Vapor Liquid Equilibrium Behavior of an Ethyl Acetate-Ethanol-Toluene System at Atmospheric Pressure

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The VLE data of 85 points for a system of ethyl acetate–ethanol–toluene were measured at atmospheric pressure. The results were examined by boilling-point calculations using two forms of the Wilson equation: one with constants of constituent binary systems and the other with constants from a least-squares fit minimizing the Q-function($g^E/RT=\sum x_i \ln \gamma_i$) of the ternary data. Two binary systems, ethyl acetate–ethanol and ethanol–toluene, show minimum azeotropic points. The normal boiling point of toluene is much higher than the boiling points of the other two substances by 32—3 K. Because the system had a complicated behavior, calculations using the Wilson equation had difficulty to accurately cover the entire area of compositions.

Distillation processes have been playing very important roles in the separation of a large number of chemical substances in various chemical industries. Accurate knowledge regarding the relations of vapor-liquid equilibria is fundamental for distillation, and is required in both designing and operating a distillation unit. In addition, briefly speaking, by carefully looking at the VLE many engineers can easily judge the extent of difficulty during separation by distillation.

Numerous VLE data for multi-component systems (mainly binary) have bee obtained, and some methods concerning VLE prediction have been proposed; however, both are not sufficient to satisfy requirements in actual chemical practice. There is thus a need to continue measurements of VLE in order to collect accurate VLE data, and to further develop new prediction methods.

Here, the VLE of an ethyl acetate–ethanol–toluene system, for which no data are available, were measured at atmospheric pressure. The system has the following complicated features: (1) Two binary systems, ethyl acetate–ethanol and ethanol–toluene, show minimum azeptropic points, though ethyl acetate–toluene does not. (2) The boiling points of pure ethyl acetate, ethanol, and toluene at 100.61 kPa are 350.04, 351.28 and 383.51 K, respectively; though the points of the former two substances are very close to each other, the point of the latter substance, toluene, are higher than the points of the former substances by 32—3 K.

The Wilson equation is most widely used to represent the relations of the VLE of binary and multi components systems, and multi-component system can be predicted from the VLE of the constituent binary systems. The following two forms of the Wilson equation were applied to our experimental results: one with constants from the constituent binary systems and the other with constants from a least-squares fit which minimized the Q-function($=\sum x_i \ln \gamma_i$) of the ternary data. The total average accuracies including the entire area of compositions as well as local accuracies of specific areas of the compositions were obtained. The applicability of the Wilson equation to the system is discussed.

Experimental

The experimental apparatus used was the same as that already described in the literature.[1)] The pressures were measured by a Fortin mercury barometer with an error of ±0.01 kPa. The temperatures were read from two mercury thermometers with 40—100 and 100—150 °C graduations calibrated at 5 K intervals with accuracies of 0.04 K.

Analyses of the liquid and vapor phases were carried out by gas chromatography on a Yanagimoto G-3600 Model unit

Table 1. Physical Properties of Chemicals

	T/K	Density ρ/g cm^{-3} Exptl	Density ρ/g cm^{-3} Lit	T/K	Refractive index n_D Exptl	Refractive index n_D Lit	Bp at atmospheric pressures	T/K Exptl	T/K Lit
Ethyl acetate	298.15	0.8943	0.89451[a)] 0.8946[b)]	293.15	1.37242	1.37243[a)]	100.53 kPa	349.99	350.03[c)]
Ethanol	298.15	0.7853	0.78508[b)] 0.78511[b)]	298.15	1.35927	1.35929[b)]	100.21 kPa	351.25	351.17[c)]
Toluene	298.15	0.8621	0.86220[a)] 0.86230[b)]	298.15	1.49411	1.49405[a)] 1.49413[b)]	100.64 kPa	383.47	383.53[c)]

a) Ref. 2. b) Ref. 3. c) The values interpolated from Ref. 4.

Table 2. Vapor–Liquid Equilibrium Data for the Ethyl Acetate(1)–Ethanol(2)–Toluene(3) System at 100.61 kPa

