1066 *J. Chem. Eng. Data* **1996,** *41,* 1066−1070

Vapor−Liquid Equilibria for Alcohol + Alcohol + Sodium Iodide at 298.15 K

Hideki Yamamoto,* Koji Fukase, and Junji Shibata

Faculty of Engineering, Department of Chemical Engineering, Kansai University, Suita, Osaka, 564 Japan

Vapor−liquid equilibria for methanol + propan-1-ol + NaI, methanol + propan-2-ol + NaI, ethanol + propan-1-ol + NaI, and ethanol + propan-2-ol + NaI systems were measured at 298.15 K using a static method. The apparatus was tested by comparing results for ethanol + water and ethanol + water + $CaCl_2$ with literature results. Results were tested for thermodynamic consistency by Herinton's area test and point test. NaI exerted a salting-in effect on all binary alcohol solutions and the order of the salt effect of NaI was methanol + ethanol < ethanol + propan-1-ol < ethanol + propan-2-ol < methanol + propan-1-ol < methanol + propan-2-ol. Hála's model was applied for the correlation of four alcohol + alcohol + salt systems using observed data. Calculated β values in Hála's equation were between 2.8 and 3.9 for the four alcohol + alcohol + NaI systems.

1. Introduction

Estimation and correlation of phase equilibria data in chemical engineering are indispensable for the design of equilibrium separation processes. If a salt, being completely nonvolatile, is added to the solvent mixture, the relative volatility generally changes; this is known as the salting-in or -out effect on vapor−liquid equilibria. If the salt effect is utilized for the distillation, it is possible to separate an azeotropic mixture (Further, 1977). There are few measurements on mixtures of organic solvents with electrolytes. In the previous studies, isothermal vapor−liquid equilibria at 298.15 K were measured for ethanol + water + $CaCl_2$. The salt effects of $CaCl_2$, NH_4I, and NaI on the vapor−liquid equilibria of methanol + ethanol and ethanol + water systems at 298.15 K were also studied (Yamamoto et al., 1995a,b).

The present results were correlated using Hála's model (Hála et al., 1983), and the β values in the Hála equation for methanol + propan-1-ol, methanol + propan-2-ol, ethanol + propan-1-ol, and ethanol + propan-2-ol systems were determined. These data were compared to those for the methanol + ethanol system (Yamamoto et al., 1995a,b).

2. Experimental Section

2.1. Experimental Apparatus. The apparatus is based on a static method (Kojima, 1969; Iino et al., 1971; Lee et al., 1991). The schematic diagram is shown in Figure 1. A 500 cm^3 degassing flask was used to degas the sample. It was equipped with a water jacket for cooling and bellows valves. The equilibrium cell, which was made of Pyrex glass, had about 100 cm^3 capacity and was equipped with a water jacket to keep the mixture at a constant temperature (298.15 ± 0.05 K). The constant temperature water bath was controlled by a temperature controller within an accuracy of ±0.01 K. The temperature of the sample was measured with the standard mercury thermometer. The sample was stirred slowly by a magnetic stirrer. The temperature of the external circulating water was controlled at about 5 K higher than the temperature of the equilibrium cell to avoid the partial condensation of vapor in the pipe arrangement. A gas sampler was used for analysis of the vapor-phase composition. It consists of a six-way ball valve and a tube of about 1 cm^3 capacity. A sample of the vapor phase was introduced into the gas chromatograph directly. The line between the gas sampler and the gas chromatograph was wrapped by a ribbon heater to avoid partial condensation. It was controlled to about 5 K higher than the temperature of the equilibrium cell by the temperature controller with an accuracy of ±0.05 K. For the measurement of vapor pressure, a digital quartz manometer DG-430KH of Tokyo Aircraft Instrument Co., Ltd. was used. Its accuracy was within ±0.01% of full scale (2 MPa). A sampling flask of 30 cm^3 was used for sampling the liquid phase in the equilibrium cell. To remove air and moisture from the system, a vacuum pump was used, and its attainable degree of vacuum was 0.1 Pa. The connector lines in the experimental apparatus (Figure 1) were made of stainless steel. Its outside and inside diameters were 6.35 mm and 3.18 mm, respectively. The bellows valves were from Nupro Co., and the ball valves by Whitey Co., respectively.

