472 J. Chem. Eng. Data **1995**, *40*, 472–477

Vapor–Liquid Equilibria for Methanol + Ethanol + Calcium Chloride, + Ammonium Iodide, and + Sodium Iodide at 298.15 K

Hideki Yamamoto,* Tamotsu Terano, Yasuharu Nishi, and Junji Tokunaga

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

Vapor–liquid equilibria for methanol + ethanol + $CaCl_2$, + NH_4I, and + NaI were measured at 298.15 ± 0.05 K using a static method. The data obtained in this apparatus were confirmed by comparison with the literature data of ethanol + water and ethanol + water + $CaCl_2$ and tested for thermodynamic consistency. Any salt used in this work exerted salting-in effect on the methanol + ethanol system, the magnitude of which was $CaCl_2 > NaI > NH_4I$. The observed data were correlated by use of Hála's equation, and β was determined for each system. The calculated result of each system reproduced experimental data within an accuracy of ±2.12% in vapor-phase mole fraction. From the results of comparison of β obtained in this work with the kind of salt additive for methanol + ethanol and ethanol + water systems, it was found that β depended mainly on the kind of salt but not on the kind of solvent mixture. The application of Hála's model for an alcohol + alcohol + salt system was confirmed at a temperature of 298.15 K.

1. Introduction

Data of phase equilibria in chemical engineering are indispensable for the design of equilibrium separation processes such as distillation, absorption, extraction, or crystallization. Recently, an alternative extractive distillation using a salt as extractive solvent has attracted attention. 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. As a result, the azeotropic point is shifted or eliminated, when the salt-free mixture has an azeotropic point. Furthermore, if the salt effect is utilized for the distillation, it is possible to separate an azeotropic mixture (*1*).

This is one reason research for salt effect has been undertaken. In comparison with vapor–liquid equilibria for nonelectrolyte systems, those for systems containing electrolytes are still insufficient from the standpoint of theoretical analysis. Also, the investigation of the kind of salts has been limited. Furthermore, a mathematical model for vapor–liquid equilibria in the presence of salt has been less established than for nonelectrolyte, because of the complex behavior of electrolytes.

In this study, to check the consistency of the experimental apparatus based on the static method, 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 at 298.15 K are examined experimentally.

The present data of vapor–liquid equilibria were correlated using Hála's model (*2*), and β values in Hála's equation for methanol + ethanol + salt were determined.

2. Experimental Section

2.1. Experimental Apparatus. The apparatus based on a static method (*3, 4*) was manufactured in our laboratory for the measurement of vapor–liquid equilibria. A schematic diagram for the experimental apparatus 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 a bellows valve. The equilibrium cell, which was made of Pyrex glass, has about 100 cm^3 capacity, and it was equipped with a water jacket to keep the mixture at constant temperature (298.15 ± 0.05 K). The constant-temperature water bath was controlled by PID controller within an accuracy of ±0.01 K. The temperature of the sample was measured with a standard mercury thermometer. 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 equilibrium to avoid partial condensation of vapor in the pipe arrangement. A gas sampler was used for analysis of vapor-phase composition. It consists of a six-way ball valve and a tube of about 1 cm^3 capacity. A vapor phase was introduced into the gas chromatograph directly. The line between the gas sampler and gas chromatograph was wrapped by a ribbon heater to avoid partial condensation. It was controlled at about 5 K higher than the temperature of the equilibrium cell by the PID controller with an accuracy of ±0.05 K. For measurement of the vapor pressure, the digital quartz manometer DG-430KH of Tokyo Aircraft Instrument Co., Ltd., was used in this experiment, and its accuracy was within ±0.01% of full scale (2 MPa). Then, a sampling flask of 30 cm^3 capacity was used for sampling of the liquid phase in the equilibrium cell. To remove air and moisture from the system, the vacuum pump was used, and its attainable degree of vacuum was 0.1 Pa. The pipe arrangement of the experimental apparatus (Figure 1) was made of stainless steel, and the outside and inside diameters were 6.35 and 3.18 mm, respectively. A clamping joint of metal ferrule manufactured by Nupro Co. was used in this apparatus. As for the valve arrangements, the bellows valve was supplied by Nupro Co. and the ball valve by Whitey Co.

