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Measurement of the Effect of Salt on Vapor−Liquid Equilibria by Using Headspace Gas Chromatography

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The effect of salt on vapor−liquid equilibria for ethyl acetate + ethanol + $CaCl_2$ and + LiCl was measured by using headspace gas chromatography (HSGC) at 313.15 K. Applying a HSGC technique to the measurement of VLE has three advantages, namely, a short measurement time, a small sample volume, and minor skills required. As a result, relative volatility was increased with salt concentrations. LiCl showed stronger effect than $CaCl_2$. The observed data were well correlated with a modified solvation model and with an electrolyte NRTL model. The azeptropic points were estimated by the modified solvation model. It was confirmed that the point was observed to shift to the ethyl acetate-rich region in $CaCl_2$ system and that LiCl broke the azeotrope.

Introduction

Vapor−liquid equilibrium (VLE) relations are changed by adding a salt to the solvent mixture, because of the salt effect. Azeotropic points are broken or shifted by this effect. Therefore, this effect can be used to break an azeotrope in azeotropic or extractive distillation. Many measurements of this effect have been carried out by using a conventional apparatus, such as a Furter type equilibrium still.[1] This is more difficult than a no-salt system because salt is a nonvolatile component. Difficulties encountered when measuring this effect include the effect of entrainment of salt and determination of liquid composition. Therefore, it often takes more time and more skill than a system without salt.

Headspace gas chromatography (HSGC) is a general analytical method for volatile components that exist in a liquid phase or solid phase that involves analyzing the vapor phase (headspace gas) by gas chromatography. The method can be divided into dynamic and static methods based on the vapor−liquid equilibrium phenomena. In the static method, the sample is enclosed in a vial (20 mL to 30 mL), and then is maintained in a thermostatic bath at constant temperature, and the vapor phase in the vial is analyzed after reaching equilibria to determine liquid composition by applying vapor−liquid equilibrium relation. Therefore, HSGC can measure vapor−liquid equilibria, and several researchers have proposed a method that uses HSGC for measurement of vapor−liquid equilibria.[2−5] The advantages of this method for measurement of VLE include shorter times, smaller sample volumes, and minor skills required. In this work, HSGC was used to measure the salt effect on vapor−liquid equilibria. The HSGC used in this work is a static method; therefore, entrainment of salt does not affect the measurements. Furthermore, the HSGC sampling system differs from other proposed methods, because it uses a gastight syringe, and it is not necessary to the correct liquid composition. Therefore, the HSGC can be applied to measure the salt effect on vapor−liquid equilibria. In this work, ethyl acetate + ethanol + $CaCl_2$ (3.6 mol %) and ethyl acetate + ethanol + LiCl (3.6 mol %) were measured by the HSGC. The ethyl acetate + ethanol system has an azeotropic point, and it is difficult to separate by distillation. At atmospheric pressure, the system containing $CaCl_2$ has been studied by Hashitani and Hirata;[6] however, data were not reported at isothermal conditions. Our measured data were compared with several models such as a modified solvation model[7,8] and the electrolyte NRTL model.[9] To check the consistency of the apparatus, ethyl acetate + ethanol system without salt was also measured at 313.15 K.

Experimental Section

Principles of Measurement. In this work, the HSGC method was used to observe vapor−liquid equilibria. In the HSGC method, a sample was placed in a small vial and then was thermostat in an aluminum block. After reaching equilibrium state, the vapor phase was automatically injected into the GC by gastight syringe. Finally, the equilibrium compositions of the vapor phase were determined from peak areas. The principles of measurement are shown below.

For ideal gas behavior and a fixed sampling volume, the relation between the vapor pressure P_i of component i and peak area $A°_i$ is a linear one

$$P_i = k_i A°_i \tag{1}$$

where k_i is the response factor of i components. Between the partial pressure p_i of i component and peak area A_i there is a similar relation to eq 1 given by

$$p_i = k_i A_i \tag{2}$$

From eq 1, a response factor k_i can be determined. The vapor composition was calculated by eqs 1 and 2.