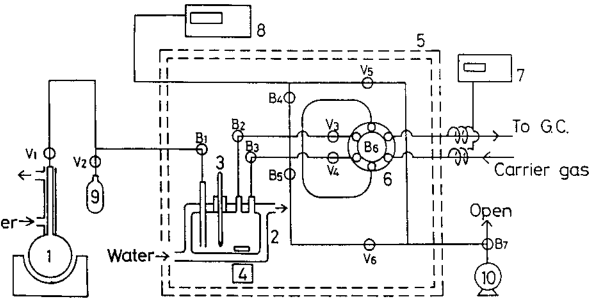

Figure 1. Schematic diagram of the experimental apparatus: (1) degassing flask; (2) equilibrium cell; (3) standard mercury thermometer; (4) magnetic stirrer; (5) constant temperature water bath; (6) gas sampler; (7) PID temperature controller; (8) digital quartz pressure gauge; (9) sampling flask; (10) vacuum pump; (B1−B5) ball valves; (V1−V6) bellows valves.

In order to analyze the liquid-phase composition in the equilibrium state using the gas chromatograph, salt and solvent must be separated. Therefore, an evaporating apparatus similar to that used by Iino et al. (1971) was consulted. The samples for vapor and liquid phases were analyzed using a gas chromatograph with a thermal conductivity detector GC-8A and an integrator C-R6A manufactured by Simazu Corp. Co., Ltd. Helium with a purity of 99.999% was used as the carrier gas, and it was provided from Sumitomo Seika Co.

2.2. Experimental Procedure. 2.2.1. Measurement of Vapor Pressure. A known mass of solvent and salt

S0021-9568(96)00096-9 CCC: $12.00

Table 1. Vapor−Liquid Equilibria of Methanol (1) + Propan-1-ol (2) at 298.15 K[a]

x_1	y_1	100δ	P/kPa
0.042	0.196	−2.96	3.41
0.153	0.535	4.33	5.10
0.304	0.731	1.44	7.25
0.351	0.778	2.05	7.87
0.434	0.824	0.37	9.16
0.541	0.886	1.03	10.65
0.605	0.908	0.53	11.62
0.723	0.947	0.57	13.21
0.878	0.980	0.16	15.42
		$100\Delta = \pm 1.46$	

[a] $\delta = \{(y_{1(\mathrm{cal}^*)} - y_{1(\mathrm{exp})}\}/y_{1(\mathrm{exp})}$. $\Delta = (1/N)\sum_{i=1}^{N}|\{(y_{1(\mathrm{cal}^*)} - y_{1(\mathrm{exp})}\}/y_{1(\mathrm{exp})}|_i$. Asterisks refer to smoothed values from Kumagae et al. (1992) using the Wilson equation.

Table 2. Vapor−Liquid Equilibria of Ethanol (1) + Propan-1-ol (2) at 298.15 K[a]

x_1	y_1	100δ	P/kPa
0.047	0.120	0.20	3.17
0.109	0.251	−0.67	3.46
0.212	0.429	0.40	3.93
0.328	0.574	−0.35	4.40
0.432	0.671	−1.32	4.96
0.553	0.767	−1.20	5.61
0.666	0.841	−0.93	6.17
0.828	0.930	−0.19	6.92
0.966	0.985	−0.28	7.59
		$100\Delta = \pm 0.62$	

[a] $\delta = \{(y_{1(\mathrm{cal}^*)} - y_{1(\mathrm{exp})}\}/y_{1(\mathrm{exp})}$. $\Delta = (1/N)\sum_{i=1}^{N}|\{(y_{1(\mathrm{cal}^*)} - y_{1(\mathrm{exp})}\}/y_{1(\mathrm{exp})}|_i$. Asterisks refer to smoothed values from Kumagae et al. (1992) using the Wilson equation.

was stirred slowly by a magnetic stirrer in the Erlenmeyer flask until the salt dissolved completely in the solvent. The sample was charged into a degassing flask and heated by a mantle heater. After the mixture was degassed by aspirator for 1 h, the degassing flask was connected to the apparatus. The experimental apparatus connecting the vapor−liquid equilibrium cell was evacuated by a vacuum pump for 1 or 2 h, and the pressure in the system was recorded. Then, the sample in the degassing flask was introduced into the equilibrium cell by the pressure difference. This sample solution was stirred slowly until it reached an equilibrium. When the temperature of the sample and pressure in the apparatus became constant, the pressure was recorded. The vapor pressure of a single solvent + salt system was obtained as the pressure difference between the initial pressure (0.1 Pa) in the apparatus and that in the equilibrium state.

2.2.2. Accuracy of Measurements. Each experiment was carried out under the condition of constant mass percent of salt. For the analysis of the vapor-phase composition, vapor in the equilibrium state was withdrawn into the gas sampler, and it was analyzed by gas chromatography. The liquid phase in the cell was introduced into a sampling flask and its mass was measured as 0.0001 g. Since the liquid phase contained a salt, the salt was separated using an evaporating apparatus. The liquid-phase composition other than the salt (salt-free basis) was analyzed by gas chromatography. And the mole fraction of salt in this liquid phase was obtained from the mass of the separated salt.

