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Measurement of Isothermal Vapor−Liquid Equilibria for Hydrocarbon + Monocarboxylic Acid Binary Systems by a Flow-Type Apparatus

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A flow-type apparatus was constructed to measure isothermal vapor−liquid equilibria. The reliability of this experimental method was confirmed by comparing the data obtained with literature values. Isothermal vapor−liquid equilibria for hydrocarbon + monocarboxylic acid binary systems were measured. Hexane, 1-hexene, cyclohexane, and benzene were adopted for the hydrocarbons, and acetic acid and propionic acid for the monocarboxylic acids. The experimental data obtained in this work are found to be thermodynamically consistent. They are correlated by applying the NRTL model to liquid-phase activity coefficients and by assuming vapor-phase association of monocarboxylic acids.

Introduction

Vapor-phase association affects physical properties of mixtures containing carboxylic acids. For example, vapor−liquid equilibria are significantly affected. From the compilation of Gmehling and Onken,[1] it is shown that thermodynamically consistent data for vapor−liquid equilibria of hydrocarbon + monocarboxylic acid binary systems are fewer than 20%. Therefore, more precise vapor−liquid equilibria data are desired to design a distillation column. We designed and constructed a flow-type apparatus for precise measurement of isothermal vapor−liquid equilibria. The apparatus was tested with measurement of vapor−liquid equilibria for ethanol + toluene and heptane + propionic acid binary systems at 323.2 K. Then, isothermal vapor−liquid equilibria for eight hydrocarbon + monocarboxylic acid binary systems (hexane + acetic acid, 1-hexene + acetic acid, cyclohexane + acetic acid, benzene + acetic acid, hexane + propionic acid, 1-hexene + propionic acid, cyclohexane + propionic acid, and benzene + propionic acid) were measured at 313.2 K. Further, they were correlated by applying the NRTL model to liquid-phase activity coefficients and by assuming the vapor-phase association of monocarboxylic acids.

Experimental Section

Materials. All chemicals, except 1-hexene, used in this study were guaranteed reagent grade. The purities of chemicals were reported by the supplier to be greater than 99.7% for acetic acid, 99.5% for propionic acid, ethanol, toluene, cyclohexane, and benzene, 99.0% for heptane, 96% for hexane, and 95% for 1-hexene. They were used without any further purification. The purity of helium used as a carrier gas was reported by the supplier to be higher than 99.995%.

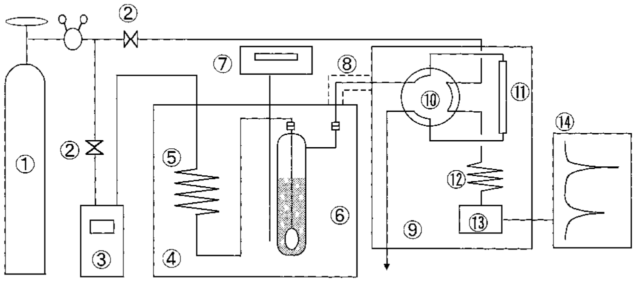

Figure 1. Schematic diagram of the flow-type apparatus: (1) carrier gas cylinder; (2) mass flow controller; (3) flow meter; (4) water bath; (5) heat exchanger; (6) equilibrium cell; (7) thermometer; (8) ribbon heater; (9) air chamber; (10) six-way valve; (11) sampling tube; (12) column; (13) TCD; (14) integrator.

Apparatus. A flow-type apparatus was constructed to measure the isothermal vapor−liquid equilibria. The apparatus was similar to that used by Uchizono et al.[2] The schematic diagram of the apparatus is shown in Figure 1. The apparatus consisted of a carrier gas cylinder, a mass flow controller, an equilibrium glass cell (about 30 mL), a water bath (±0.05 K), a thermometer (±0.05 K), a sampling tube (about 1 mL) with a six-way valve, a gas chromatograph with a thermal conductivity detector (TCD), and an integrator. Helium gas was used as carrier gas, because it is inert and has a high thermal conductivity. The sampling tube was in the air chamber of the gas chromatograph. The connecting line from the cell to the sampling tube was heated and maintained 50 K higher than the temperature of the water bath (323.2 K or 313.2 K) to avoid any condensation. The air chamber of the gas chromatograph was maintained at 473 K and 493 K in experiments for the systems containing acetic acid and propionic acid, respectively.

