

Measurement of Isothermal Vapor–Liquid Equilibria for Binary and Ternary Systems Containing Monocarboxylic Acid

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Isothermal vapor–liquid equilibria for 15 binary systems and 7 ternary systems containing monocarboxylic acid were measured. For the binary systems, water, ethanol, butanol, methyl ethyl ketone, ethyl acetate, ethyl propionate, butyl aldehyde, and dibutyl ether were adopted for the polar compounds and acetic acid and propionic acid for the monocarboxylic acids. For the ternary systems, formic acid, acetic acid, propionic acid, and butyric acid were adopted for the monocarboxylic acids and hexane, water, ethanol, methyl ethyl ketone, and ethyl acetate for the other compounds. The experimental data of the binary systems obtained in this work were correlated by applying the NRTL model to liquid-phase activity coefficients and by assuming vapor-phase association. Furthermore, the vapor–liquid equilibria of the ternary systems were predicted by using the interaction parameters determined for the constituent binary systems.

Introduction

Vapor-phase association affects various physical properties of mixtures containing monocarboxylic acids. For example, vapor–liquid equilibria are significantly affected. In the compilation of Gmehling and Onken,¹ 295 sets among 350 sets of vapor–liquid equilibrium data for polar compound (such as alcohols) + monocarboxylic acid binary systems are thermodynamically inconsistent. That is, only 10 sets for polar compound + monocarboxylic acid binary systems and 45 sets for water + monocarboxylic acid binary systems are consistent. Therefore, accurate and reliable vapor–liquid equilibria of mixtures containing monocarboxylic acid are needed. In previous work,^{2,3} a flow-type apparatus was proposed. The experimental vapor–liquid equilibrium data for ethanol + toluene and heptane + propionic acid systems obtained with the apparatus agree well with the literature data.¹ Furthermore, the vapor–liquid equilibria for hydrocarbon + monocarboxylic acid binary systems and monocarboxylic acid + monocarboxylic acid binary systems were measured with the flow-type apparatus. In this work, the isothermal vapor–liquid equilibria for polar compound + monocarboxylic acid binary systems were measured. In addition, the isothermal vapor–liquid equilibria for ternary systems containing two or three kinds of monocarboxylic acids were measured. The vapor–liquid equilibria for the binary systems were correlated by applying the NRTL model to liquid-phase activity coefficients and by assuming vapor-phase association. The vapor–liquid equilibria for the ternary systems were predicted by using the interaction parameters determined for the constituent binary systems.

Experimental Section

Materials. All of the organic chemicals used in this study were of guaranteed reagent grade. The purities of chemicals were reported by the supplier, Kishida Chemical Co., as follows: >95.0% for butyl aldehyde and hexane, 98.0% for formic acid, 99.0% for ethyl propionate and butyric acid, and, 99.5% for the other chemicals. Formic acid was purified by fractional freezing. Water used in this work was purified by distillation. Other chemicals were used without further purification. The purities of all compounds were checked by the authors with GC; the percent area of each compound was >99.7%. The purity of helium used as a carrier gas was reported by the supplier, Nippon Sanso Co., to be >99.995%.

Apparatus and Procedures. A flow-type apparatus was used. A detailed description of the equipment and operating procedure was given previously.³ The apparatus consisted of a carrier gas cylinder, a mass flow controller, an equilibrium glass cell, a water bath, a thermometer, a condensation glass cell, and a dry ice–2-propanol bath. Helium gas was used as a carrier gas, because it is inert and has a high thermal conductivity. A liquid mixture of known composition was charged into the equilibrium cell. Helium gas was then charged into the equilibrium cell. Helium gas containing the vapor phase components passed through the condensation cell and discharged into the atmosphere. When the vapor phase in the equilibrium cell was carried into the condensation cell, the vapor components except helium were nearly completely trapped in the condensation cell. The pressures in the equilibrium cell and the condensation cell were considered to be ambient pressure. After the carrier gas flow was stopped, the total amount of supplied helium gas was recorded. The decrease of the liquid sample's mass was determined by weighing the equilibrium cell, and the mass of the liquid mixture