To analyze the liquid-phase composition in equilibrium state using the gas chromatograph, salt and solvent must be separated from the liquid phase. Therefore, an evaporating apparatus similar to that devised by Iino et al. (*5*) was newly manufactured for this purpose. A schematic diagram is shown in Figure 2. The samples for vapor and liquid phases were analyzed using gas chromatography with thermal conductivity detector GC-8A and integrator C-R6A manufactured by Simadzu Corp. Co., Ltd. Helium with a purity of 99.999% was used as carrier gas, and it was provided from Sumitomo Seika Co. The operating

0021-9568/95/1740-0472$09.00/0

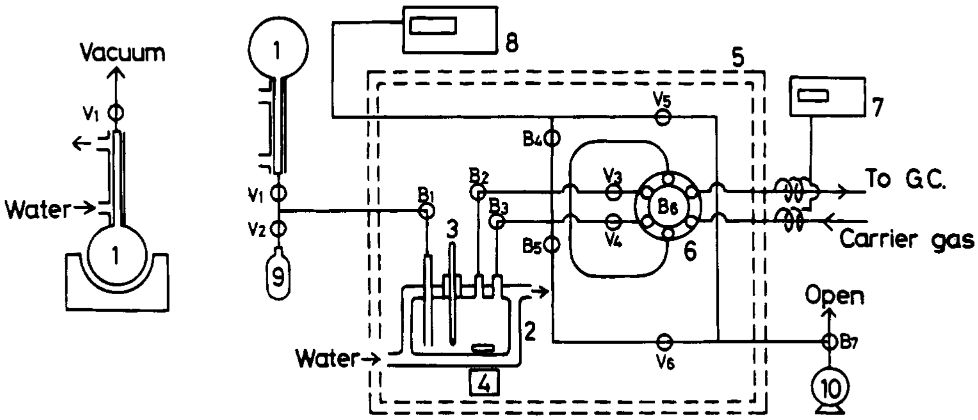

Figure 1. Schematic diagram of the experimental apparatus: 1, degassing flask; 2, equilibrium cell; 3, standard mercury thermometer; 4, magnetic stirrer; 5, constant temperature water bath; 6, gas sampler; 7, PID temperature controller; 8, digital quartz pressure gauge; 9, sampling flask; 10, vacuum pump; B_1–B_5, ball valve; V_1–V_6, bellows valve.

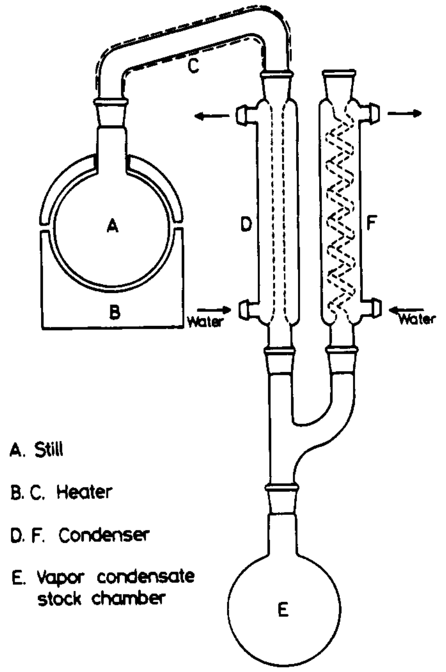

Figure 2. Schematic diagram of the evaporating apparatus for separation of salt.

Table 1. Operating Conditions of the Gas Chromatograph

column	SUS i.d. 3 mm × 2 m
packing	Gaskuropack 54 60/80
carrier gas	He (30 mL/min)
sample size	0.6 μL
injection/detector temp	493 K
column temp	393 K
current	90 mA

conditions of the gas chromatograph are given in Table 1.

2.2. Experimental Procedures. 2.2.1. Measurement of Vapor Pressure for Single Solvent + Salt. A weighed solvent and salt were stirred slowly by a magnetic stirrer in the Erlenmeyer flask until the salt dissolved completely in the solvent. The sample was charged in a degassing flask being heated by mantle heater. After the mixture was degassed by aspirator for 1 h, the degassing flask was installed in a fixed position of the apparatus. The experimental apparatus connecting the vapor–liquid equilibrium cell was evacuated by vacuum pump for 1 or 2 h, and the pressure in the system was recorded. Then, the sample in the degassing flask was introduced to the cell. This sample solution was stirred slowly to reach an equilibrium state. When the temperature of the sample and the pressure in the apparatus became constant, the sample was regarded as in equilibrium state and the pressure was recorded. The vapor pressure of a single solvent + salt system was obtained as the pressure difference between initial pressure in the apparatus and that in equilibrium state.

