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Vapor−Liquid Equilibrium of Propan-2-ol + Propan-1-ol + Sodium Iodide at 298.15 K

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This paper presents vapor−liquid equilibrium data for the propan-2-ol (1) + propan-1-ol (2) + NaI (3) ternary system measured at 298.15 K using a static method. The salting-out effect was observed for this ternary system. The VLE data were correlated by use of a semiempirical model proposed by Hála. The parameters in Hála's equation were determined to be $\beta = 3.8$, $E_{13} = 35.14$, $E_{23} = 36.56$, $\Lambda_{12} = 1.3404$, $\Lambda_{21} = 0.7464$, $\Lambda_{13} = \Lambda_{31} = 0.0774$, and $\Lambda_{23} = \Lambda_{32} = 0.1796$, respectively. This equation can describe the experimental values with an average deviation of 1.47%.

Introduction

Vapor−liquid equilibrium data of solvent mixtures are necessary for the design of distillation and absorption processes in the chemical industry. Especially, the effect of electrolytes on phase equilibria has been utilized in many equilibrium separation processes (Furter, 1977). However, these VLE data are scarcely measured and few investigations on the effect of salt have been published (Hongo et al., 1989, 1992; Mishima et al., 1987; Kumagae et al., 1992, 1993; Lee et al., 1991).

In previous work, vapor−liquid equilibria (VLE) of alcohol (1) + water (2) + salt (3) and alcohol (1) + alcohol (2) + salt (3) ternary systems were measured at 298.15 K (Yamamoto et al., 1995a,b). $CaCl_2$, NaI, and NH_4I were chosen as the salts. In the case of the solvent mixture containing NaI, the VLE of five binary alcohol mixtures (methanol (1) + ethanol (2), methanol (1) + propan-1-ol (2), methanol (1) + propan-2-ol (2), ethanol (1) + propan-1-ol (2), and ethanol (1) + propan-2-ol (2)) were measured at 298.15 K (Yamamoto et al., 1995b, 1997).

This paper is concerned with the measurement of VLE for the propan-2-ol (1) + propan-1-ol (2) + NaI (3) ternary system at 298.15 K. The experimental data for the ternary system were correlated by the use of a semiempirical model proposed by Hála (1983), and the optimized β value and other parameters in Hála's equation were determined.

Materials

Reagent grade propan-1-ol, propan-2-ol, and NaI used in this investigation were supplied by Wako Pure Chemicals Co. Their purities were, according to the supplier, all higher than 99.5%. Since the principal impurity in both alcohols was water, they were dehydrated over 3A molecular sieves (1/16 in.), and a minimum purity of 99.9% was confirmed by gas chromatography. For the purpose of removing moisture contained in the salt, NaI was dried by heating at 353 K for 3 h in an oven. The physical properties, the water content, and the purity of the solvent used in this work are presented in Table 1 alongside literature values (Riddick et al., 1970).

Experimental Section

An experimental apparatus which was based on a static method was applied to these measurements. The experimental apparatus, the procedure, and the accuracy of the measurement were described in previous publications (Yamamoto et al., 1995a).

The measured vapor pressures of pure solvents (propan-1-ol and propan-2-ol) are presented in Table 2 with literature values (Singh and Benson, 1968; Singh et al., 1969). The deviations of the vapor pressures from the literature values are 0.11% for propan-1-ol and −1.14% for propan-2-ol. The reproducibility for the vapor pressure measurement for pure solvent was within ±0.36%. The vapor pressures of propan-1-ol + NaI and propan-2-ol + NaI binary solutions have been presented in a previous publication (Yamamoto et al., 1997). The accuracy and the thermodynamic consistency of the vapor−liquid equilibrium measurement were discussed in previous work (Yamamoto et al., 1995a,b).

Results and Discussion

Measurement of Vapor−Liquid Equilibrium. The vapor−liquid equilibrium of the propan-2-ol (1) + propan-1-ol (2) binary mixture was measured at 298.15 K (±0.05 K), and the experimental data are presented in Table 3. Figure 1 illustrates the comparison between measured and literature values (Polak et al., 1970). Satisfactory agreement within an average deviation of 1.28% was obtained.