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Table 1. Kinds of Molecular Species of Dimer in Ternary Systems

component 1	component 2	component 3	homo-dimer	heterodimer
hexane	acetic acid	propionic acid	2, 3	2 + 3
water	acetic acid	propionic acid	2, 3	2 + 3
ethanol	acetic acid	propionic acid	2, 3	1 + 2, 1 + 3, 2 + 3
methyl ethyl ketone	acetic acid	propionic acid	2, 3	1 + 2, 1 + 3, 2 + 3
ethyl acetate	acetic acid	propionic acid	2, 3	1 + 2, 1 + 3, 2 + 3
formic acid	acetic acid	propionic acid	1, 2, 3	1 + 2, 1 + 3, 2 + 3
acetic acid	propionic acid	butyric acid	1, 2, 3	1 + 2, 1 + 3, 2 + 3

Table 2. Vapor–Liquid Equilibria for Polar Compound + Acetic Acid Binary Systems

x_1	y_1	p/kPa	x_1	y_1	p/kPa
water (1) + acetic acid (2) at 343.2 K			ethyl acetate (1) + acetic acid (2) at 323.2 K		
0.019	0.042	19.0	0.028	0.090	8.8
0.048	0.095	19.9	0.055	0.173	9.8
0.096	0.169	21.0	0.091	0.270	11.1
0.295	0.398	24.0	0.285	0.630	17.6
0.495	0.601	26.2	0.486	0.820	25.5
0.695	0.784	28.4	0.689	0.925	30.4
0.899	0.927	30.0	0.895	0.983	36.1
0.949	0.966	30.5	0.948	0.993	37.8
0.979	0.987	30.8	0.979	0.998	38.9
ethanol (1) + acetic acid (2) at 323.2 K			butyl aldehyde (1) + acetic acid (2) at 323.2 K		
0.029	0.055	8.2	0.026	0.114	9.3
0.058	0.110	8.4	0.053	0.214	10.2
0.096	0.180	9.0	0.091	0.322	12.1
0.290	0.503	12.1	0.280	0.648	20.9
0.488	0.763	16.0	0.481	0.815	27.1
0.686	0.919	21.0	0.687	0.915	33.3
0.894	0.986	27.2	0.894	0.978	40.3
0.947	0.995	28.7	0.946	0.991	42.0
0.978	0.998	29.6	0.979	0.997	41.6
butanol (1) + acetic acid (2) at 323.2 K			dibutyl ether (1) + acetic acid (2) at 343.2 K		
0.021	0.007	7.5	0.030	0.033	18.9
0.052	0.020	7.3	0.080	0.072	18.8
0.103	0.042	6.8	0.255	0.157	17.7
0.309	0.162	5.4	0.572	0.310	15.1
0.501	0.365	4.6	0.807	0.539	12.0
0.746	0.748	4.1	0.927	0.775	9.9
0.896	0.936	4.3	0.974	0.911	9.2
0.949	0.975	4.5			
0.980	0.991	4.5			
methyl ethyl ketone (1) + acetic acid (2) at 323.2 K					
0.028	0.077	8.4			
0.056	0.148	9.1			
0.094	0.243	10.2			
0.284	0.597	15.6			
0.484	0.810	21.5			
0.688	0.926	27.4			
0.895	0.985	33.3			
0.947	0.994	35.1			
0.979	0.998	36.0			

trapped was also measured by weighing the condensation cell. The recovery rates were checked and were >99 % in all experiments. The compositions of the liquid mixture trapped in the condensation cell were determined by gas chromatography. Vapor–liquid equilibrium relations for the binary and ternary systems were determined with the following procedure.

An average vapor-phase composition y_1^{av} was first determined as the composition of the liquid trapped in the condensation cell. Next, the average liquid-phase composition x_1^{av} was determined as follows. The following equations can be derived from Rayleigh's equation for a simple distillation:

Table 3. Vapor–Liquid Equilibria for Polar Compound + Propionic Acid Binary Systems

x_1	y_1	p/kPa	x_1	y_1	p/kPa
water (1) + propionic acid (2) at 343.2 K			ethyl acetate (1) + propionic acid (2) at 323.2 K		
0.014	0.204	8.8	0.022	0.219	3.1
0.037	0.335	11.0	0.048	0.385	4.1
0.072	0.466	14.1	0.082	0.533	5.4
0.261	0.709	22.7	0.281	0.851	13.7
0.478	0.813	28.1	0.484	0.940	21.6
0.689	0.876	31.1	0.687	0.976	28.3
0.899	0.928	32.1	0.895	0.994	35.6
0.950	0.953	32.3	0.947	0.997	36.5
0.980	0.979	32.3	0.979	0.999	38.5
ethanol (1) + propionic acid (2) at 323.2 K			ethyl propionate (1) + propionic acid (2) at 323.2 K		
0.022	0.183	3.0	0.025	0.138	2.7
0.046	0.317	3.6	0.051	0.252	3.2
0.080	0.445	4.7	0.087	0.379	3.9
0.271	0.764	9.2	0.280	0.735	7.3
0.478	0.902	14.2	0.481	0.878	10.6
0.684	0.967	20.2	0.686	0.949	13.5
0.895	0.995	27.0	0.894	0.987	16.2
0.947	0.998	28.9	0.947	0.994	16.9
0.979	0.999	30.2	0.978	0.998	17.4
butanol (1) + propionic acid (2) at 343.2 K			butyl aldehyde (1) + propionic acid (2) at 323.2 K		
0.030	0.042	6.5	0.020	0.228	3.3
0.059	0.081	6.4	0.045	0.428	4.7
0.098	0.133	6.8	0.084	0.594	6.9
0.295	0.393	7.3	0.280	0.865	16.2
0.490	0.649	8.8	0.478	0.941	24.9
0.690	0.860	10.3	0.684	0.974	32.8
0.895	0.974	12.9	0.894	0.993	39.7
0.946	0.990	13.5	0.947	0.997	41.2
0.979	0.996	13.3	0.978	0.999	42.6
methyl ethyl ketone (1) + propionic acid (2) at 323.2 K			dibutyl ether (1) + propionic acid (2) at 343.2 K		
0.022	0.198	3.0	0.019	0.035	6.6
0.045	0.355	4.0	0.048	0.086	6.8
0.080	0.500	5.3	0.097	0.158	7.3
0.276	0.832	12.5	0.296	0.384	8.2
0.479	0.930	19.2	0.496	0.563	8.8
0.686	0.975	26.2	0.698	0.726	9.1
0.895	0.996	33.1	0.900	0.897	9.2
0.942	0.998	34.7	0.951	0.945	9.2
0.973	0.999	35.8	0.979	0.976	8.8

$$\ln \frac{L^s}{L^f} = \frac{1}{\beta_{12}^{\text{av}} - 1} \ln \left\{ \frac{x_1^s(1 - x_1^f)}{x_1^f(1 - x_1^s)} \right\} + \ln \frac{(1 - x_1^f)}{(1 - x_1^s)} \quad (1)$$

In eq 1, L is the amount of sample in the equilibrium cell, and x_1 and y_1 are the compositions of component 1 in the liquid phase and vapor phase, respectively. Superscripts s and f denote the start and final states of the experiment, respectively. The average relative volatility β_{12}^{av} is defined by

$$\beta_{12}^{\text{av}} = (y_1^{\text{av}}/x_1^{\text{av}})/[(1 - y_1^{\text{av}})/(1 - x_1^{\text{av}})] \quad (2)$$

L^f and x_1^f were obtained from the material balance and y_1^{av} . The average liquid-phase composition x_1^{av} corresponding to y_1^{av} was determined by using eqs 1 and 2. Then, the average total pressure p^{av} was determined as follows. In the determination of p^{av} , the kinds of molecular species in the vapor phase should be considered. Yamamoto et al.⁴ found that ethanol associates with acetic acid in supercritical carbon dioxide by FTIR analysis. Therefore, in this work, a heterodimer of polar compound and monocarboxylic acid was considered in the vapor phase. That is, for polar compound + monocarboxylic acid binary systems, it was assumed that monomers of each component, homodimers of monocarboxylic acids, and heterodimers of polar com-