2.3. Determination of Composition. In order to obtain a calibration curve from the gas chromatograph, various compositions of methanol + ethanol were prepared, these mixtures were introduced into the gas chromatograph, and the area fraction of the peak in the gas chromatogram was measured. The accuracy for the observed calibration curves was within an average deviation of ±0.0075.

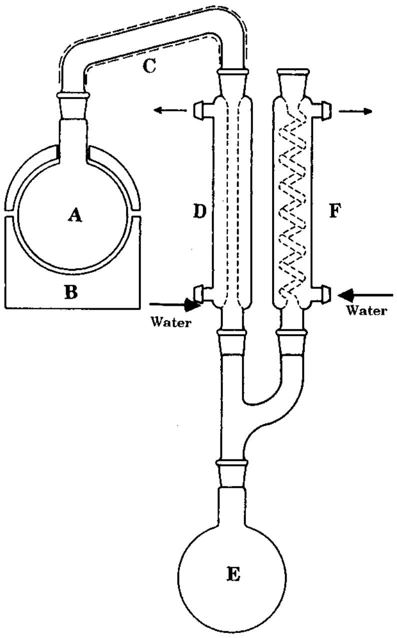

Figure 2. Schematic diagram of the evaporating apparatus for the separation of salt: (A) still; (B) mantle heater; (C) ribbon heater; (D, F) condenser; (E) vapor condensate stock chamber.

3. Materials

Methanol, ethanol, propan-1-ol, propan-2-ol, and NaI in this study were guaranteed reagents from Wako Chemicals Co., and their minimum purities were 99.8%, 99.5%, 99.5%, 99.5%, and 99.5%, respectively. Since the impurity in the alcohols was mostly water, they were dehydrated by molecular sieves 3A, $^1/_{16}$ in. A minimum purity of 99.9% was confirmed by gas chromatography. $CaCl_2$ was dried by heating at 573 K for more than 24 h. NaI was dried by heating at 353 K for 3 h.

4. Results and Discussion

4.1. Accuracy. The apparatus was checked by comparisons of vapor−liquid equilibrium measurements for ethanol + water and ethanol + water + $CaCl_2$ with literature values at 298.15 (±0.05) K (Hála, 1983). Observed data had satisfactory agreement with data from the references. Furthermore, vapor−liquid equilibria for methanol (1) + propan-1-ol (2) and ethanol (1) + propan-1-ol (2) was measured at 298.15 (±0.05) K. These results are given in Tables 1 and 2 with average deviations from litarature values. The average deviation between experiment and literature (Kumagae et al.,1992; Mishima et al., 1987) was ±1.2% in the vapor-phase mole fraction and ±1.5% in the total pressure.

4.2. Thermodynamic Consistency. The thermodynamic consistency of the results was determined using the area test of Herington's method (Herington et al., 1951; Kojima et al., 1990). The result of Herington's area test was $A = 0.028$, and the point test was $P = 0.027$. (Results are considered generally $A < 0.03$, $P < 0.05$, respectively.)

In order to check the reproducibility of the results, samples of the liquid-phase compositions (0.2, 0.4, 0.6, and 0.8 mole fraction of ethanol) were measured three times. The reproducibility was within ±1.4% for vapor-phase composition and within ±0.9% for total pressure. In view of the above results, it appears that the vapor−liquid equilibrium result obtained from this experimental apparatus should be reliable.

4.3. Evaporating Apparatus. The evaporating apparatus (Figure 2) was checked by the yield of solvents (mole fraction) and the material balance before and after

Table 3. Vapor Pressures and Activities of Solvent + NaI at 298.15 K

solvent^a	x_1	vapor pressure P/kPa	activity^b a
methanol			
$B_i = -2081$	1.000	16.96	1.000
$\nu_i^0 = 40.72$	0.990	16.77	0.989
	0.979	16.34	0.964
	0.961	15.57	0.919
	0.952	14.90	0.880
	0.935	13.62	0.803
	0.919	11.95	0.708
	0.899	10.69	0.634
ethanol			
$B_i = -2965$	1.000	7.87	1.000
$\nu_i^0 = 58.69$	0.980	7.63	0.970
	0.960	7.33	0.932
	0.943	7.08	0.901
	0.923	6.61	0.842
	0.907	6.16	0.785
	0.894	5.79	0.738
1-propanol			
$B_i = -2620$	1.000	2.81	1.000
$\nu_i^0 = 75.13$	0.980	2.73	0.972
	0.961	2.65	0.944
	0.943	2.55	0.908
	0.926	2.47	0.880
	0.915	2.39	0.852
2-propanol			
$B_i = -3294$	1.000	5.71	1.000
$\nu_i^0 = 76.89$	0.980	5.68	0.985
	0.988	5.77	0.999
	0.961	5.52	0.967
	0.944	5.39	0.945
	0.925	5.23	0.917
	0.918	5.17	0.906

[a] B_i: second virial coefficient of solvent, cm^3/mol, smoothed values from Smith et al. (1986). ν_{i}^0: saturated liquid volume of solvent, cm^3/mol, smoothed values from Smith et al. (1986). [b] Activity was calculated by eq 1.