Vapor pressures of pure solvents were calculated from the Antoine equation with Antoine constants obtained from Ohe's data book of vapor pressure.[10]

Apparatus. The apparatus used in this work has the following components. The gas chromatograph (GC) was a Shimadzu GC-14A with a flame ionization detector (FID). The column was an HP Ultra 1 (Capillary Column, 25 m

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Table 1. Experimental Vapor−Liquid Equilibrium Data of Ethyl Acetate + Ethanol + Salt System at 313.15K, Liquid Mole Fraction of Ethyl Acetate on a Salt-Free Basis (x_i'), and Vapor Mole Fraction of Ethyl Acetate (y_1)

no salt				$CaCl_2$ (3 mol %)		$CaCl_2$ (6 mol %)		LiCl (3 mol %)		LiCl (6 mol %)	
x_1	y_1	x_1	y_1	x_1'	y_1	x_1'	y_1	x_1'	y_1	x_1'	y_1
0.030	0.116	0.471	0.571	0.062	0.283	0.063	0.301	0.062	0.294	0.062	0.325
0.062	0.210	0.524	0.593	0.130	0.403	0.129	0.424	0.131	0.424	0.130	0.467
0.129	0.334	0.580	0.617	0.204	0.470	0.202	0.497	0.204	0.509	0.205	0.572
0.203	0.417	0.640	0.646	0.287	0.521	0.285	0.550	0.285	0.571	0.285	0.632
0.274	0.473	0.703	0.675	0.374	0.574	0.372	0.596	0.374	0.617	0.375	0.682
0.283	0.477	0.771	0.716	0.473	0.622	0.468	0.639	0.474	0.669	0.472	0.738
0.327	0.502	0.842	0.771	0.583	0.688	0.586	0.698	0.584	0.721	0.582	0.788
0.372	0.527	0.918	0.857	0.706	0.750	0.709	0.752	0.705	0.789	0.705	0.857
0.420	0.547			0.844	0.840						

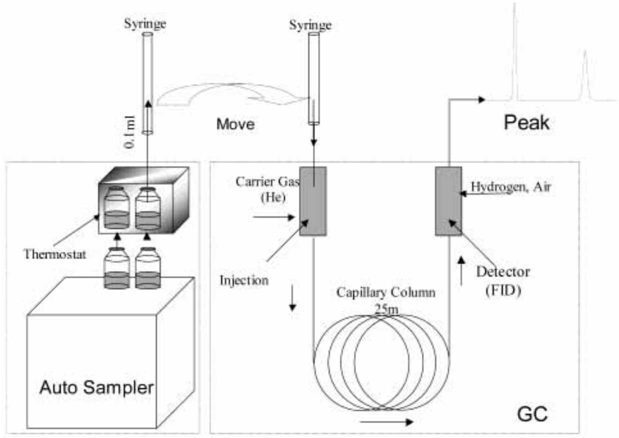

Figure 1. Diagram of apparatus.

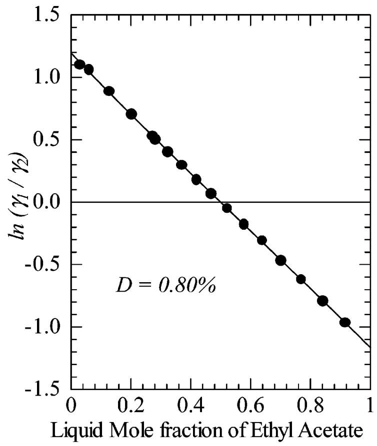

Figure 2. Area test for ethyl acetate + ethanol system at 313.15K.