Procedures. A binary liquid mixture of known composition was charged into the equilibrium cell. The equilibrium

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cell and the preheating line were set in the water bath. After the temperature of the sample reached that of the water bath, helium gas was flowed into the cell. Helium gas was slowly passed (about 30 mL·min^{-1}) through the liquid mixture to establish equilibrium. Helium gas containing vapor phase passed through the sampling tube and discharged into the atmosphere. The temperature of the gaseous mixture in the sampling tube was the same as that of the air chamber of the gas chromatograph. The pressure drop from the equilibrium cell to the atmosphere was so small that the pressures in the cell and the sampling tube were considered to be ambient pressure. Changing the six-way valve, the vapor phase in the sampling tube was analyzed with a gas chromatograph. After the experiment, the liquid mixture in the cell was analyzed with the same gas chromatograph. Since helium was also used as the carrier gas of the gas chromatograph, helium was not detected on the recorder. Only two peaks for two compounds were observed in the experiment for a binary system. The equilibrium compositions of both liquid and vapor phases and the vapor pressure were determined by the peak areas. The analysis method for the system containing carboxylic acid (associating component) is different from that for the system containing nonassociating components.

(a) Nonassociating Component + Nonassociating Component Binary Systems. The following assumptions are valid, because the total pressure in this experiment is atmospheric pressure. (I) The solubility of helium in a liquid mixture can be negligible. (II) The vapor phase can be treated as an ideal gaseous mixture.

In brief, helium can be treated as inert. When the vapor phase in the equilibrium glass cell is carried into the sampling tube, it may expand because the temperature of the tube is higher than that of the cell. On the basis of the above assumption II, however, the composition and the partial pressure of each component do not change. Both liquid- and vapor-phase compositions can be determined by the peak areas and the relative sensitivities (factors) of the gas chromatograph. The factors were determined by using standard solutions with known compositions. To obtain accurate factors, compositions and amounts of the standard solutions were prepared to give almost the same peak areas of the samples.

On the other hand, the total pressure was obtained from the peak areas of the vapor sample. Absolute sensitivity between the peak area and the partial pressure is necessary. If the peak area A_i for component i is approximated by a quadratic function of the amount of substance n_i^* carried into the sampling tube, the relationship between the partial pressure in the sampling tube p_i^* (=p_i in the cell) and the peak area is expressed by

$$p_i^* = \frac{n_i^* R T^*}{V^*} = a_i A_i + b_i A_i^2 \qquad (1)$$

where the volume of the sampling tube V^* (about 1 mL) and the temperature of the gaseous mixtures in the sampling tube T^* (473 K or 493 K) were constant throughout the experiment. The subscript i denotes component 1 or 2. a_i and b_i are the coefficients of the absolute sensitivities of the gas chromatograph. The coefficients a_i and b_i were determined by the following procedure. Each pure component was charged into the equilibrium cell, and the peak areas were obtained at several temperatures. Since the saturated vapor pressure p_i^s (=p_i^*) was changed with temperature, various peak areas were obtained. The saturated vapor pressures can be calculated by the Antoine equation whose parameters are presented in Table 1.[3,4] Namely, the coefficients a_i and b_i can be obtained as the relationship between the vapor pressures and the peak areas.

Table 1. Antoine Constants[a] for Saturated Vapor Pressure

	A	*B*	*C*
acetic acid[b]	15.192 34	3654.622	45.392
propionic acid[b]	15.296 86	3670.949	70.545
ethanol[c]	16.896 59	3803.986	41.670
toluene[c]	13.998 42	3096.516	53.668
heptane[c]	13.858 44	2911.320	56.514
hexane[c]	13.804 08	2691.077	48.940
1-hexene[c]	13.793 67	2654.814	47.301
cyclohexane[c]	13.737 44	2766.627	50.503
benzene[c]	13.885 61	2788.507	52.360

[a] $\ln(p^s/\mathrm{kPa}) = A - B/[(T/K) - C]$. [b] Ambrose and Ghiassee.[3] [c] Yaws.[4]

The partial pressures of each component in a binary system were obtained by the peak areas measured and the coefficients a_i and b_i. The total pressure can be obtained by the following equation, based on assumption II:

$$p = p_1 + p_2 \qquad (2)$$

The vapor-phase composition can also be obtained by the partial pressures. However, the precision of the absolute sensitivity becomes lower as the partial pressure becomes lower, because the peak area is smaller. Therefore, the error of the composition obtained from the partial pressure may be large though the effect of the error in compositions on the total pressure is small. Accordingly, both vapor- and liquid-phase compositions were determined by using the relative sensitivities, though the total pressure was obtained by using the absolute sensitivities.