2.2.2. Accuracy of Vapor–Liquid Equilibria Measurement. Each experiment was carried out under the condition of constant mass percent of salt. In the subsequent operation, vapor pressure was measured by the method described under 2.2.1.

For the analysis of the vapor-phase composition, vapor in equilibrium state was withdrawn into the gas sampler, and it was analyzed by gas chromatography. On the other hand, liquid phase in the cell was introduced into a sampling flask and its weight was measured exactly. Since the liquid phase contained a salt, the salt was completely separated using an evaporating apparatus (Figure 2). The liquid-phase composition other than salt (salt-free basis) was analyzed by gas chromatography. The mole fraction of salt in this liquid phase was also obtained from the weight of separated salt.

2.3. Determination of Composition. To obtain the calibration curve, 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 obtained. The obtained mole fraction (x) and area fraction(s) were interpolated using a fifth-order function as follows:

$$x = 1.370(s - s^5) - 0.865(s^2 - s^5) + 1.290(s^3 - s^5) - 1.314(s^4 - s^5) + s^5 \quad (1)$$

The observed data were fitted to pass through two points, (0,0) and (1,1). Accuracy for this calibration curve was within an average deviation of ±1.06%. Each composition obtained in this work was determined by interpolation of the calibration curve (eq 1).

3. Materials

Methanol, ethanol, $CaCl_2$, NH_4I, and NaI in this study were guaranteed reagents from Wako Chemicals Co., and their minimum purities were 99.8%, 99.5%, 99.0%, 99.5%, and 99.5%, respectively. Since the impurity in methanol or ethanol was water, it was dehydrated by 3A molecular sieves, $^1/_{16}$ inch, and then minimum purities 99.9% were confirmed by gas chromatography. For the purpose of removing of moisture contained in the salt, $CaCl_2$ was dried

Table 2. Vapor–Liquid Equilibria of Ethanol (1) + Water (2) at 298.15 K

mole fraction				
liquid phase	vapor-phase		total pressure	
x_1	y_1	$100\ \delta^a{}_{y_1/y_1}$	p/(kPa)	$100\ \delta^b\ p/p$
0.063	0.365	0.55	4.56	−2.98
0.115	0.486	3.85	5.51	1.47
0.205	0.581	4.12	6.37	3.24
0.291	0.614	1.15	6.67	0.91
0.327	0.633	1.61	6.81	0.89
0.424	0.662	0.00	7.08	0.28
0.495	0.679	−1.45	7.27	0.28
0.650	0.752	−0.13	7.49	−1.45
0.701	0.785	1.03	7.63	−0.78
0.838	0.867	1.17	7.81	−0.76
0.973	0.971	0.00	7.87	−0.25
		$100\Delta^c = \pm 1.37$		$100\Delta\delta = \pm 1.21$

[a] $\delta_{y_1} = (y_1^{\text{exptl}} - y_1^{\text{calcd*}})$. [b] $\delta_p = (p^{\text{exptl}} - p^{\text{calcd*}})$. [c] $\Delta = (1/N)\text{-}\sum_{i=1}^{N}|[(\text{exptl}) - (\text{calcd*})]/(\text{calcd*})]$. *, Smoothed values from Hall et al. using the Wilson equation (Wilson parameter: $\Lambda_{12} = 0.2805$, $\Lambda_{21} = 0.7264$).

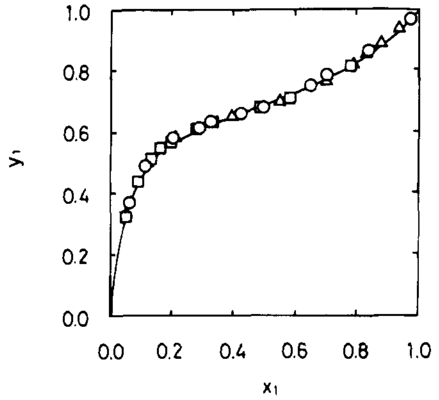

Figure 3. Vapor–liquid equilibria of ethanol (1) + water (2) at 298.15 K: ○, present work; □, Dobson (*10*); △, Hall (*11*); −, smoothed value by Wilson's equation using observed data.

by heating at 573 K for more than 24 h. NH_4I and NaI were dried by heating at 353 K for 3 h. Water was purified by use of Milli-Q Labo manufactured by Millipore Ltd., after distillation and ion exchange.