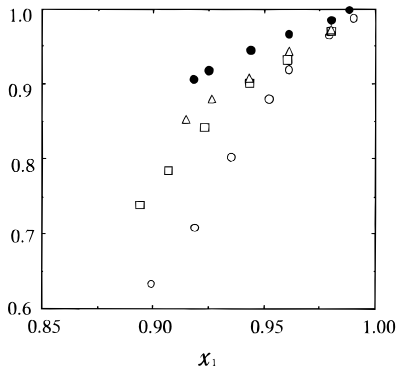

Figure 3. Activities of solvent in solvent + NaI systems at 298.15 K: (○) methanol; (□) ethanol; (△) propan-1-ol; (●) propan-2-ol.

Table 4. Vapor–Liquid Equilibria of Methanol (1) + Propan-1-ol (2) + NaI (3) at 298.15 K^a

x_1	x_3	y_1	100δ	P/kPa
0.113	0.000	0.224	8.13	6.66
0.201	0.000	0.381	−1.47	7.50
0.300	0.000	0.524	−0.07	8.54
0.344	0.000	0.581	−0.95	9.05
0.514	0.000	0.754	0.30	11.03
0.596	0.000	0.814	−0.74	12.00
0.758	0.000	0.904	−0.43	13.72
0.803	0.000	0.925	−0.70	14.46
0.935	0.000	0.979	−0.38	16.11
			$100\Delta = \pm 1.46$	

x_1°	x_3	y_1	100δ	P/kPa	γ_1	γ_2
0.084	0.143	0.301	−2.55	3.23	0.765	1.021
0.171	0.129	0.493	0.49	4.23	0.813	1.032
0.332	0.132	0.704	1.03	5.85	0.850	1.035
0.485	0.119	0.817	1.32	7.57	0.892	1.054
0.583	0.116	0.869	0.97	8.71	0.906	1.067
0.661	0.118	0.898	1.15	9.63	0.908	1.079
0.788	0.113	0.945	0.37	11.63	0.921	1.123
0.867	0.107	0.968	0.11	12.55	0.933	1.170
0.920	0.091	0.984	−0.20	13.75	0.933	1.170
			$100\Delta = \pm 0.91$			

[a] x_1° = mole fraction of salt-free base. γ is the activity coefficient using Hála's equation. $\delta = \{(y_{1(\mathrm{cal}^*)} - y_{1(\mathrm{exp})}\}/y_{1(\mathrm{exp})}$. $\Delta = (1/N) \sum_{i=1}^{N} |\{(y_{1(\mathrm{cal}^*)} - y_{1(\mathrm{exp})}\}/y_{1(\mathrm{exp})}|_i$. Asterisks refer to smoothed values from experimental values using Hála's equation ($\beta = 3.1$, $E_{13} = 37.18$, $\Lambda_{13} = 0.7882$, $E_{23} = 15.25$, $\Lambda_{23} = 0.1431$, $\Lambda_{12} = 1.8698$, $\Lambda_{21} = 0.3611$).

evaporating. A solution of fixed composition (alcohol (1) + alcohol (2) + NaI (3)) was charged into a still. After the salt was separated from the solution, the material balance and the yield of the solvents were calculated. The above operation was repeated three times. The maximum deviation of the solvents composition (mole fraction) was −0.80%, and its yield was more than 99.40%. Accordingly, it was considered that the salt and solvents were sufficiently separated.

4.4. Vapor Pressure of Single Solvent + NaI. To correlate salt effect, vapor pressure data for a single solvent (methanol, ethanol, propan-1-ol, propan-2-ol) + NaI were measured at 298.15 (±0.05) K. The activity (a_i) of the solvent could be expressed as

$$a_i = \frac{P_i}{P_i^0} \exp\left\{\frac{(B_i - \nu_i^0)(P_i - P_i^0)}{RT}\right\} \qquad i = 1, 2 \qquad (1)$$

where P_i^0 and P_i are the vapor pressure of pure component and partial pressure of component i, respectively. B_i and ν_i^0 are the second virial coefficient and saturated liquid volume; smoothed values for 298.15 K (Smith et al., 1986) were used for calculation of the activity. The vapor pressure and activity data for methanol + salt, ethanol + salt, propanol + salt, and propanol + salt systems are given in Table 3. The degree of vapor pressure lowering against molarity is given in Figure 3. The following order of vapor pressure lowering was obtained for the systems: propan-2-ol + NaI < propan-1-ol + NaI < ethanol + NaI < methanol + NaI were obtained.