Table 4. Thermodynamic Consistency^a for Polar Compound + Monocarboxylic Acid Binary Systems

component 1	component 2	temp/K	$\Delta H_{12}/\text{kJ}\cdot\text{mol}^{-1}$	area test	point test	γ
water	acetic acid	343.2	- <i>b</i>	2	0.001	$1.02 < \gamma < 3.84$
ethanol	acetic acid	323.2	-46.0	1	0.003	$0.70 < \gamma < 1.02$
butanol	acetic acid	323.2	-46.0	41	0.002	$0.89 < \gamma < 1.01$
methyl ethyl ketone	acetic acid	323.2	-43.5	1	0.001	$1.01 < \gamma < 1.26$
ethyl acetate	acetic acid	323.2	-41.0	1	0.004	$1.02 < \gamma < 1.80$
butyl aldehyde	acetic acid	323.2	-45.5	1	0.002	$0.99 < \gamma < 1.72$
dibutyl ether	acetic acid	343.2	- <i>b</i>	6	0.005	$1.02 < \gamma < 4.19$
water	propionic acid	343.2	- <i>b</i>	2	0.008	$1.01 < \gamma < 8.95$
ethanol	propionic acid	323.2	-46.0	66	0.001	$0.65 < \gamma < 1.19$
butanol	propionic acid	343.2	-46.0	1	0.001	$0.75 < \gamma < 1.05$
methyl ethyl ketone	propionic acid	323.2	-43.5	∞^c	0.002	$0.61 < \gamma < 1.13$
ethyl acetate	propionic acid	323.2	-41.0	8	0.001	$0.98 < \gamma < 1.88$
ethyl propionate	propionic acid	323.2	-41.0	23	0.003	$1.00 < \gamma < 1.97$
butyl aldehyde	propionic acid	323.2	-45.5	90	0.005	$0.95 < \gamma < 1.31$
dibutyl ether	propionic acid	343.2	- <i>b</i>	8	0.006	$1.01 < \gamma < 3.44$
thermodynamic consistency ^a				≤ 10	≤ 0.01	

^a Gmehling and Onken.¹ ^b No heterodimer. ^c No intersection on $\ln(\gamma_1/\gamma_2) = 0$ axis.

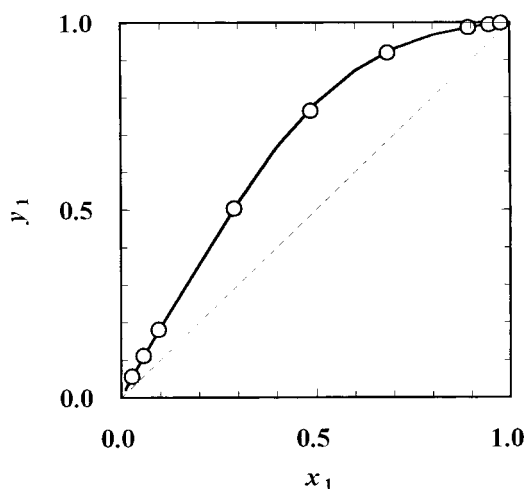


Figure 1. Vapor-liquid equilibria for the ethanol (1) + acetic acid (2) binary system at 323.2 K: \circ , present data; —, correlation with NRTL model with vapor-phase association.

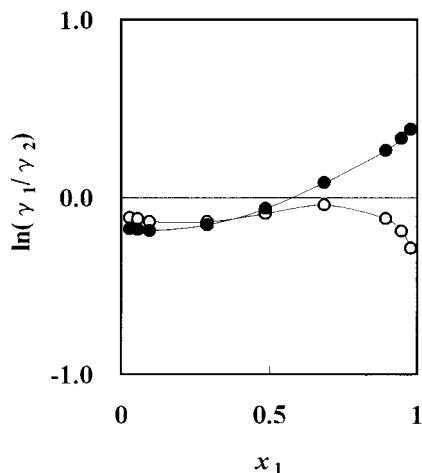


Figure 2. Area test for the ethanol (1) + acetic acid (2) binary system at 323.2 K: \circ , no heterodimer considered; \bullet , heterodimer considered.