(b) Nonassociating Component + Associating Component Binary Systems. The total pressures and equilibrium compositions for hydrocarbon and monocarboxylic acid binary systems were measured as follows. The procedure was similar to that for the nonassociating component and nonassociating component binary systems mentioned above. However, monocarboxylic acid associates in the vapor phase. Therefore, this association effect should be taken into account.

For a carboxylic acid, it is assumed that a monomer and a dimer of the carboxylic acid exist in the vapor phase, and they compose an ideal gaseous mixture.[5] Therefore, the following assumptions are valid for a nonassociating component and associating component binary system. (I) The solubility of helium in a liquid mixture can be negligible. (II) A monomer and a dimer of carboxylic acid, hydrocarbon, and helium exist in the vapor phase. (III) The association constant of a carboxylic acid is not affected by the presence of helium and hydrocarbon.

In the experiment for a mixture containing carboxylic acid, when the vapor phase in the equilibrium glass cell is carried into the sampling tube, it may expand and a part of the dimer of carboxylic acid may decompose because the temperature is higher than that of the cell. On the other hand, the peak area of the gas chromatograph corresponds to the amount of substance (mole), evaluated by the molecular weight of monomeric acid. The vapor-phase compositions in the sampling tube accounting for monomeric acid are the same as that in the cell. Therefore, the vapor- and liquid-phase compositions can be determined by the peak areas with the relative sensitivities (factors) of the gas chromatograph. Since the partial pressures for each component (monomer and dimer) in the sampling tube are different from those in the cell, they cannot be obtained by the peak areas directly. The relationship between the partial pressure in the equilibrium cell p_i and that in the sampling tube p_i^* can be obtained by the compositions of the monomer and dimer in both the cell and the tube on the basis of the material balance. The compositions of the monomer and dimer for carboxylic acid can be estimated from the association constant. A relationship between the peak areas and the partial pressures in the sampling tube p_i^* is necessary. It was obtained by the experiment using the pure component. In this case, component 1 is considered to be a nonassociating component and component 2 is an associating component. The subscripts m and d indicate the monomer and dimer of carboxylic acid, respectively. Equation 1 is valid for hydrocarbons, and coefficients a_1 and b_1 can be obtained by the above-mentioned procedure. Further, eq 3 is valid for carboxylic acids

$$p_{2m}^* + 2p_{2d}^* = \frac{(n_{2m}^* + 2n_{2d}^*)RT^*}{V^*} = c_2 A_2 + d_2 A_2^2 \quad (3)$$

The coefficients c_2 and d_2 were determined by the flowing procedure. In general, the association constant is given as a function of the temperature as follows[6]

$$K_2(T) = \exp\left(\frac{\Delta S_2}{R} - \frac{\Delta H_2}{RT}\right) \cong \frac{p_{2d}}{(p_{2m})^2} \quad (4)$$

where ΔS_2 and ΔH_2 are the entropy and the enthalpy for association, respectively. We used -136.0 J·mol^{-1}·K^{-1} for ΔS_2 and -58.5 kJ·mol^{-1} for ΔH_2, for both acetic acid and propionic acid.[5] The relationships between the partial pressures of the monomer and dimer, both in the equilibrium cell (T) and in the sampling tube (T^*), were estimated with the association constant by eq 4 and the equation

$$K_2(T^*) \cong \frac{p_{2d}^*}{(p_{2m}^*)^2} \quad (5)$$

On the other hand, the saturated vapor pressure p_2^s of the pure carboxylic acid in the cell is obtained from the partial pressures for the monomer and dimer by[6]

$$p_2^s = p_{2m} + p_{2d} \quad (6)$$

The saturated vapor pressure p_2^s for the pure carboxylic acid changed with the temperature. The peak areas of the pure carboxylic acid were obtained at several temperatures. The saturated vapor pressures can be calculated by the Antoine equation whose parameters are presented in Table 1. On the basis of the material balance for carboxylic acid (monomer and dimer) and helium both in the equilibrium cell and in the sampling tube, the partial pressures in the sampling tube were obtained by using eqs 4−6. The coefficients c_2 and d_2 were determined with eq 3.