4. Results and Discussion

4.1. Consistency of Experimental Apparatus. The consistency of the experimental apparatus for vapor pressure measurement was already checked by comparisons of vapor pressures of pure components (methanol, ethanol, 1-propanol, 2-propanol, and water) with literature values at 298.15 (±0.05) K. Observed vapor pressure had satisfactory agreement with data from the refs 6−9 within an accuracy of ±1.5%. The reproducibility was within ±0.6%.

To check the consistency of the experimental apparatus used in this work, vapor–liquid equilibria for ethanol (1) + water (2) was measured at 298.15 (±0.05) K. The experimental data for ethanol + water are given in Table 2 and shown in Figure 3, where they are compared with the literature data (*10*, *11*). The average deviation between experimental and literature value was ±1.37% in vapor-phase mole fraction and ±1.21% in total pressure. Thermodynamic consistency of the data was ascertained by the area test of Herington's method (*12*, *13*). The result of Herington's area test was $A = 0.028$, and the point test was $P = 0.027$ (consistency tests of data were generally $A < 0.03$, $P < 0.05$, respectively).

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

Table 3. Accuracy of Separation of Ethanol (1) + Water (2) Containing $CaCl_2$ using Evaporating Apparatus

mole fraction of ethanol			
$x_1{}^{*1a}$	$x_1{}^{*2b}$	$100\delta_{x_1/x_1}{}^c$	yield of solvent
0.486	0.482	−0.82	99.33
	0.483	−0.62	99.36
	0.482	−0.82	99.54

[a] Mole fraction of ethanol determined before salt mixing. [b] Mole fraction of ethanol determined after separation using the evaporating apparatus. [c] $\delta_{x_1} = x_1{}^{*2} - x_1{}^{*1}$.

4.2. Consistency of Evaporating Apparatus. The consistency of the evaporating apparatus (Figure 2) was checked by yield of solvents (mole fraction) and material balance before and after evaporating. The solution of fixed composition (ethanol (1) + water (2) + $CaCl_2$ (3)) was charged into a still. After salt was separated from the solution, material balance and yield of the solvents were calculated. The above operation was repeated three times. The results are given in Table 3. For ethanol (1) + water (2) + $CaCl_2$ (3), maximum deviation of solvent composition (mole fraction) was −0.82%, and its yield was more than 99.3%. Accordingly, it was considered that salt and solvents were sufficiently separated from solution.

4.3. Vapor Pressure of Single Solvent + Salt. To correlate salt effect, vapor pressure data for single solvent (methanol or ethanol) + salt ($CaCl_2$, NH_4I, or NaI) were measured at 298.15 (±0.05) K. Activity (a_i) of the solvent could be expressed as

$$a_i = p_i/p_i^0 \qquad i = 1, 2 \tag{2}$$

where p_i^0 and p_i are the vapor pressure of pure component and the partial pressure of component i, respectively. The vapor pressure and activity data for the methanol + salt ethanol + salt systems are given in Tables 4 and 5. As for the degree of vapor pressure lowering against molarity, it was found that ethanol + NaI was the largest among ethanol + salt, and there was not much difference between ethanol + NH_4I and ethanol + $CaCl_2$.

The order of vapor pressure lowering for methanol + salt was methanol + $CaCl_2$ > methanol + NaI > methanol + NH_4I.

4.4. Vapor–Liquid Equilibria for Methanol (1) + Ethanol (2) + Salt (3). To check the reliability of the apparatus for the measurement of salt effect, the vapor–liquid equilibria for ethanol (1) + water (2) with 5 mass % $CaCl_2$, as already reported, was measured at 298.15 (±0.05) K. Table 6 gives the obtained experimental data. These data are also shown in Figure 4, where they are compared with the literature data (*14*). As shown in Table 6, the average deviation of these experimental data was within ±1.6% in vapor-phase composition from the literature data. It was considered that this experimenal apparatus was reliable for the measurement of salt effect.

In turn, the vapor–liquid equilibria for the methanol (1) + ethanol (2) + $CaCl_2$ (3) (10 mass %), methanol (1) + ethanol (2) + NH_4I (3) (20 mass %), and methanol (1) + ethanol (2) + NaI (3) (20 mass %) systems were newly measured at 298.15 (±0.05) K. The mole fraction (x_3) of NH_4I and NaI were 0.09−0.13, similar to that of $CaCl_2$ (10 mass %). The experimental data for these systems are