× 0.32 mm × 0.52 μm). A headspace sampler (HSS-2B) with an aluminum block thermostat (with an accuracy of ±0.1 K) was used. Shimadzu C-R4A computer was connected to the GC and the headspace sampler. The volume of the vial was 26 mL, and the sample volume was 10 mL. The conditions of analysis were as follows: the column temperature was 323.15K; the injection temperature was 473.15K; the detector temperature was 473.15K; and the thermostat temperature was 313.15K. Helium was used as a carrier gas. Heating time was 40 min. The uncertainty of vapor composition was less than 1%. A diagram of the apparatus is shown in Figure 1.

The headspace sampler used in this work was built by Shimadzu Co. Ltd. The automatic sampling method used a gastight syringe for sampling the vapor phase, which differs from previous methods. In the sampling method proposed by Perkin-Elmer,[2] a carrier gas flowed into the vial to pressurize it for sampling. Therefore, it was necessary to correct the liquid composition. In this method, the syringe is held at the same temperature as the vial, which prevented partial condensation in the syringe and maintained an equilibrium in the vial. Sampling volume was set with a bar that was moved by an electromagnetic valve set in the upper part of the cylinder. Furthermore, before sampling, nitrogen gas flowed into the syringe to improve reproducibility. Therefore, the method can sample a fixed volume and maintain an equilibrium in the vial during sampling.

The composition of the liquid phase at equilibrium was taken to be the original composition determined from a gravimetric procedure. This assumption is reasonable because the sample of liquid was 10 mL, the volume of the vapor in the vial was 16 mL, and the sampling volume of the headspace gas was about 0.3 mL. Furthermore, some vials were weighed before and after the measurement, and the change in mass was less than 0.1 %. Vaporization from the liquid phase is very small and can be neglected. Therefore, it was not necessary to correct the liquid composition. Samples were weighed directly into the vial by using an analytical balance with an accuracy of ±0.5 mg. The uncertainty of liquid composition is less than 1%.

Measurement Procedures. The measurement procedure was as follows: (1) prepare sample by gravimetric procedure; (2) set the vial on an auto sampler; (3) heat vial for a constant time in an aluminum block thermostat; (4) after heating, inject vapor phase into the GC; and (5) determine vapor composition from peak area.

Chemicals. The measurement were made with high purity (more than 99%) chemicals. Ethyl acetate was a special grade with a purity of more than 99.5%. Ethanol was a dehydrated reagent (99.5%). Salts were special grade with purities of 99%. Kanto Chemical Co. manufactured all chemicals used in this work.

Results and Disccussion

Observed Data. Vapor−liquid equilibrium data of ethyl acetate + ethanol without the salt system is presented in Table 1. For this system without salt, thermodynamic consistency was verified by Herington's area test,[11] which is shown in Figure 2. An *x-y* curve for these data is shown in Figure 3. For the area test, the deviation *D* was 0.80%. The observed data were compared with literature data for the same system reported by Murtin et al., obtained from Hirata, Ohe, and Nagahama's vapor−liquid data collection.[12] The comparison is shown in Figure 3. Good agreement was observed for the vapor−liquid equilibria of the ethyl acetate + ethanol system.

In the system containing salt, the measurement results are presented in Table 1 and Figure 3. Relative volatility increased with the mole fraction of salt. This phenomenon was observed for both salts. When comparing calcium

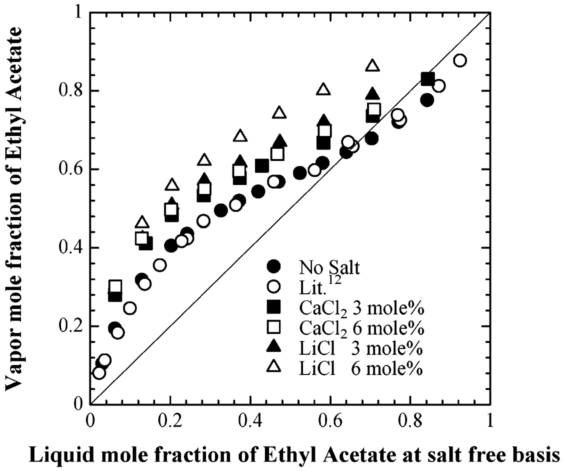

Figure 3. *x-y* curve for ethyl acetate + ethanol + LiCl and +$CaCl_2$ system at 313.15K.