The vapor−liquid equilibrium of propan-2-ol (1) + propan-1-ol (2) + NaI (3) (20 mass % NaI) was measured at 298.15 K (±0.05 K). Table 4 contains measured vapor−liquid equilibrium values for the ternary system. Experimental data are illustrated in Figure 2 with those of five other alcohol (1) + alcohol (2) + NaI (3) systems. The dotted and full lines in this figure show the calculated values by Wilson and Hála's equations, respectively. A salting-out effect was observed for the propan-2-ol (1) + propan-1-ol (2) binary mixture. A salting-in effect was confirmed for the five other alcohol (1) +alcohol (2) + NaI (3) systems.

Correlation of Vapor−Liquid Equilibria using Hála's Equation. Hála proposed the following semiempirical model for the normalized Gibbs energy using a constant exponent β value (Hála, 1983). The excess Gibbs

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Table 1. Physical Properties of Materials at 298.15 K

material	density ($kg\cdot m^{-3}$) exp	density ($kg\cdot m^{-3}$) lit[a]	refractive index exp	refractive index lit[a]	water content (mass %)	purity[b] (%)
propan-1-ol	0.79963×10^3	0.79975×10^3	1.3833	1.3837	0.0671	99.9
propan-2-ol	0.78082×10^3	0.78126×10^3	1.3758	1.3752	0.0852	99.9

[a] Riddick et al. (1970). [b] Determined by gas-chromatography.

Table 2. Vapor Pressure of Pure Solvents at 298.15 K

material	vapor pressure (kPa) exp	vapor pressure (kPa) lit[a]	reproducibility[b] (%)	deviation[c] (%)
propan-1-ol	2.811	2.808	±0.36	0.11
propan-2-ol	5.714	5.780	±0.07	−1.14

[a] Singh et al. (1968, 1969). [b] $\pm 100(1/2)[(p_{max} - p_{min})/p_{ave}]$. [c] $100[(p_{exp} - p_{lit})/p_{lit}]$.

Table 3. Vapor−Liquid Equilibrium of Propan-2-ol (1) + Propan-1-ol (2) at 298.15 K

x_1	y_1	100δ[a]	π (kPa)
0.000	0.000		2.811
0.100	0.172	5.37	3.131
0.193	0.335	−3.25	3.402
0.325	0.494	−0.06	3.791
0.424	0.596	0.74	4.063
0.573	0.737	−0.27	4.449
0.637	0.780	0.63	4.682
0.718	0.848	−0.69	4.890
0.807	0.901	−0.29	5.209
0.907	0.952	0.23	5.518
1.000	1.000		5.714
		$100\Delta = 1.28$	

[a] $\delta = (y_1^{cal*} - y_1^{exp})/y_1^{exp}$. $\Delta = (1/N)\sum_{i=1}^{N}|(y_1^{cal*} - y_1^{exp})/y_1^{exp}|_i$.

Table 4. Vapor−Liquid Equilibrium of Propan-2-ol (1) + Propan-1-ol (2) + NaI (3) at 298.15 K

x°_1	x_3	y_1	100δ[a]	π (kPa)
0.097	0.140	0.182	1.43	2.79
0.212	0.138	0.366	−0.03	3.04
0.308	0.152	0.480	2.31	3.33
0.413	0.141	0.618	−1.87	3.66
0.495	0.144	0.698	−1.95	3.78
0.641	0.140	0.825	−3.01	4.17
0.791	0.157	0.907	−1.08	4.49
0.902	0.141	0.956	−0.05	4.79
			$100\Delta = 1.47$	

[a] $\delta = (y_1^{cal*} - y_1^{exp})/y_1^{exp}$. $\Delta = (1/N)\sum_{i=1}^{N}|(y_1^{cal*} - y_1^{exp})/y_1^{exp}|_i$.

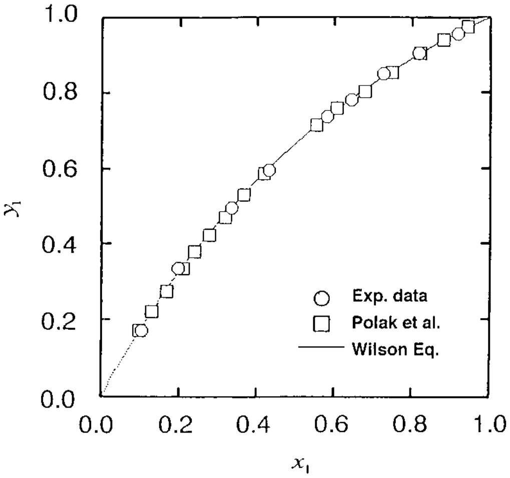

Figure 1. Vapor−liquid equilibrium of propan-2-ol (1) + propan-1-ol (2) at 298.15 K: (○); this work; (□); Polak et al. (1970).

energy G^E of a solvent mixture containing an electrolyte can be represented by

$$G^E = G_a^{\ E} + G_b^{\ E} \tag{1}$$

where $G_a^{\ E}$ is the electrostatic contribution term assumed empirically and is expressed as

$$G_a^{\ E} = \sum_{ij} E_{ij} x_i x_j^{\ \beta} \tag{2}$$

where E is an adjustable constant for the electrostatic long range interaction and the value of the exponent β is originally given as 3/2 by Hála (1983).