4.5. Vapor–Liquid Equilibria for Alcohol (1) + Alcohol (2) + NaI (3). The vapor–liquid equilibria for methanol (1) + propan-1-ol (2) + NaI (3) (20 mass %), methanol (1) + propan-2-ol (2) + NaI (3) (20 mass%), ethanol (1) + propan-1-ol (2) + NaI (3), (20 mass %), and ethanol (1) + propan-2-ol (2) + NaI (3) (20 mass %), were measured at 298.15 (±0.05) K. The results for these systems are shown in Tables 4–7 and Figures 4–7. NaI exerted a salting-in effect on all binary systems. The order of the salt effect of NaI was methanol + ethanol < ethanol + propan-1-ol < ethanol + propan-2-ol < methanol + propan-1-ol < methanol + propan-2-ol.

4.6. Correlation of Vapor–Liquid Equilibria for Methanol (1) + Ethanol (2) + Salt (3) Using Hála's Model. Kojima et al., (1990) and Sada et al. (1973) have reported on the method of estimation and correlation for vapor–liquid equilibria in the presence of a salt. Hála (1983) proposed a semiempirical model using a value of β of $^3/_2$. For some systems, the difference between Hála's parameter and the experimental value was as much as 20% (Lee et al., 1991). Recently, Mishima (1987) proposed that β be treated as a parameter. In this work, b was treated as a parameter, and it was determined from observed data.

The excess Gibbs energy G^E of the solvent mixture containing an electrolyte can be represented by

$$G^E = G_a^E + G_b^E \qquad (2)$$

where G_a^E is the electrostatic contribution term assumed

Table 5. Vapor−Liquid Equilibria of Methanol (1) + Propan-2-ol (2) + NaI (3) at 298.15 K[a]

x_1	x_3	y_1	100δ	P/kPa
0.113	0.000	0.224	2.94	6.66
0.201	0.000	0.381	0.12	7.50
0.300	0.000	0.524	0.13	8.54
0.344	0.000	0.581	−0.13	9.05
0.514	0.000	0.754	0.04	11.03
0.596	0.000	0.814	0.54	12.00
0.758	0.000	0.904	1.16	13.72
0.803	0.000	0.925	1.08	14.46
0.935	0.000	0.979	0.37	16.11
			$100\Delta = \pm 0.72$	

x_1°	x_3	y_1	100δ	P/kPa	γ_1	γ_2
0.100	0.134	0.158	−7.65	5.75	0.552	1.058
0.219	0.129	0.332	0.05	6.46	0.636	1.054
0.308	0.127	0.450	2.72	7.10	0.688	1.045
0.387	0.124	0.546	3.76	7.70	0.730	1.034
0.485	0.115	0.654	4.01	8.64	0.785	1.018
0.580	0.115	0.738	4.34	9.48	0.822	0.993
0.691	0.104	0.827	3.61	10.74	0.875	0.959
0.805	0.106	0.897	2.95	12.11	0.906	0.912
0.921	0.086	0.957	1.85	13.86	0.958	0.852
			$100\Delta = \pm 3.44$			

[a] x_1° = mole fraction of salt-free base. γ is the activity coefficient using Hála's equation. $\delta = \{(y_{1(\mathrm{cal}*)} - y_{1(\mathrm{exp})}\}/y_{1(\mathrm{exp})}$. $\Delta = (1/N) \sum_{i=1}^{N} |\{(y_{1(\mathrm{cal}*)} - y_{1(\mathrm{exp})}\}/y_{1(\mathrm{exp})}|_i$. Asterisks refer to smoothed values from experimental values using Hála's equation ($\beta = 3.1$, $E_{13} = 37.18$, $\Lambda_{13} = 0.7882$, $E_{23} = 14.66$, $\Lambda_{23} = 0.0594$, $\Lambda_{12} = 1.4704$, $\Lambda_{21} = 0.8849$).