Table 4. Vapor Pressures and Activities of Methanol (1) + Salt (3) at 298.15 K

system	molality m_3/(mol·kg^{-1})	vapor pressure p_1/(kPa)	activity a_1
methanol + $CaCl_2$	0.328	16.62	0.980
	0.450	16.54	0.975
	0.551	16.41	0.968
	0.725	16.17	0.954
	0.914	15.77	0.930
	1.262	15.17	0.895
	1.493	14.73	0.869
	1.793	14.03	0.827
	1.862	13.91	0.820
	2.258	13.24	0.781
methanol + NaI	0.316	16.77	0.989
	0.663	16.34	0.964
	1.255	15.57	0.919
	1.586	14.90	0.879
	2.159	13.62	0.803
	2.753	11.95	0.705
	3.404	10.69	0.630
methanol + NH_4I	0.346	16.72	0.986
	0.675	16.42	0.968
	0.943	16.12	0.951
	1.296	15.77	0.930
	1.639	15.24	0.899
	2.337	14.39	0.849
	2.757	13.96	0.823

Table 5. Vapor Pressures and Activities of Ethanol (2) + Salt (3) at 298.15 K

system	molality m_3/(mol·kg^{-1})	vapor pressure p_2/(kPa)	activity a_2
ethanol + $CaCl_2$	0.311	7.73	0.983
	0.740	7.57	0.962
	0.916	7.43	0.944
	1.179	7.32	0.930
	1.525	7.01	0.891
	1.879	6.77	0.861
ethanol + NaI	0.448	7.63	0.970
	0.908	7.33	0.932
	1.320	7.08	0.900
	1.555	6.68	0.849
	1.778	6.28	0.798
	2.221	5.87	0.746
ethanol + NH_4I	0.299	7.77	0.988
	0.606	7.59	0.965
	0.910	7.43	0.944
	1.227	7.24	0.920
	1.519	7.01	0.891

shown in Table 7. The vapor–liquid equilibria for all systems show a salting-in effect, and their magnitude of salt effect was $CaCl_2$ > NaI > NH_4I.

4.5. *Correlation of Vapor–Liquid Equilibria for Methanol (1) + Ethanol (2) + Salt (3) Using Hála's Model.* Some methods (*15*) of estimation and correlation for vapor–liquid equilibria in the system in the presence of a salt were already reported. Hála (*2*) proposed the semiempirical model and equation by a comparatively simple method and gave better results for estimation. However, in this application for some systems, the deviation from the observed data was as much as about 20% (*16*). β in Hála's equation is treated as a constant value (β = 1.5). Recently, Misima (*14*) proposed that if β were treated as a parameter, Hála's equation would be applicable for many systems. In this work, β was treated as a parameter, and it was determined from observed data.

The excess Gibbs energy Q of solvent mixtures containing electrolytes is represented as

$$Q = Q_a + Q_b \tag{3}$$

Table 6. Vapor–Liquid Equilibria of Ethanol (1) + Water (2) + $CaCl_2$ (3) at 298.15 K

mole fraction				
liquid phase		vapor phase		total pressure
x_1^0	x_3	y_1	$100\delta^a_{y_1/y_1}$	p/(kPa)
0.064	0.025	0.386	−1.78	4.94
0.131	0.029	0.537	2.29	6.00
0.218	0.032	0.616	1.82	6.60
0.318	0.036	0.671	1.51	6.96
0.447	0.040	0.717	0.28	7.24
0.648	0.049	0.786	−1.63	7.51
0.756	0.050	0.827	−3.16	7.61
0.862	0.055	0.913	−0.54	7.68
0.927	0.058	0.947	−1.46	7.72
			$100\Delta^b = \pm 1.61$	

[a] $\delta_{y_1} = (y_1^{\text{exptl}} - y_1^{\text{calcd}})$. [b] $\Delta = (1/N)\sum_{i=1}^{N}|(y_1^{\text{exptl}} - y_1^{\text{calcd*}})/y_1^{\text{calcd*}}|$. *, Smoothed values from Mishima et al. using Hala's equation ($\beta = 3.9$, $E_{13} = 18.0$, $\Lambda_{13} = 0.0677$, $E_{23} = 54.2$, $\Lambda_{23} = 3.22$, $\Lambda_{12} = 0.294$, $\Lambda_{21} = 0.644$).