$G_b^{\ E}$ is the short-range interaction term and is expressed by the use of a Wilson-type equation:

$$G_b^{\ E} = \sum_k x_k \ln(\sum_l x_l \Lambda_{kl}) \tag{3}$$

where Λ are adjustable constants for short-range interaction and x_i can be calculated by the assumption of complete dissociation of salt in the liquid phase. For a binary mixture containing an electrolyte, the expression for the normalized excess Gibbs energy in the system becomes

$$G^E = E_{13}x_1x_3^{\ \beta} + E_{23}x_2x_3^{\ \beta} - x_1 \ln(x_1 + x_2\Lambda_{12} + x_3\Lambda_{13}) - x_2 \ln(x_1\Lambda_{21} + x_2 + x_3\Lambda_{23}) - x_3 \ln(x_1\Lambda_{31} + x_2\Lambda_{32} + x_3) \tag{4}$$

The activity coefficients of both solvents in the system are given by

$$\ln \gamma_1 = E_{13}\{(1 - \beta x_1)x_3^{\ \beta}\} + E_{23}(-\beta x_2 x_3^{\ \beta}) - \ln(x_1 + x_2\Lambda_{12} + x_3\Lambda_{13}) + 1 - x_1/(x_1 + x_2\Lambda_{12} + x_3\Lambda_{13}) - x_2\Lambda_{21}/(x_1\Lambda_{21} + x_2 + x_3\Lambda_{23}) - x_3\Lambda_{31}/(x_1\Lambda_{31} + x_2\Lambda_{32} + x_3) \tag{5}$$

$$\ln \gamma_2 = E_{13}(-\beta x_1 x_3^{\ \beta}) + E_{23}\{(1 - \beta x_2)x_3^{\ \beta}\} - \ln(x_1\Lambda_{21} + x_2 + x_3\Lambda_{23}) + 1 - x_1\Lambda_{12}/(x_1 + x_2\Lambda_{12} + x_3\Lambda_{13}) - x_2/(x_1\Lambda_{21} + x_2 + x_3\Lambda_{23}) - x_3\Lambda_{32}/(x_1\Lambda_{31} + x_2\Lambda_{32} + x_3) \tag{6}$$

The Wilson parameters between solvent i and salt 3 are simply assumed to be given by

$$\Lambda_{i3} = \Lambda_{3i} \qquad [i = 1, 2] \tag{7}$$

Measured vapor−liquid equilibrium data for the ternary system were correlated using Hála's equation. In this work, the exponent β value was treated as a parameter (Kumagae et al., 1992; Lee et al., 1991), and the optimized β value was determined using the vapor−liquid equilibrium data of the ternary system. The parameters in Hála's equation and the accuracy of this calculation are presented in Table 5, and the calculated values are illustrated by the full line in Figure 2. This equation could reproduce the experimen-