Table 2. Correlation Results for Salt-Free System

model	interaction parameter (cal·mol^{-1}·K^{-1})		nonrandomness factor α	$\lvert\Delta y_1\rvert_{av}$ [a]
	$g_{12}-g_{11}$	g_{21}-g_{22}		
Wilson	109.43	798.93		0.003
NRTL	421.57	411.65	0.3	0.004
UNIQUAC	246.88	153.59		0.004

[a] $\lvert\Delta y_1\rvert_{av} = 1/n\ \sum\lvert y_{1,obs} - y_{1,cal}\rvert$; n is the number of data points; $y_{1,obs}$ is the observed vapor composition of ethyl acetate; $y_{1,cal}$ is the calculated data of vapor composition of ethyl acetate.

Table 3. Correlated Result for Modified Solvation Model for System Containing Salt

salt	solvation number		$\lvert\Delta y_1\rvert_{av.}$
	ethyl acetate	ethanol	
$CaCl_2$ 3 mol %	0	12.7	0.005
$CaCl_2$ 6 mol %	0	7.53	0.004
LiCl 3 mol %	0	17.8	0.009
LiCl 6 mol %	0	11.6	0.007

Table 4. Correlated Result of Electrolyte NRTL Model[a]

salt	interaction parameter				$\lvert\Delta y_1\rvert_{av.}$
	$\tau_{ca,m1}$	$\tau_{m1,ca}$	$\tau_{ca,m2}$	$\tau_{m2,ca}$	
$CaCl_2$ 3 mol %	5.933	12.116	−1.254	3.645	0.008
$CaCl_2$ 6 mol %					0.009
LiCl 3 mol %	8.176	10.600	−2.658	1.102	0.008
LiCl 6 mol %					0.007

[a] Nonrandomness factor $\alpha_{ca,m1} = \alpha_{ca,m2} = 0.3$.

chloride and lithium chloride, lithium chloride had a larger salt effect on the system.

Correlated. The experimental data containing no salt was correlated with the Wilson,[13] NRTL,[14] and UNIQUAC[15] models. The parameters and correlation deviations are given in Table 2. Good correlations were obtained. The salt systems were correlated with a modified solvation model and the electrolyte NRTL model. Model parameters and deviation are presented in Tables 3 and 4. These models represented experimental data with a high accuracy.

The azeotropic points of these mixtures were estimated by a modified solvation model with the solvation numbers determined from experimental data. The azeotropic point of the salt-free system $x_{1,az}$ was estimated 0.659 by the Wilson model. In the system containing calcium chloride, the azeotropic point was estimated to be 0.823 for 3 mol % and 0.896 for 6 mol %. The system containing lithium chloride showed no azeotoropic point. In the system containing calcium chloride, the azeotropic point shifted to the ethyl acetate-rich region with a higher mole fraction of salt. Lithium chloride can break the azeotrope for ethyl acetate + ethanol.

Conclusion

The ethyl acetate + ethanol + $CaCl_2$ and ethyl acetate + ethanol + LiCl systems at 313.15 K were measured by headspace gas chromatography. For the ethyl acetate + ethanol system containing no salt, good agreement with literature data and thermodynamics consistency by the area test were confirmed. For the system containing salt, relative volatility increased with the mole fraction of salt. The effect of lithium chloride was larger than that of calcium chloride. The measured vapor−liquid equilibrium data was correlated with several models. Good correlations were shown. The azeotropic points were estimated by a modified solvation model. It was confirmed that the point was observed to shift to the ethyl acetate-rich region in $CaCl_2$ system and that LiCl broke the azeotrope.

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