0.821	0.817	0.817	0.802	0.807	0.808	0.805	0.787		
Y	Pred	0.923	0.901	0.888	0.883	0.877	0.873	0.870	0.868	0.867	0.867	0.864	0.863	0.862	0.858	0.817		
	Pred/Expt	0.973	0.979	0.996	1.012	1.034	1.038	1.054	1.057	1.061	1.061	1.065	1.070	1.067	1.065	1.038	0.038	0.033
	Pred-Expt																0.030	0.027
	Expt	83.2	83.4	83.5	83.6	83.9	84.3	84.9	85.4	85.9	86.6	88.5	90.5	90.8	95.2	102.0		
T, °C	Pred	82.1	82.2	82.4	82.6	82.9	83.0	83.4	83.6	83.6	83.7	84.0	84.2	84.3	85.0	91.2		
	Pred/Expt	0.987	0.986	0.987	0.988	0.987	0.985	0.982	0.978	0.974	0.967	0.950	0.930	0.929	0.893	0.894	0.961	0.034
	Pred-Expt																−3.6	3.4

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* Experimental.
** Predicted.

tem were found to be thermodynamically consistent even with the more stringent Jaques and Furter (1972) criteria of $K > D$. However, for the calcium nitrate system, the data satisfied Herrington's criteria of $D\text{-}J < 10$ (Hala et al., 1958), but not the Jaques and Furter criteria of $K > D$.

Correlation with the Modified Wilson Equation

Masashi et al.'s values of A_{12} and A_{21} (Hirata et al. 1975) were used for the present correlation. The salt-solvent interaction parameters, A_{31} and A_{32}, were determined by nonlinear regression of the excess free energy of mixing function. Table 1 gives the correlation results for the two systems. The derived expression was found to predict the vapor composition to within a mean error of −0.005 mole fraction of alcohol for the potassium nitrate system and to within 0.03 for the calcium nitrate system. For the bubble point, the equation gave a mean error of 0.8 and 3.6°C for the two systems, respectively. The observed salt effect and the corresponding values of the salt-solvent interaction parameters agree well with the interpretations by Tan (1984), in that for A_{31} close to 1.0, as in both the present systems, the effect of the salt on the relative volatility would be larger, with a higher value of A_{32}. The calcium nitrate system is therefore characterized by a high value of A_{32} of about 4 for its very large salt effect, while potassium nitrate with a moderate to negligible effect on the system is characterized by a low value of about 1.2.

CONCLUSIONS

Calcium nitrate, a more soluble salt than potassium nitrate in isopropanol–water system, showed a more pronounced effect on the vapor–liquid equilibria of the system than potassium nitrate. The azeotrope was completely eliminated with dissolved calcium nitrate, whereas saturated potassium nitrate merely shifted it slightly toward higher alcohol content. The proposed modified Wilson equation was found to give good correlation for the two systems.

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NOTATION

A = solution interaction parameters in modified Wilson Eq. 1
D = Herrington's consistency test parameter = $100|I|/\Sigma$
ΔG^E = excess free energy of mixing
I = difference in the areas under $\gamma_{S1}/\gamma_{S2} - X_1$ curve
J = Herrington consistency test parameter = $150(T_{\max} - T_{\min})/T_{\min}$
K = Jaques and Furter's consistency test parameter = $\frac{1}{2}J$
P^o = vapor pressure of pure component
R = gas constant
T = temperature
X = liquid composition on salt-free basis
Y = vapor composition
m,c = vapor pressure correlation parameters as defined in Eq. 4

Greek Letters

α = relative volatility
γ = activity coefficient based on vapor pressure of pure component saturated with salt
σ = standard deviation

Subscripts

1 = alcohol
2 = water
3 = salt
0 = system without dissolved salt
S = system with dissolved salt

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