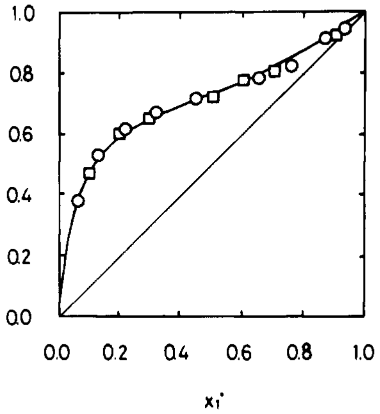

Figure 4. Vapor–liquid equilibria of ethanol (1) + water (2) + $CaCl_2$ (3) at 298.15 K: ○, present work; □, Mishima (*14*); —, smoothed value by Hála's equation using observed data; x_i^0, mole fraction on a salt-free basis.

where Q_a is the electrostatic contribution term assumed empirically and is expressed as

$$Q_a = \sum_i E_{ij} x_i x_j^{\beta} \tag{4}$$

where E is an adjustable constant for electrostatic long-range interaction, β is an empirical parameter defined by Hála (*2*), and i and j represent nonelectrolyte and electrolyte, respectively.

Q_b is the interaction term and is expressed by use of Wilson's equation as

$$Q_b = -\sum_k x_k \ln(\sum_l x_l \Lambda_{kl}) \tag{5}$$

where Λ is an adjustable constant for short-range interaction, x is mole fraction in the case that complete dissociation of salt in liquid is assumed, and β is 1.5 as in the original description by Hála. k and l represent components. However, β was treated as a parameter in this work. For simplification, Wilson parameters including a salt are assumed as

$$\Lambda_{i3} = \Lambda_{3i} \qquad i = 1, 2 \tag{6}$$

Only for alcohol + water and alcohol + alcohol systems with added $CaCl_2$ has its application been confirmed so far (*14*). It has not been reported yet for the system with other added salts. In this study, isothermal vapor–liquid equi-

Table 7. Vapor–Liquid Equilibria of Methanol (1) + Ethanol (2) + Salt (3) at 298.15 K

	mole fraction				
	liquid-phase		vapor-phase		total pressure
salt	x_1^0	x_3	y_1	$100\delta^a{}_{y_1/y_1}$	p/(kPa)
$CaCl_2$	0.116	0.117	0.199	−0.13	8.38
	0.246	0.129	0.389	0.78	9.20
	0.398	0.127	0.543	−3.78	10.32
	0.491	0.109	0.656	0.01	11.20
	0.613	0.108	0.752	−0.79	12.22
	0.729	0.089	0.836	−0.20	13.24
	0.842	0.103	0.909	−0.30	14.49
	0.918	0.104	0.956	0.09	15.04
NaI	0.161	0.136	0.275	−0.48	7.87
	0.255	0.108	0.406	−0.10	8.79
	0.338	0.102	0.502	−1.15	9.54
	0.477	0.111	0.646	−0.47	10.51
	0.593	0.099	0.752	0.54	11.68
	0.708	0.110	0.833	0.30	12.38
	0.838	0.104	0.923	1.26	13.67
	0.930	0.098	0.962	−0.11	14.50
NH_4I	0.085	0.110	0.170	10.95	7.82
	0.181	0.107	0.302	0.22	8.51
	0.278	0.104	0.416	−3.75	9.19
	0.377	0.099	0.545	−0.16	10.09
	0.487	0.097	0.656	0.11	10.78
	0.621	0.094	0.758	−1.18	12.03
	0.740	0.093	0.851	0.12	13.18
	0.854	0.088	0.940	2.15	14.34
	0.948	0.082	0.977	0.46	15.28

[a] $\delta_{y_1} = (y_1^{exptl} - y_1^{calcd})$. *, Smoothed values from experimental values using Hála's equation.

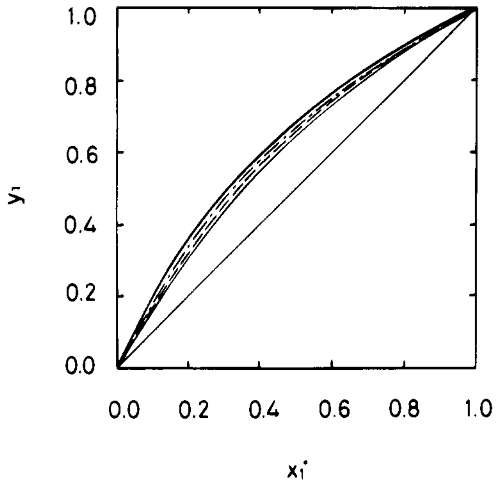

Figure 5. Correlation of salt effect of $CaCl_2$, NH_4I, and NaI on vapor–liquid equilibria of methanol (1) + ethanol (2) at 298.15 K by Hála's model: thick line, no salt; —, $CaCl_2$; – – –, NaI; – - –, NH_4I; x_i^0, mole fraction on a salt-free basis.

libria were measured for the methanol + ethanol system with not only $CaCl_2$ added but also NH_4I or NaI, and the application of Hála's model was investigated. The results of correlation are shown in Figure 5. The parameters and the accuracies of correlation for each system are given in Table 8. The calculated results could reproduce the experimental data within ±2.1% (average deviation) in the vapor phase for these three systems. Therefore, it is considered that Hála's model can correlate the vapor–liquid equilibria for the methanol + ethanol system with added NH_4I or NaI as well as $CaCl_2$ with sufficient accuracy.