For a binary system, the partial pressure p_i^* of each component in the sampling tube can be evaluated by each peak area by adopting eq 1 or 3. The partial pressure in the equilibrium cell p_i can be determined on the basis of the material balance and eqs 4 and 5. The total pressures can be obtained by the equation

$$p = p_1 + p_{2m} + p_{2d} \quad (7)$$

Results and Discussion

Experimental Data. To confirm the reliability of this experiment, the results obtained in this work were compared with the literature. For a binary system containing nonassociating components, vapor−liquid equilibrium data obtained at 323.2 K for ethanol + toluene are listed in Table 2. The p−x−y relation is shown in Figure 2 together with that reported by Zharov et al.[7] For a binary system containing an associating component, vapor−liquid equilibrium data obtained at 323.2 K for heptane + propionic acid are listed in Table 2. The p−x−y relation is shown in Figure 3 together with that reported by Schuberth.[8] Both data in the literature were evaluated by Gmehling and Onken,[1] and they are considered to be thermodynamically consistent. Good agreement between the present data and the literature values for both systems is shown, which confirms the reliability of the apparatus and the procedure.

The vapor−liquid equilibria obtained in this work for hydrocarbon and monocarboxylic acid binary systems are

Table 2. Vapor−Liquid Equilibria for Ethanol + Toluene and Heptane + Propionic Acid Systems at 323.2 K

x_1	y_1	p (kPa)	x_1	y_1	p (kPa)
		Ethanol (1) + Toluene (2)			
0.008	0.170	14.6	0.645	0.715	32.4
0.025	0.347	18.5	0.756	0.753	32.8
0.027	0.360	18.7	0.804	0.777	32.5
0.027	0.358	18.7	0.904	0.852	32.0
0.043	0.443	21.4	0.904	0.853	32.0
0.143	0.590	28.0	0.904	0.853	31.9
0.310	0.646	30.7	0.954	0.913	30.9
0.474	0.677	31.5	0.982	0.961	30.2
0.477	0.678	31.8	0.991	0.980	30.0
0.479	0.679	31.8			
		Heptane (1) + Propionic Acid (2)			
0.091	0.673	8.7	0.490	0.863	15.6
0.289	0.817	13.6	0.689	0.904	17.0
0.291	0.815	13.5	0.897	0.955	18.3
0.488	0.864	15.7			

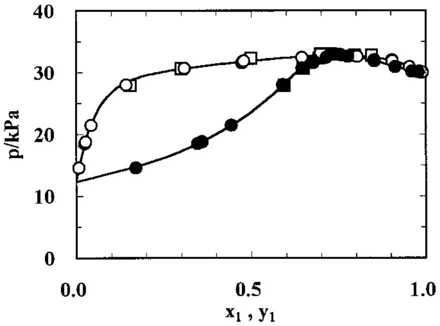

Figure 2. Vapor−liquid equilibria for the ethanol (1) + toluene (2) system at 323.2 K: (□, ■) Zharov et al.;[7] (○, ●) present work; (−) correlation with NRTL model.

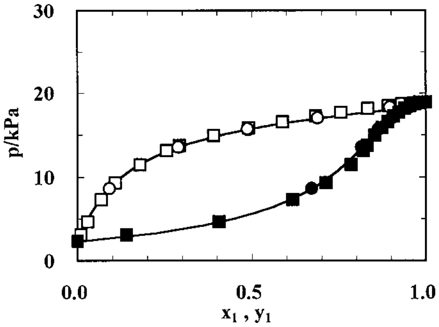

Figure 3. Vapor−liquid equilibria for the heptane (1) + propionic acid (2) system at 323.2 K: (□, ■) Schuberth;[8] (○, ●) present work; (−) correlation with NRTL + vapor-phase association model.