Table 6. Vapor−Liquid Equilibria of Ethanol (1) + Propan-1-ol (2) + NaI (3) at 298.15[a]

x_1	x_3	y_1	100δ	P/kPa
0.047	0.000	0.120	−0.20	3.17
0.109	0.000	0.251	0.68	3.46
0.212	0.000	0.429	−0.40	3.93
0.328	0.000	0.574	0.35	4.40
0.432	0.000	0.671	1.33	4.96
0.553	0.000	0.767	1.22	5.61
0.666	0.000	0.841	0.94	6.17
0.828	0.000	0.930	0.19	6.92
0.966	0.000	0.985	0.28	7.59
			$100\Delta = \pm 0.62$	

x_1°	x_3	y_1	100δ	P/kPa	γ_1	γ_2
0.071	0.139	0.147	1.99	2.76	0.848	1.027
0.201	0.134	0.374	−0.42	3.28	0.877	1.042
0.309	0.130	0.528	−2.01	3.70	0.899	1.052
0.399	0.127	0.619	−0.46	4.07	0.916	1.060
0.489	0.128	0.701	−0.22	4.40	0.928	1.067
0.599	0.124	0.785	0.22	4.97	0.945	1.074
0.705	0.119	0.857	−0.07	5.46	0.962	1.079
0.779	0.123	0.898	−0.01	5.81	0.968	1.085
0.910	0.120	0.968	−0.58	6.39	0.984	1.091
			$100\Delta = \pm 0.66$			

[a] x_1° = mole fraction of salt-free base. γ is the activity coefficient using Hála's equation. $\delta = \{(y_{1(\mathrm{cal}*)} - y_{1(\mathrm{exp})}\}/y_{1(\mathrm{exp})}$. $\Delta = (1/N) \sum_{i=1}^{N} |\{(y_{1(\mathrm{cal}*)} - y_{1(\mathrm{exp})}\}/y_{1(\mathrm{exp})}|_i$. Asterisks refer to smoothed values from experimental values using Hála's equation ($\beta = 3.9$, $E_{13} = 36.95$, $\Lambda_{13} = 0.5551$, $E_{23} = 35.19$, $\Lambda_{23} = 0.2192$, $\Lambda_{12} = 1.2084$, $\Lambda_{21} = 0.8275$).

empirically and is expressed as

$$G_{\mathrm{a}}^{\mathrm{E}} = \sum_{i} E_{ij} x_i x_j^{\beta} \tag{3}$$

i = nonelectrolyte

j = electrolyte

where E is an adjustable constant for the electrostatic long range interaction and β is the empirical parameter defined by Hála (1983).

Table 7. Vapor−Liquid Equilibria of Ethanol (1) + Propan-2-0l (2) + NaI (3) at 298.15 K[a]

x_1	x_3	y_1	100δ	P/kPa
0.136	0.000	0.159	2.51	5.96
0.243	0.000	0.284	1.64	6.04
0.430	0.000	0.489	2.03	6.29
0.497	0.000	0.553	3.13	6.43
0.619	0.000	0.682	1.66	6.62
0.684	0.000	0.744	1.43	6.77
0.832	0.000	0.871	1.18	7.22
0.923	0.000	0.942	0.76	7.51
0.958	0.000	0.968	0.52	7.71
			$100\Delta = \pm 1.65$	

x_1°	x_3	y_1	100δ	P/kPa	γ_1	γ_2
0.093	0.142	0.093	−1.12	5.16	0.768	1.061
0.249	0.137	0.258	−0.17	5.29	0.821	1.069
0.380	0.132	0.397	1.32	5.47	0.861	1.069
0.500	0.128	0.523	2.08	5.65	0.895	1.064
0.606	0.125	0.633	2.12	5.84	0.941	1.044
0.774	0.125	0.796	2.01	6.16	0.957	1.031
0.847	0.117	0.864	1.73	6.40	0.975	1.013
0.946	0.116	0.954	0.59	6.71	0.990	0.987
			$100\Delta = \pm 1.51$			

[a] x_1° = mole fraction of salt-free base. γ is the activity coefficient using Hála's equation. $\delta = \{(y_{1(\mathrm{cal}*)} - y_{1(\mathrm{exp})}\}/y_{1(\mathrm{exp})}$. $\Delta = (1/N) \sum_{i=1}^{N} |\{(y_{1(\mathrm{cal}*)} - y_{1(\mathrm{exp})}\}/y_{1(\mathrm{exp})}|_i$. Asterisks refer to smoothed values from experimental values using Hála's equation ($\beta = 3.7$, $E_{13} = 34.61$, $\Lambda_{13} = 0.3820$, $E_{23} = 31.34$, $\Lambda_{23} = 0.0735$, $\Lambda_{12} = 1.7055$, $\Lambda_{21} = 0.5863$).

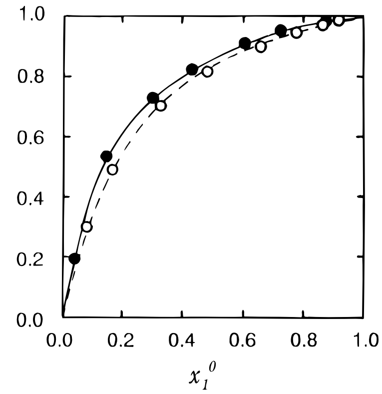

Figure 4. Vapor−liquid equilibria of methanol (1) + propan-1-ol (2) +NaI (3) at 298.15 K: (●) no salt; (○) NaI.