However, it appears that Hála's model is neither the simplest nor the most applicable model, since data reduction and determination of parameters require much time on the correlation analysis for one system. If β was predicted by any method, the vapor–liquid equilibria of a ternary system could be estimated by use of the data of binary systems only, as ternary systems include a binary one.

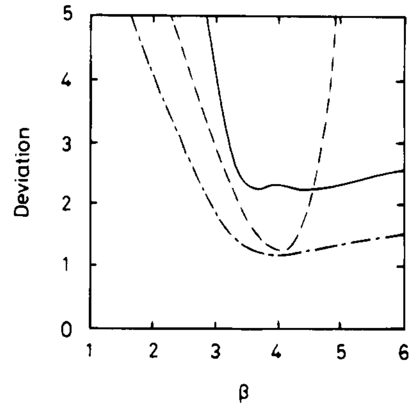

Figure 6. Relation between β value and accuracy of Hála's model for solvent + solvent + $CaCl_2$: —, ethanol (1) + water (2) + $CaCl_2$ (3); – – –, methanol (1) + ethanol (2) + $CaCl_2$ (3); – - –, methanol (1) + water (2) + $CaCl_2$ (3). Deviation = $(1/N)\Sigma|(y_1^{exptl} - y_1^{calcd})/y_1^{calcd}|$.

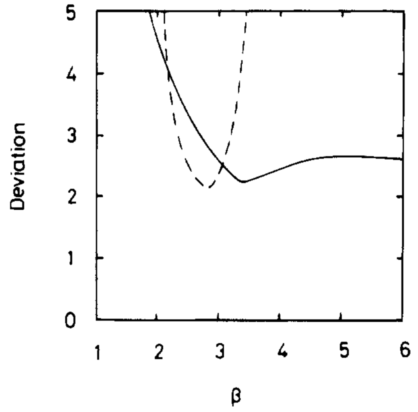

Figure 7. Relation between β value and accuracy of Hála's model for solvent + solvent + NH_4I: —, ethanol (1) + water (2) + NH_4I (3); – – –, methanol (1) + ethanol (2) + NH_4I (3). Deviation = $(1/N)\Sigma|(y_1^{exptl} - y_1^{calcd})/y_1^{calcd}|$.

To predict β value, β vs accuracy of correlation for a ternary system is plotted. Figure 6 shows the relation of β value and deviation for ethanol (1) + water (2), methanol (1) + ethanol (2), and methanol (1) + water (2) (*14*) containing $CaCl_2$. In Figure 6, the β value for each system is the same. Furthermore, Figures 7 and 8 show the deviation plots for methanol (1) + ethanol (2) and ethanol (1) + water (2) in the presence of NH_4I and NaI, in which the same tendency is observed. It was found that β value mainly depended on the kind of salt, not on the kind of solvent mixture. There is a possibility to estimate salt effect on vapor–liquid equilibria for other solution systems containing salt.

5. Conclusion

Salt effect on vapor–liquid equilibria for methanol (1) + ethanol (2) was measured at 298.15 (±0.05) K using the experimental apparatus based on a static method. $CaCl_2$, NH_4I, and NaI were chosen as salt additives for this system. The reliability of data obtained in this apparatus was confirmed by a good agreement with the literature data (ethanol + water and ethanol + water + $CaCl_2$) and the test of thermodynamic consistency. Any salt used in this study exerted salting-in effect on methanol (1) + ethanol