pound and monocarboxylic acid exist in the vapor phase. They comprise an ideal gaseous mixture. On the basis of pVT relations of an ideal gaseous mixture in the equilibrium cell, the partial pressures are calculated as follows:

$$p_{1m}^{\text{av}} V = n_{1m} RT \quad (3)$$

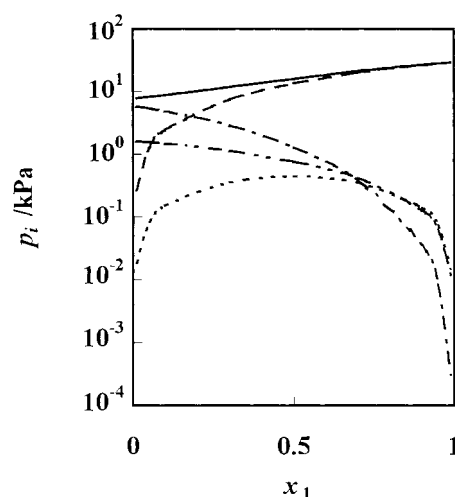


Figure 3. Partial pressures of monomers and dimers in the ethanol (1) + acetic acid (2) binary system at 323.2 K: —, monomer of ethanol; - - -, monomer of acetic acid; - · - ·, homodimer of acetic acid; · · · ·, heterodimer of ethanol and acetic acid; —, total pressure.

$$p_{2m}^{\text{av}} V = n_{2m} RT \quad (4)$$

$$p_{2d}^{\text{av}} V = n_{2d} RT \quad (5)$$

$$p_{12d}^{\text{av}} V = n_{12d} RT \quad (6)$$

$$p_{\text{He}}^{\text{av}} V = n_{\text{He}} RT \quad (7)$$

where p_i^{av} is the average partial pressure of each component i , and V is the volume all components occupy at temperature T and atmospheric pressure π . n is the amount of substance. Subscripts 1 and 2 indicate the polar component and the monocarboxylic acid, respectively. Subscripts m and d indicate the monomer and dimer, respectively. Subscript He denotes helium. Material balances can give the following relationships:

$$n_1 = n_{1m} + n_{12d} \quad (8)$$

$$n_2 = n_{2m} + 2n_{2d} + n_{12d} \quad (9)$$

The total pressure is obtained from

$$\pi = p_{1m}^{\text{av}} + p_{2m}^{\text{av}} + p_{2d}^{\text{av}} + p_{12d}^{\text{av}} + p_{\text{He}}^{\text{av}} \quad (10)$$

Table 5. Vapor–Liquid Equilibria for Ternary Systems

x_1	x_2	y_1	y_2	p/kPa
hexane (1) + acetic acid (2) + propionic acid (3) at 323.2 K				
0.152	0.209	0.853	0.064	31.9
0.149	0.420	0.814	0.129	36.3
0.105	0.655	0.756	0.211	36.5
0.339	0.217	0.890	0.060	43.2
0.342	0.434	0.843	0.130	47.3
0.565	0.215	0.895	0.075	50.0
water (1) + acetic acid (2) + propionic acid (3) at 343.2 K				
0.160	0.202	0.508	0.180	19.6
0.163	0.405	0.410	0.365	20.7
0.186	0.605	0.354	0.532	22.3
0.376	0.205	0.674	0.140	25.6
0.385	0.407	0.586	0.305	25.9
0.589	0.205	0.776	0.125	29.5
ethanol (1) + acetic acid (2) + propionic acid (3) at 323.2 K				
0.184	0.201	0.550	0.182	7.8
0.182	0.403	0.455	0.360	8.6
0.186	0.606	0.390	0.518	9.9
0.384	0.204	0.773	0.113	12.6
0.383	0.409	0.700	0.237	13.1
0.587	0.206	0.899	0.066	18.0
methyl ethyl ketone (1) + acetic acid (2) + propionic acid (3) at 323.2 K				
0.180	0.202	0.627	0.154	9.5
0.181	0.405	0.546	0.305	10.8
0.182	0.609	0.481	0.444	11.7
0.380	0.205	0.832	0.086	17.2
0.382	0.410	0.772	0.184	18.2
0.580	0.209	0.917	0.056	23.8
ethyl acetate (1) + acetic acid (2) + propionic acid (3) at 323.2 K				
0.182	0.202	0.660	0.142	10.9
0.183	0.405	0.583	0.281	12.0
0.182	0.610	0.517	0.414	13.0
0.380	0.205	0.846	0.080	19.1
0.380	0.412	0.788	0.171	20.1
0.584	0.207	0.922	0.054	27.0
formic acid (1) + acetic acid (2) + propionic acid (3) at 343.2 K				
0.182	0.197	0.394	0.226	15.8
0.185	0.399	0.345	0.414	17.6
0.190	0.602	0.310	0.573	20.6
0.382	0.201	0.594	0.183	22.9
0.391	0.403	0.543	0.346	25.3
0.592	0.202	0.729	0.162	29.5
acetic acid (1) + propionic acid (2) + butyric acid (3) at 358.2 K				
0.185	0.198	0.420	0.226	10.0
0.184	0.399	0.371	0.410	11.9
0.184	0.604	0.333	0.566	13.7
0.386	0.201	0.641	0.175	15.6
0.389	0.404	0.587	0.326	17.7
0.592	0.203	0.774	0.146	22.0