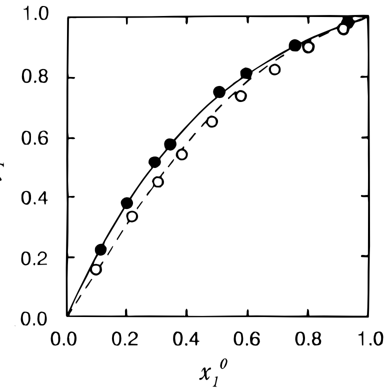

Figure 5. Vapor−liquid equilibria of methanol (1) + propan-2-ol (2) + NaI (3) at 298.15 K: (●) no salt; (○) NaI.

$G_{\mathrm{b}}^{\mathrm{E}}$ is the interaction term and is expressed by use of Wilson's equation as follows:

$$G_{\mathrm{b}}^{\mathrm{E}} = -\sum_{k} \ln\left(\sum_{i} x_i \Lambda_{kl}\right) \tag{4}$$

k, l = component k and l

where L is an adjustable constant for the short range

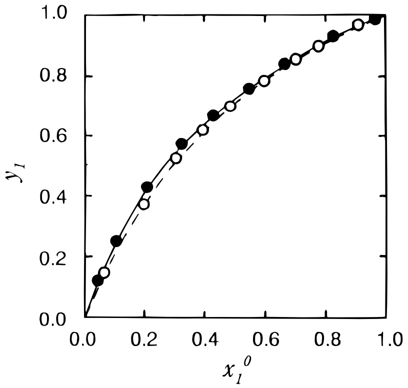

Figure 6. Vapor−liquid equilibria of ethanol (1) + propan-1-ol (2) + NaI (3) at 298.15 K: (●) no salt: (○) NaI.

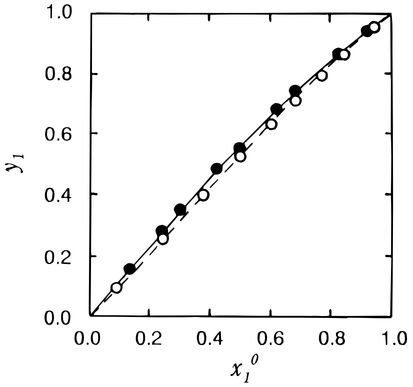

Figure 7. Vapor−liquid equilibria of ethanol (1) + propan-2-ol (2) + NaI (3) at 298.15 K: (●) no salt; (○) NaI.

interaction, x_i is the mole fraction of component i assuming complete dissociation of salt in the liquid, and $\beta = {}^3/_2$ as in the original description by Hála. Wilson parameters including a salt are assumed as

$$\Lambda_{i3} = \Lambda_{3i} \qquad i = 1, 2 \tag{5}$$

The approach has only been tested for alcohol + water and alcohol + alcohol systems with $CaCl_2$. The results of the above correlation are shown in Figures 4−7 by the dotted line. The parameters and the accuracies of correlation for each system are given in Table 8. The equation could reproduce the experimental data within 3.44% (average deviation) in the vapor phase for the four systems. Therefore, it is considered that the Hála model can correlate the vapor−liquid equilibria for four alcohol + alcohol systems with NaI as well as $CaCl_2$ with sufficient accuracy.

Table 8. Parameters for Correlation of Vapor−Liquid Equilibria for Alcohol + Alcohol + NaI Using Hála's Equation

solvents	parameters	mass % of salt	av deviation[a]
methanol + propan-1-ol	$\beta^b = 3.1$		
	$E_{13} = 37.18$, $E_{23} = 15.25$	0	±1.46
	$\Lambda_{12} = 1.8698$, $\Lambda_{21} = 0.3611$		
	$\Lambda_{13} = 0.7882$, $\Lambda_{23} = 0.1431$	20	±0.91
methanol + propan-2-ol	$\beta^b = 3.1$		
	$E_{13} = 37.18$, $E_{23} = 14.66$	0	±0.72
	$\Lambda_{12} = 1.4704$, $\Lambda_{21} = 0.8849$		
	$\Lambda_{13} = 0.7882$, $\Lambda_{23} = 0.0594$	20	±3.44
ethanol + propan-1-ol	$\beta^b = 3.9$		
	$E_{13} = 36.95$, $E_{23} = 35.19$	0	±0.62
	$\Lambda_{12} = 1.2084$, $\Lambda_{21} = 0.8275$		
	$\Lambda_{13} = 0.5551$, $\Lambda_{23} = 0.2192$	20	±0.67
ethanol + propan-2-ol	$\beta^b = 3.7$		
	$E_{13} = 34.61$, $E_{23} = 31.34$	0	±1.65
	$\Lambda_{12} = 1.7055$, $\Lambda_{21} = 0.5863$		
	$\Lambda_{13} = 0.3820$, $\Lambda_{23} = 0.0735$	20	±1.51
methanol + ethanol[c]	$\beta^b = 2.8$		
	$E_{13} = 31.56$, $E_{23} = 19.68$	0	±2.12
	$\Lambda_{12} = 1.7149$, $\Lambda_{21} = 0.4566$		
	$\Lambda_{13} = 0.2750$, $\Lambda_{23} = 0.08431$	20	±0.59