Table 8. Correlation Parameters for Vapor–Liquid Equilibria of Methanol (1) + Ethanol (2) + Salt (3) at 298.15 K by Hála's Model

system	β^{*a}	Wilson parameters	av deviation $100\Delta^b$
methanol + ethanol + $CaCl_2$	3.8	$E_{13} = 45.44$, $\Lambda_{13} = 0.2818$ $E_{23} = 21.15$, $\Lambda_{23} = 0.0614$ $\Lambda_{12} = 1.715$, $\Lambda_{21} = 0.4566$	±0.76
methanol + ethanol + NaI	2.8	$E_{13} = 31.56$, $\Lambda_{13} = 0.2750$ $E_{23} = 19.68$, $\Lambda_{23} = 0.0843$ $\Lambda_{12} = 1.715$, $\Lambda_{12} = 0.4566$	±0.55
methanol + ethanol + NH_4I	2.8	$E_{13} = 15.81$, $\Lambda_{13} = 0.1941$ $E_{23} = 19.53$, $\Lambda_{23} = 0.0484$ $\Lambda_{12} = 1.715$, $\Lambda_{12} = 0.4566$	±2.12

[a] These values were optimized by vapor–liquid equilibria of ternary system. [b] $\Delta = (1/N)\sum_{i=1}^{N} |(y_1^{\text{exptl}} - y_1^{\text{calcd}*})/y_1^{\text{calcd}*}|$.

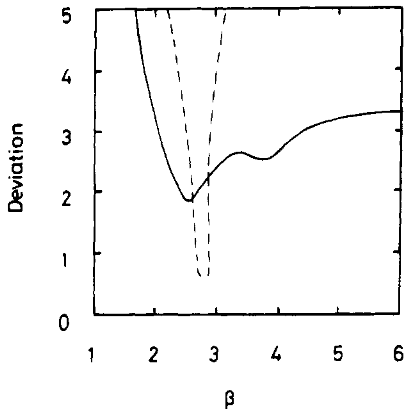

Figure 8. Relation between β value and accuracy of Hála's model for solvent + solvent + NaI: —, ethanol (1) + water (2) + NaI (3); – – –, methanol (1) + water (2) + NaI (3). Deviation = $(1/N)\sum|(y_1^{\text{exptl}} - y_1^{\text{calcd}})/y_1^{\text{calcd}}|$.

(2), the magnitude of which was $CaCl_2 > NaI > NH_4I$. The experimental data were correlated by Hála's model, and the calculated result of every system was reproduced with sufficient accuracy. Therefore, the application of Hála's model for the alcohol + alcohol + salt system was confirmed. From the results of comparison of β value obtained in this work, it was considered that β as a parameter mainly depended on the kind of salt, not on the solvent mixture.

Literature Cited

(1) Further, W. F. Salt Effect in Distillation: Literature Review II. *Can. J. Chem. Eng.* **1977**, *55*, 229–239.
(2) Hála, E. *Fluid Phase Equilib.* **1983**, *13*, 311–319.
(3) Hála, E.; Pick, J.; Fried, V.; Vilim, O. *Vapor-Liquid Equilibrium*, 2nd ed.; Pergamon Press: Oxford, U.K., 1967.
(4) Kojima, K. *Kagaku Kogaku* **1969**, *33*, 1201–1204.
(5) Iino, M.; Nakae, N.; Sudoh, J.; Hirose, Y. *Kagaku Kogaku* **1971**, *35*, 1017–1021.
(6) Gibbard, H.; Creek, J. L. *J. Chem. Eng. Data* **1974**, *19*, 308–310.
(7) Nagata, I. *J. Chem. Eng. Data.* **1985**, *30*, 201–203.
(8) Singh, J.; Benson, G. C. *Can. J. Chem.* **1968**, *46*, 2065–2069.
(9) Singh, J.; Pflug, H. D.; Benson, G. C. *Can. J. Chem. Eng.* **1969**, *47*, 543–546.
(10) Dobson, H. J. E. *J. Chem. Soc.* **1925**, *128*, 2886–2890.
(11) Hall, D. J.; Mash, C. J; Pemberton, R. C. "NPL Report Chemistry"; Jan 1979 p 95.
(12) Herington, E. F. G. *J. Inst. Petrol.* **1951**, *37*, 457–470.
(13) Kojima, K.; Moon, H.; Ochi, K. *Fluid Phase Equilib.* **1990**, *56*, 269–284.
(14) Misima, K.; Matsubara, K.; Arai, Y.; Hongo, M. *Kagaku Kogaku Ronbunshu* **1987**, *13*, 850–853.
(15) Sada, E.; Kito, S.; Morisue, T. *Kagaku Kogaku* **1973**, *37*, 983–986.
(16) Lee, L. S.; Tsao, Y. Z.; Yang, B. L. M. *Can. J. Chem. Eng.* **1991**, *69*, 788–793.

Received for review August 29, 1994. Revised November 14, 1994. Accepted November 22, 1994.®

JE940180Q

® Abstract published in *Advance ACS Abstracts,* January 15, 1995.