Table 3. Vapor−Liquid Equilibria for Hydrocarbon + Carboxylic Acid Systems at 313.2 K

x_1	y_1	p (kPa)	x_1	y_1	p (kPa)
Hexane (1) + Acetic Acid (2)			Hexane (1) + Propionic Acid (2)		
0.014	0.426	10.5	0.017	0.627	4.2
0.033	0.618	17.9	0.044	0.792	8.2
0.070	0.724	25.8	0.088	0.871	13.3
0.263	0.800	34.0	0.274	0.940	24.4
0.463	0.815	36.4	0.479	0.958	29.3
0.675	0.841	37.6	0.676	0.970	32.6
0.896	0.913	38.1	0.893	0.986	36.0
0.948	0.947	37.9	0.945	0.991	36.7
0.978	0.975	37.3	0.978	0.995	37.2
1-Hexene (1) + Acetic Acid (2)			1-Hexene (1) + Propionic Acid (2)		
0.014	0.390	9.6	0.018	0.596	4.0
0.036	0.591	15.8	0.045	0.776	7.7
0.072	0.708	22.9	0.088	0.865	13.0
0.248	0.817	34.8	0.270	0.945	26.2
0.457	0.847	37.9	0.467	0.965	32.7
0.672	0.880	40.0	0.681	0.978	37.9
0.889	0.940	42.6	0.885	0.990	42.3
0.945	0.964	43.3	0.943	0.994	43.7
0.978	0.984	44.9	0.977	0.997	44.0
Cyclohexane (1) + Acetic Acid (2)			Cyclohexane (1) + Propionic Acid (2)		
0.015	0.346	8.6	0.019	0.527	3.2
0.040	0.537	13.5	0.047	0.723	5.8
0.083	0.656	18.8	0.095	0.826	9.7
0.281	0.748	24.8	0.288	0.919	17.0
0.488	0.764	25.8	0.491	0.943	20.2
0.690	0.785	26.2	0.689	0.959	22.1
0.900	0.862	26.4	0.899	0.979	23.9
0.952	0.913	26.2	0.949	0.987	24.3
0.981	0.955	25.6	0.979	0.993	24.6
Benzene (1) + Acetic Acid (2)			Benzene (1) + Propionic Acid (2)		
0.019	0.179	6.1	0.020	0.347	2.2
0.047	0.341	8.1	0.048	0.581	3.7
0.095	0.491	10.8	0.096	0.738	5.7
0.292	0.712	17.0	0.296	0.907	12.3
0.492	0.806	20.6	0.492	0.952	16.8
0.695	0.872	22.3	0.685	0.974	20.0
0.898	0.946	23.4	0.900	0.990	23.0
0.950	0.969	23.7	0.950	0.994	23.5
0.979	0.985	24.0	0.979	0.997	23.9

Table 4. Thermodynamic Consistency[a] of Present Data

component 1	component 2	area test	point test
ethanol	toluene	0.2	0.002
heptane	propionic acid	1.0	0.002
hexane	acetic acid	0.9	0.009
1-hexene	acetic acid	4.2	0.007
cyclohexane	acetic acid	0.8	0.009
benzene	acetic acid	2.5	0.004
hexane	propionic acid	1.1	0.004
1-hexene	propionic acid	4.7	0.003
cyclohexane	propionic acid	0.9	0.003
benzene	propionic acid	1.5	0.003
thermodynamic consistency[a]		≤10	≤0.01

[a] Gmehling and Onken.[1]

listed in Table 3. It is estimated that the uncertainties of this experiment are ±0.1 K for temperature, ±0.3 kPa for pressure, and ±0.005 mole fraction for composition. As shown in Table 4, all experimental data obtained in this work are eligible for the thermodynamic consistency test.[1] The vapor−liquid equilibrium for hexane + acetic acid is shown in Figure 4 as a typical illustration. The data obtained at 313.2 K for the benzene + propionic acid system were compared with those reported by Kogan et al.[9] They show good agreement for $p-y$ relations and fair agreement for $p-x$ relations. Their data have been evaluated to be inconsistent by Gmehling and Onken.[1]

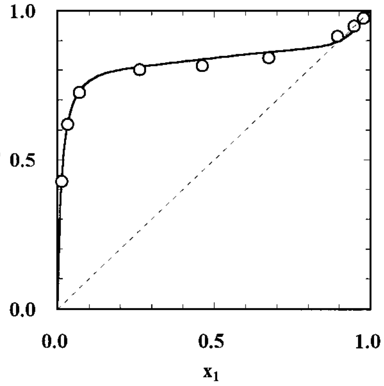

Figure 4. Vapor−liquid equilibria for the hexane (1) + acetic acid (2) system at 313.2 K: (○) present work; (—) correlation with NRTL + vapor-phase association model.