The partial pressures of the monomer and the homodimer of monocarboxylic acids are calculated with an association constant. In general, the association constant of each homodimer is given as a function of temperature⁵ by

$$K_i = \frac{P_{id}^{av}}{(P_{im}^{av})^2} f^{\phi} = \exp\left(\frac{\Delta S_i}{R} - \frac{\Delta H_i}{RT}\right) \quad (11)$$

where $f^0 = 101.3\text{kPa}$ and ΔS_i and ΔH_i are the entropy change and the enthalpy change for the association, respectively. We used $-149.0\text{ J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$ for ΔS_i and $-58.5\text{ kJ}\cdot\text{mol}^{-1}$ for ΔH_i for formic acid and $-136.0\text{ J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$ for ΔS_i and $-58.5\text{ kJ}\cdot\text{mol}^{-1}$ for ΔH_i for the other acids, which were determined in a previous work.⁵ On the other hand, the association constant for the heterodimer of polar compound and monocarboxylic acid is

$$K_{ij} = \frac{P_{ijd}}{P_{im}P_{jm}} f^{\phi} = 2 \exp\left(\frac{\Delta S_{ij}}{R} - \frac{\Delta H_{ij}}{RT}\right) \quad (12)$$

Because the entropy change ΔS_{ij} of the heterodimer can be assumed to be similar to the entropy change ΔS_i of the

homodimer of monocarboxylic acid, we used $-136.0\text{ J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$ for ΔS_{ij} . On the other hand, the enthalpy change ΔH_{ij} was determined from the data regression of vapor–liquid equilibria that satisfy the thermodynamic consistency area test. From eqs 3–12 can be obtained the average partial pressure p_i^{av} . The average total pressure p^{av} can be calculated with

$$p^{av} = p_{1m}^{av} + p_{2m}^{av} + p_{2d}^{av} + p_{12d}^{av} \quad (13)$$

The vapor–liquid equilibrium relationship can be given by $p^{av} - x_1^{av} - y_1^{av}$, because a small amount of the liquid sample was carried away by the helium.

For the ternary systems, vapor–liquid equilibrium relationships were also given by $p^{av} - x_1^{av} - x_2^{av} - y_1^{av} - y_2^{av}$ according to the similar procedure for the binary systems. The kinds of molecular species in the vapor phase assumed are shown in Table 1. The association constant for a heterodimer of two monocarboxylic acids³ is

$$K_{ij} = \frac{P_{ijd}}{P_{im}P_{jm}} f^{\phi} = 2\sqrt{K_i K_j} \quad (14)$$

The temperatures were regulated so that the total pressures were between 3 and 40 kPa. If the total pressure is $<3\text{ kPa}$, the measurement of one datum takes $>10\text{ h}$. On the other hand, when the total pressure is $>40\text{ kPa}$, the experimental error of the pressure measured is $>0.5\text{ kPa}$ because the total amount of helium gas supplied is very small.