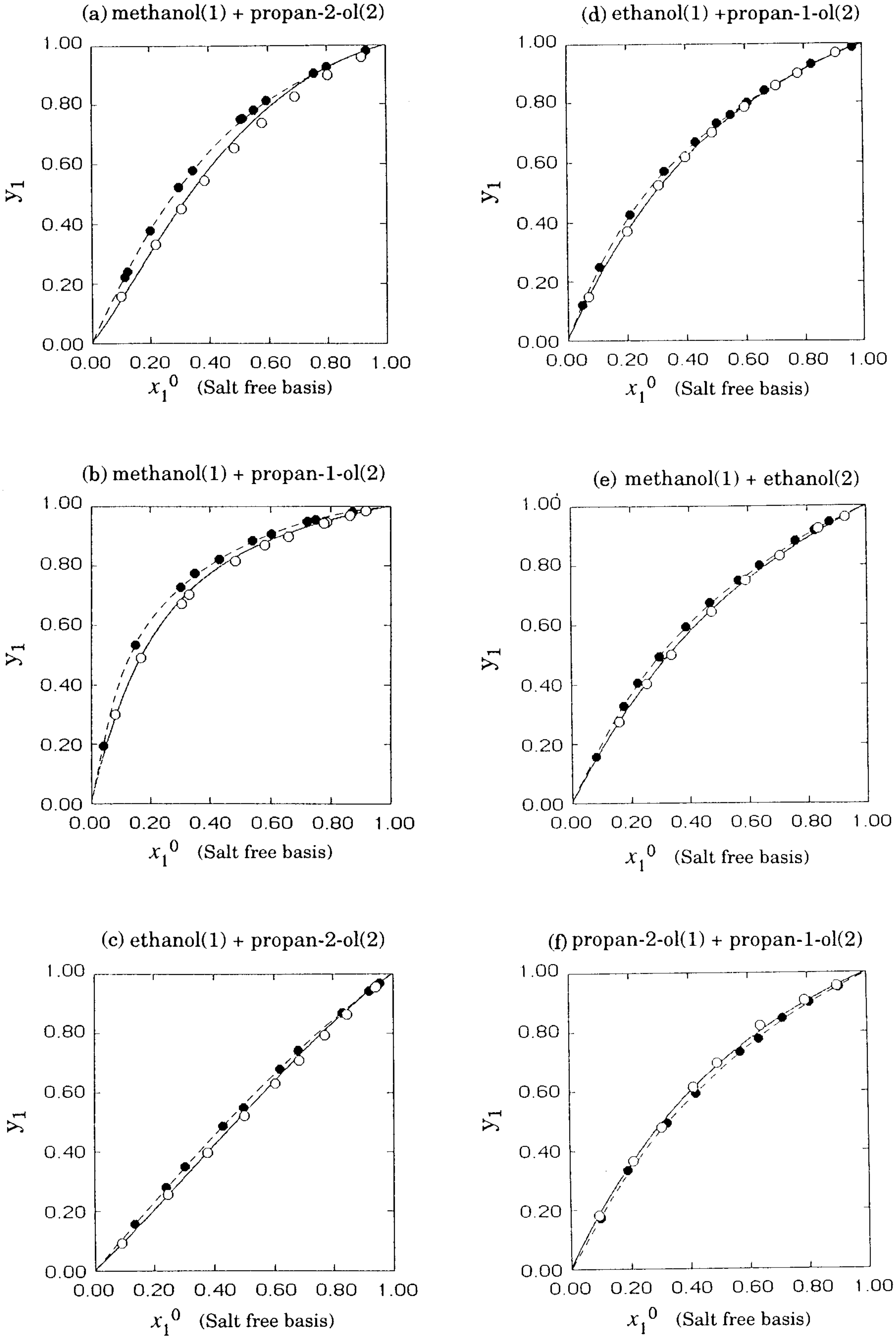

Figure 2. Effect of NaI on vapor−liquid equilibria of alcohol (1) + alcohol (2) systems: (○) NaI (20 mass %); (●) no salt; dotted and full lines are calculated values by Wilson and Hála's equations, respectively; (a) methanol + propan-2-ol; (b) methanol + propan-1-ol; (c) ethanol + propan-2-ol; (d) ethanol + propan-1-ol; (e) methanol + ethanol; (f) propan-2-ol + propan-1-ol.

tal data with an average deviation of 1.47% in the vapor-phase composition.

Effect of NaI on Alcohol (1) + Alcohol (2) Binary Mixtures. Generally speaking, a salt effect for a low-

Table 5. Correlation Parameters of Hála's Equation for Vapor−Liquid Equilibrium for Propan-2-ol (1) + Propan-1-ol (2) + NaI (3) at 298.15 K

NaI mass %	parameters							$100\Delta^a$ (%)
	β	E_{13}	$\Lambda_{13} = \Lambda_{31}$	E_{23}	$\Lambda_{23} = \Lambda_{32}$	Λ_{12}	Λ_{21}	
20	3.8	35.14	0.0774	36.56	0.1796	1.3404	0.7464	1.47

[a] $\Delta = (1/N)\sum_{i=1}^{N}|(y_1^{\text{cal}*} - y_1^{\text{exp}})/y_1^{\text{exp}}|_i$.

Table 6. Solubilities of NaI in Pure Solvents at 298.15 K

solvent	boiling point (K)	solubility[a] (mass %)
water	373.15	64.67
methanol	337.85	47.64
ethanol	351.44	29.86
propan-1-ol	370.35	22.01
propan-2-ol	355.41	20.84

[a] Stephen and Stephen, 1963.