[a] $\pm(1/N)|\{(y_{1(\mathrm{cal})} - y_{1(\mathrm{exp}^*)}\}/y_{1(\mathrm{exp})}| \times 100$. The asterisk refers to smoothed values. [b] Optimized values by vapor−liquid equilibria of ternary system. [c] Yamamoto et al. (1995a).

Literature Cited

Further, W. F. Salt Effect in Distillation: Literature Review II. *Can. J. Chem. Eng.* **1977**, *55*, 229−239.

Hála, E. Vapor-Liquid Equilibrium of Electrolytes in Systems Containing Mixed Solvent. *Fluid Phase Equilib.* **1983**, *13*, 311−319.

Hála, E.; Pick, J.; Fried, V.; Vilim, O. *Vapor-Liquid Equilibrium*, 2nd ed.; Pergamon Press: Oxford, U.K., 1967; 312−315.

Herington, E. F. G. Tests for The Consistency of Experimental Isobaric Vapor-Liquid Equilibrium Data *J. Inst. Petrol.* **1951**, *37*, 457- 470.

Iino, M.; Nakae, N.; Sudoh, J.; Hirose, Y. Separation of Isopropyl Alcohol-Water Azeotropic Mixture by Salting Out. *Kagaku Kogaku* **1971**, *35*, 1017−1021.

Kojima, K. Experimental Apparatus for Measurement of Vapor-Liquid Equilibrium. *Kagaku Kogaku* **1969**, *33*, 1201−1204.

Kojima, K.; Moon, H.; Ochi, K. Thermodynamic Consistency Test of Vapor-Liquid Equilibrium Data. *Fluid phase Equilib.* **1990**, *56*, 269−284.

Kumagae, Y.; Mishima, K.; Hongo, K.; Kusunoki, K.; Arai, Y. Effect of Calcium Chloride on Vapor-Liquid Equilibria of Alcohol-Alcohol and Alcohol-Water Binary Systems. *Can. J. Chem. Eng.* **1992**, *70*, 1181−1183.

Lee, L. S.; Tsao, Y. Z.; Yang, B. L. M. Improving Prediction of the Salt Effect on VLE of Isopropyl Alcohol-Water-Salt and Methanol-Water-Salt Systems with Perferential Association. *Can. J. Chem. Eng.* **1991**, *69*, 788−793.

Mishima, K.; Matsubara, K.; Arai, Y.; Hongo, M. Measurement and Correlation of Vapor-Liquid Equilibria of Ethanol-Water-Calcium Chloride and Methanol-Ethanol-Calcium Chloride Systems. *Kagaku Kogaku Ronbunshu* **1987**, *13*, 850−853.

Sada, E.; Kito, S.; Morisue, T. Salt Effect for Vapor-Liquid Equilibrium. *Kagaku Kogaku* **1973**, *37*, 983−986.

Smith, B. D.; Srivastava, R *Physical Science Data 25, Thermodynamic Data for Pure Compounds Part B. -halogenated hydrocarbons and alcohols*; Elsevier: New York, 1986; pp 282−285.

Yamamoto H.; Terano, T.; Nishi, Y.; Tokunaga, J. Vapor-Liquid Equilibria for Methanol+Ethanol+Calcium Chloride, +Ammonium Iodide and +Sodium Iodide at 298.15 K. *J. Chem. Eng. Data* **1995a**, *40*, 2, 472−477.

Yamamoto H.; Terano, T.; Tokunag, T. Salt effect of $CaCl_2$, NH_4I and on Vapor-Liquid Equilibrium of Ethanol + Water System at 298.15 K. *Can. J. Chem. Eng.* **1995**, *73*, 779−783.

Received for review March 11, 1996. Accepted June 24, 1996.[⊗]

JE9600966

[⊗] Abstract published in *Advance ACS Abstracts*, August 1, 1996.