Results and Discussion

Experimental Data. Before the measurement, the flow rate of helium was changed from 10 to 50 mL·min⁻¹. The experimental result did not depend on the flow rate. As a result, the flow rate of helium was controlled at $\sim 30\text{ mL}\cdot\text{min}^{-1}$ throughout the experiment. The vapor–liquid equilibria for polar compound + monocarboxylic acid binary systems obtained are summarized in Tables 2 and 3. A typical illustration is shown in Figure 1 for the ethanol + acetic acid binary system. Two thermodynamic consistency tests¹ (area test and point test) were performed and are shown in Table 4 with the values of ΔH_{ij} optimized for the present binary systems. The ranges of activity coefficients are also shown in Table 4. It seems to be difficult to clear the thermodynamic consistency area test because all of the binary systems except the systems containing water and dibutyl ether are close to an ideal solution. However, all of the present systems are eligible for the point test and 10 systems among all 15 systems are eligible for the area test. A typical illustration of the area test is shown in Figure 2 for the ethanol + acetic acid binary system. In this figure, two cases are shown, one considering the heterodimer of the polar compound and monocarboxylic acid and one neglecting the heterodimer. If the presence of the heterodimer is not considered, the system is not eligible for the area test. If the heterodimer and the optimized ΔH_{ij} are taken into account, the system is eligible for the area test. Ethanol, butanol, methyl ethyl ketone, ethyl acetate, ethyl propionate, and butyl aldehyde seem to associate with monocarboxylic acid. It is not clear that water and dibutyl ether associate with monocarboxylic acid. The partial pressures of each molecular species are evaluated from the association constants and are shown in Figure 3. The percentage of the heterodimer seems to be $<2\%$. Therefore, the effect of the heterodimer on the total pressure is very small.

Table 6. Saturated Vapor Pressure Equations

	eq type ^a	A	B	C	D	E
formic acid ^b	1	15.40560	-3894.764	-13.000		
acetic acid ^b	1	15.19234	-3654.622	-45.392		
propionic acid ^b	1	15.29686	-3670.949	-70.545		
butyric acid ^b	1	15.09674	-3599.963	-93.307		
water ^c	2	62.12291	-7258.200	-7.304	4.1653 × 10 ⁻⁶	2
ethanol ^d	1	16.89659	-3803.986	-41.670		
butanol ^c	2	81.64691	-9185.900	-9.746	4.7796 × 10 ⁻¹⁸	6
methyl ethyl ketone ^c	2	61.17191	-6143.600	-7.578	5.6476 × 10 ⁻⁶	2
ethyl acetate ^c	2	55.29791	-6227.600	-6.410	1.7914 × 10 ⁻¹⁷	6
ethyl propionate ^c	2	94.11391	-8007.000	-12.477	9.0000 × 10 ⁻⁶	2
butyl aldehyde ^c	2	87.80392	-7083.600	-11.733	1.0027 × 10 ⁻⁵	2
dibutyl ether ^c	2	62.58591	-7694.600	-7.306	8.7952 × 10 ⁻¹⁸	6
hexane ^d	1	13.80408	-2691.077	-48.940		

^a Vapor pressure equations: (1) $\ln[p^{\text{sat}}(\text{kPa})] = A + \{B/(T + C)\}$; (2) $\ln[p^{\text{sat}}(\text{kPa})/101.3] = A + (B/T) + C \ln(T) + DT^E$. ^b Ambrose and Ghiassaei. ^c DIPPR. ^d Yaws.⁸

Table 7. Parameters for NRTL Model and Average Deviations for Polar Compound + Monocarboxylic Acid Binary Systems

component 1	component 2	temp/K	$[(g_{12} - g_{22})/R]/K$	$[(g_{21} - g_{11})/R]/K$	α_{12}	Δy	$\Delta p/\text{kPa}$
water	acetic acid	343.2	444.976	269.867	1.303	0.004	0.4
ethanol	acetic acid	323.2	-287.184	483.886	0.649	0.002	0.3
butanol	acetic acid	323.2	-247.658	370.252	0.486	0.003	0.1
methyl ethyl ketone	acetic acid	323.2	243.903	-114.762	0.788	0.002	0.3
ethyl acetate	acetic acid	323.2	281.225	-108.966	0.494	0.004	0.1
butyl aldehyde	acetic acid	323.2	206.137	-44.494	0.417	0.002	0.4
dibutyl ether	acetic acid	343.2	370.106	454.072	0.928	0.002	0.4
water	propionic acid	343.2	685.363	378.723	0.695	0.005	0.6
ethanol	propionic acid	323.2	-303.852	528.918	0.434	0.001	0.2
butanol	propionic acid	343.2	-235.582	413.826	0.707	0.002	0.2
methyl ethyl ketone	propionic acid	323.2	229.232	-102.499	0.705	0.001	0.2
ethyl acetate	propionic acid	323.2	339.257	-107.145	0.718	0.001	0.3
ethyl propionate	propionic acid	323.2	360.876	-102.553	0.532	0.002	0.4
butyl aldehyde	propionic acid	323.2	387.070	-134.625	0.456	0.005	0.3
dibutyl ether	propionic acid	343.2	386.621	193.069	1.189	0.002	0.3
					av	0.002	0.3