Correlation. The fugacities of each component in the vapor phase and the liquid phase are equal under vapor−liquid equilibrium conditions. According to the theory of associated solutions, the fugacity of the monomer is equal to that of the component.[10] Therefore, vapor−liquid equilibrium for the nonassociating component and associating component binary system is expressed by the equations[11]

$$f_1^{\mathrm{L}} = f_1^{\mathrm{V}} \tag{8}$$

$$f_2^{\mathrm{L}} = f_2^{\mathrm{V}} = f_{2\mathrm{m}}^{\mathrm{V}} \tag{9}$$

If the mole fractions of the monomer and dimer are denoted by η, the fugacities of each component in the vapor phase and liquid phase are given by eqs 10−13.

$$f_1^{\mathrm{V}} = p\eta_1\varphi_1 \tag{10}$$

$$f_{2\mathrm{m}}^{\mathrm{V}} = p\eta_{2\mathrm{m}}\varphi_{2\mathrm{m}} \tag{11}$$

$$f_1^{\mathrm{L}} = \gamma_1 x_1 f_1^{0\mathrm{L}} \tag{12}$$

$$f_2^{\mathrm{L}} = \gamma_2 x_2 f_2^{0\mathrm{L}} \tag{13}$$

If we can assume that hydrocarbon, carboxylic acid monomer, and dimer exist in the vapor phase and they are an ideal gaseous mixture, the fugacity coefficients can be obtained by the following equation because the total pressure is sufficiently low

$$\varphi_1 = 1 \qquad \varphi_{2\mathrm{m}} = 1 \tag{14}$$

The relationship among the mole fraction η, the association constant K, and the mole fraction of substance y is given by

$$\eta_1 + \eta_{2\mathrm{m}} + \eta_{2\mathrm{d}} = 1 \tag{15}$$

$$K_2 = \frac{p_{2\mathrm{d}}}{p_{2\mathrm{m}}^{2}} = \frac{\eta_{2\mathrm{d}}}{p\eta_{2\mathrm{m}}^{2}} \tag{16}$$

$$y_1 = \frac{\eta_1}{\eta_1 + \eta_{2\mathrm{m}} + 2\eta_{2\mathrm{d}}} \tag{17}$$

The liquid-phase fugacity for a pure component can be obtained by the following equations by adopting the mole fraction of the monomer $\eta_{2\mathrm{m}}^{0}$ in the saturated vapor phase

Table 5. Parameters for NRTL Model and Average Deviations

component 1	component 2	$(g_{12} - g_{22})/R$ (K)	$(g_{21} - g_{11})/R$ (K)	α_{12}	Δy	Δp (kPa)
ethanol	toluene	341.330	580.142	0.531	0.002	0.09
heptane	propionic acid	481.002	413.321	0.637	0.002	0.10
hexane	acetic acid	592.386	603.682	0.477	0.012	0.55
1-hexene	acetic acid	405.462	483.535	0.504	0.008	0.16
cyclohexane	acetic acid	649.725	551.780	0.467	0.009	0.35
benzene	acetic acid	524.845	279.014	0.735	0.006	0.13
hexane	propionic acid	605.025	353.925	0.666	0.005	0.37
1-hexene	propionic acid	624.530	265.866	0.721	0.004	0.56
cyclohexane	propionic acid	623.376	326.105	0.646	0.006	0.22
benzene	propionic acid	545.562	166.625	0.967	0.005	0.10

at the same temperature of the binary system ($\varphi_1^0 = 1$, $\varphi_{2m}^0 = 1$)

$$f_1^{0L} = f_1^{0V} = p_1^s \varphi_1^0 = p_1^s \tag{18}$$

$$f_2^{0L} = f_{2m}^{0V} = p_2^s\, \eta_{2m}^0\, \varphi_{2m}^0 = p_2^s\, \eta_{2m}^0 \tag{19}$$

$$\eta_{2m}^0 + \eta_{2d}^0 = 1 \tag{20}$$

$$K_2 = \frac{p_{2d}}{p_{2m}^2} = \frac{\eta_{2d}^0}{p_2^s (\eta_{2m}^0)^2} \tag{21}$$