Table 7. Effect of NaI on VLE for Binary Solvent Mixtures at 298.15 K

solvent (1)	solvent (2)	solubility of NaI	$\ln(S_2/S_1)$	salt effect
ethanol	water	1 < 2	0.77	out[a]
methanol	ethanol	1 > 2	−0.46	in[b]
methanol	propan-1-ol	1 > 2	−0.78	in[c]
methanol	propan-2-ol	1 > 2	−0.82	in[c]
ethanol	propan-1-ol	1 > 2	−0.30	in[c]
ethanol	propan-2-ol	1 > 2	−0.36	in[c]
propan-2-ol	propan-1-ol	1 < 2	0.06	out[d]

[a] Yamamoto et al. (1995a). [b] Yamamoto et al. (1995b). [c] Yamamoto et al. (1997). [d] This work.

solubility salt on a solvent is small, and that of a high-solubility salt on a solvent is large. The degree of vapor pressure depression for a high-solubility salt is larger than that of a low-solubility salt (Ohe, 1991). In other words, a salt effect is closely connected with the relative volatility change among the components in the mixture (Kumagae, 1992). In this paper, the component with the lower boiling point is designated solvent 1 and the higher one is solvent 2. The salt effect is defined as the ratio of relative volatility (α_s/α) of solvent 1 to solvent 2, where α_s and α are the relative volatility with and without salt. This ratio is enhanced (salting-out) or reduced (salting-in) according to the interaction between the electrolyte and the nonelectrolyte component.

Table 6 contains the solubility of NaI in four alcohols and in water. The order of solubility of NaI is the following: water > methanol > ethanol > propan-1-ol > propan-2-ol. Thus, the degree of vapor pressure depression would be as follows: water > methanol > ethanol > propan-1-ol > propan-2-ol. In previous work, the salting-in effect was observed for many alcohol (1) + alcohol (2) binary mixtures (Yamamoto et al., 1997) while the salting-out effect was shown for the alcohol (1) + water (2) binary mixtures (Yamamoto et al., 1995a). The present VLE data of the propan-2-ol (1) + propan-1-ol (2) + NaI (3) ternary system showed a salting-out effect. Table 7 contains the comparison between the solubility ratio and the salt effect for seven binary mixtures. In the case of the salt effect of ethanol (1) + water (2) and propan-2-ol (1) +propan-1-ol (2) binary mixtures, the solubility of NaI in solvent 1 was greater than that in solvent 2, and salting-out effects were observed for these two systems.

Furthermore, as shown in Figure 2, the order of the salt effect is as follows: methanol + propan-2-ol > methanol + propan-1-ol > ethanol + propan-2-ol ≥ ethanol + propan-1-ol ≥ methanol + ethanol. This order agreed reasonably with the solubility difference of NaI between solvent 1 and solvent 2. The value of $\ln(S_2/S_1)$ shows an important trend for the salt effect on VLE of binary solvent mixtures.

Conclusion

This paper presented vapor−liquid equilibrium data for propan-2-ol + propan-1-ol + NaI at 298.15 K. The salting-out effect was observed for the propan-2-ol + propan-1-ol binary mixture. The isothermal vapor−liquid equilibrium data of the ternary system were correlated using Hála's equation. The parameters in Hála's equation were determined, and this equation could describe the experimental values with sufficient accuracy. The ratio of the solubility of NaI in solvent 1 and solvent 2 indicated the salt effect (salting-in or salting-out) on VLE of binary alcohol mixtures.

Nomenclature

E	adjustable constant for electrostatic long-range interaction
N	number of data
G^E	normalized excess Gibbs energy
G_a^E	electrostatic contribution term
G_b^E	short-range interaction term
$p°$	vapor pressure of pure component, Pa
S	solubility in mass percent
T	temperature, K
x	liquid-phase mole fraction (complete dissociation of salt is assumed)
$x°$	liquid-phase mole fraction (salt-free basis)
y	vapor-phase mole fraction
α	relative volatility
β	empirical parameter
γ	liquid-phase activity coefficient
Δ	average deviation in percent
Λ	adjustable constant for short-range interactions
π	total pressure, kPa

Subscripts

1	solvent 1 (lower boiling point)
2	solvent 2 (higher boiling point)
3	electrolyte (NaI)
i	nonelectrolyte
j	electrolyte
k,l	components k and l

Superscripts

cal	calculated value
exp	experimental value
lit	literature value

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