Table 8. Prediction of Vapor-Liquid Equilibria for Ternary Systems

component 1	component 2	component 3	temp/K	Δy	$\Delta p/\text{kPa}$
hexane	acetic acid	propionic acid	323.2	0.003	1.4
water	acetic acid	propionic acid	343.2	0.005	0.3
ethanol	acetic acid	propionic acid	323.2	0.005	0.4
methyl ethyl ketone	acetic acid	propionic acid	323.2	0.002	0.5
ethyl acetate	acetic acid	propionic acid	323.2	0.009	0.3
formic acid	acetic acid	propionic acid	343.2	0.005	0.4
acetic acid	propionic acid	butyric acid	358.2	0.001	0.5
			av	0.004	0.5

For the ternary systems, ethanol, methyl ethyl ketone, and ethyl acetate are considered to associate with monocarboxylic acid. ΔH_{ij} values shown in Table 4 for the heterodimer between polar compound and monocarboxylic acid were used. Table 5 shows the vapor-liquid equilibria for the ternary systems.

Correlation and Prediction. The fundamental equation of vapor-liquid equilibria is given by

$$p\eta_{im} = \gamma_i x_i p_i^{\text{sat}} \eta_{im}^0 \quad (15)$$

where η_{im} is the monomer mole fraction of mixture in the vapor phase, η_{im}^0 is the monomer mole fraction of pure component at the same temperature of mixture, and p^{sat} is the saturated vapor pressure at the same temperature of mixture. The parameters of the saturated vapor pressure equations⁶⁻⁸ are presented in Table 6. η_{im}^0 is obtained from p^{sat} and the association constant of pure component.³ The activity coefficients γ_1 and γ_2 were obtained from p - x - y measured and eq 15. They were correlated by the NRTL model⁹ with the procedure given previously.³ The optimized parameters are listed in Table 7. The vapor-

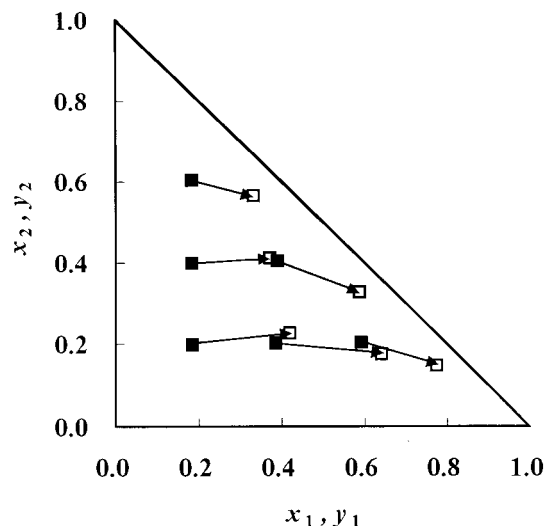


Figure 4. Vapor-liquid equilibria for the acetic acid (1) + propionic acid (2) + butyric acid (3) ternary system at 358.2 K: ■, x_{exptl} ; □, y_{exptl} ; →, prediction of tie line.

phase compositions and the total pressures calculated by applying the NRTL model to liquid-phase activity coefficients and by assuming vapor-phase association at given liquid-phase compositions were compared with the experimental data. The correlation performance Δy and Δp values for all binary systems are listed in Table 7. The average Δy and Δp values are 0.002 and 0.3 kPa, respectively. A typical illustration for the ethanol + acetic acid binary system is shown in Figure 1 with good agreement.

Then the vapor-liquid equilibria for the ternary systems were predicted by applying the NRTL model to liquid-phase activity coefficients and by assuming vapor-phase associa-

tion. The NRTL parameters and the association constants for the binary systems obtained in this work and previous work^{2,3} were used. In the present calculation, x_1 , x_2 , and T were given by the experimental data. The overall performance for prediction of Δy and Δp values for all ternary systems is given in Table 8. The average values of Δy and Δp are 0.004 and 0.5 kPa, respectively. A typical illustration for the acetic acid + propionic acid + butyric acid ternary system is shown in Figure 4 with good agreement.

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