Finally, the following equations can be derived.

$$p\eta_1 = \gamma_1\, x_1\, p_1^s \tag{22}$$

$$p\eta_{2m} = \gamma_2\, x_2\, p_2^s\, \eta_{2m}^0 \tag{23}$$

The activity coefficients γ_1 and γ_2 were evaluated by eqs 15−17 and 20−23 with the present experimental data. The activity coefficients obtained were correlated by the NRTL model.[12] Parameters for the NRTL model were optimized by the objective function

$$\text{O.F.} = \sum_{j=1}^{N} [(\gamma_{1,\text{exptl}} - \gamma_{1,\text{calcd}})^2 + (\gamma_{2,\text{exptl}} - \gamma_{2,\text{calcd}})^2]_j \tag{24}$$

The parameters optimized are listed in Table 5. The vapor-phase compositions and the total pressures were calculated by the NRTL model with eqs 15−17 and 20−23. The calculated results were compared with the experimental data. The results for all binary systems (containing ethanol + toluene and heptane + propionic acid binary systems) are listed in Table 5; a typical illustration for hexane + acetic acid is shown in Figure 4. They show good agreement.

Literature Cited

(1) Gmehling, J., Onken, U. A., Eds. *Vapor-Liquid Equilibrium Data Collection; Chemistry Data Series*; DECHEMA: Frankfurt/Main, 1977.

(2) Uchizono, Y.; Kai, M.; Tashima, Y.; Arai, Y. Activity for Some Alcohols in Alcohol Solutions Containing Calcium Chloride (in Japanese). *Kagaku Kogaku Ronbunshu* **1983**, *9*, 485−489.

(3) Ambrose, D.; Ghiassee, N. B. Vapor Pressures and Critical Temperatures and Critical Pressures of Some Alkanoic Acids: C_1 to C_{10}. *J. Chem. Thermodyn.* **1987**, *19*, 505−519.

(4) Yaws, C. L. *Thermodynamic and Physical Property Data*; Gulf Publishing Company: Houston, 1992.

(5) Miyamoto, S.; Nakamura, S.; Iwai, Y.; Arai, Y. Measurement of Vapor-Phase Compressibility Factors of Monocarboxylic Acids Using a Flow-Type Apparatus and Their Association Constants. *J. Chem. Eng. Data* **1999**, *44*, 48−51.

(6) Jasperson, L. V.; Wilson, L. C.; Brady, C. J.; Wilding, W. V.; Wilson, G. M. Vapor Association of Monocarboxylic Acids from Heat of Vaporization and PVT Measurements. *AIChE Symp. Ser., Phase Equilibria and Pure Component Properties (DIPPR)* **1989**, *85*, 102−139.

(7) Zharov, V. T.; Morachevsky, A. G.; Shapil, L. G.; Buevich, T. A. One of the Form of the Dependence of the Partition Function on the Composition of the Solution and the Use of the Equations for Calculating Data of Liquid−Vapor Equilibria in Ternary Systems. *Zh. Prikl. Khim.* **1968**, *41*, 2443−2450.

(8) Schuberth, H. Das Dampf-Fluessigkeits-Gleichgewichtsverhalten des Systems *n*-Propionsaeure/*n*-Heptan bei 50 °C (Vapor-Liquid-Equilibria for Propionic Acid + *n*-Heptane System at 50 °C). *Z. Phys. Chem. (Leipzig)* **1981**, *262*, 945−952.

(9) Kogan, E. A.; Belogurova, N. V.; Yarym-Agaev, N. L. Saturated Vapor Pressure and Composition of Binary Systems with Chemical Interaction of the Components in Vapor. XI. Propionic Acid + Benzene System. *Zh. Fiz. Khim.* **1973**, *47*, 2148−2149.

(10) Saito, S. *Fundamentals for Prediction of Equilibrium Properties Based on Statistical Thermodynamics (in Japanese)*; Baifukan: Tokyo, 1983.

(11) Tochigi, K.; Kojima, K. Activity Coefficients at Infinite Dilution for Binary Systems Containing an Association Substance. *J. Chem. Eng. Jpn.* **1977**, *10*, 343−348.

(12) Renon, H.; Prausnitz, J. M. Local Composition in Thermodynamic Excess Function for Liquid Mixtures. *AIChE J.* **1968**, *14*, 135−144.

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