Run No.	T/K	Mole fraction								
		x_1	x_2	x_3	y_1	y_2	y_3	γ_1	γ_2	γ_3
1	348.10	0.275	0.463	0.262	0.296	0.578	0.126	1.140	1.411	1.057
2	352.52	0.164	0.242	0.594	0.177	0.578	0.245	0.995	2.279	1.092
3	351.33	0.286	0.241	0.473	0.304	0.501	0.195	1.017	2.075	1.100
4	349.19	0.425	0.257	0.318	0.424	0.451	0.125	1.022	1.901	1.129
5	347.64	0.576	0.250	0.174	0.553	0.380	0.067	1.034	1.748	1.167
6	349.50	0.168	0.445	0.387	0.182	0.630	0.188	1.097	1.516	1.381
7	346.98	0.389	0.449	0.162	0.403	0.518	0.079	1.138	1.362	1.513
8	348.21	0.149	0.631	0.220	0.183	0.670	0.147	1.296	1.195	1.987
9	347.15	0.240	0.627	0.133	0.294	0.618	0.088	1.337	1.156	2.042
10	350.75	0.369	0.219	0.412	0.382	0.448	0.170	1.009	2.087	1.123
11	348.43	0.504	0.255	0.241	0.493	0.410	0.097	1.027	1.793	1.186
12	347.99	0.137	0.743	0.120	0.198	0.700	0.102	1.535	1.069	2.549
13	346.47	0.608	0.299	0.093	0.570	0.391	0.039	1.048	1.574	1.324
14	349.77	0.148	0.432	0.420	0.158	0.640	0.202	1.071	1.570	1.354
15	348.93	0.210	0.465	0.325	0.221	0.613	0.166	1.085	1.443	1.481
16	347.50	0.332	0.460	0.208	0.352	0.551	0.097	1.145	1.386	1.421
17	349.03	0.107	0.619	0.274	0.131	0.696	0.173	1.258	1.226	1.824
18	348.09	0.173	0.639	0.188	0.216	0.658	0.126	1.322	1.164	2.001
19	346.49	0.288	0.636	0.076	0.356	0.595	0.049	1.380	1.126	2.037
20	348.74	0.079	0.816	0.105	0.126	0.767	0.107	1.654	1.036	2.978
21	347.60	0.151	0.798	0.051	0.238	0.713	0.049	1.697	1.029	2.922
22	348.18	0.111	0.843	0.046	0.189	0.761	0.050	1.799	1.017	3.241
23	348.44	0.113	0.742	0.145	0.158	0.720	0.122	1.464	1.082	2.483
24	349.06	0.121	0.588	0.291	0.143	0.682	0.175	1.214	1.263	1.736
25	350.81	0.133	0.373	0.494	0.139	0.622	0.239	1.016	1.698	1.314
26	355.70	0.157	0.150	0.693	0.190	0.502	0.308	1.013	2.836	1.024
27	354.53	0.297	0.131	0.572	0.361	0.403	0.236	1.054	2.727	0.988
28	349.73	0.280	0.324	0.396	0.291	0.541	0.168	1.045	1.772	1.196
29	347.73	0.248	0.545	0.207	0.282	0.603	0.115	1.220	1.268	1.680
30	346.95	0.226	0.702	0.072	0.302	0.642	0.056	1.470	1.080	2.419
31	346.00	0.377	0.559	0.064	0.418	0.544	0.038	1.258	1.193	1.909
32	347.26	0.436	0.375	0.189	0.433	0.486	0.081	1.082	1.512	1.317
33	350.97	0.472	0.157	0.371	0.497	0.362	0.141	1.020	2.311	1.026
34	349.66	0.593	0.153	0.254	0.598	0.316	0.086	1.019	2.194	0.956
35	346.37	0.582	0.321	0.097	0.549	0.412	0.039	1.058	1.550	1.274
36	348.42	0.694	0.155	0.151	0.665	0.282	0.053	1.007	2.028	1.034
37	347.20	0.514	0.336	0.150	0.495	0.443	0.062	1.050	1.544	1.272
38	346.73	0.343	0.531	0.126	0.376	0.554	0.070	1.214	1.243	1.740
39	347.41	0.190	0.697	0.113	0.256	0.659	0.085	1.457	1.098	2.300
40	348.85	0.072	0.831	0.097	0.118	0.780	0.102	1.691	1.030	3.060
41	349.04	0.073	0.727	0.200	0.099	0.738	0.163	1.392	1.106	2.355
42	348.43	0.171	0.594	0.235	0.202	0.653	0.145	1.237	1.226	1.820
43	348.37	0.308	0.411	0.281	0.320	0.550	0.130	1.091	1.496	1.367
44	350.29	0.524	0.164	0.312	0.543	0.341	0.116	1.026	2.156	1.027
45	352.95	0.414	0.125	0.461	0.473	0.349	0.178	1.042	2.617	0.975
46	350.28	0.225	0.336	0.439	0.237	0.569	0.194	1.042	1.759	1.223
47	349.80	0.094	0.516	0.390	0.105	0.686	0.209	1.121	1.407	1.508
48	351.35	0.082	0.364	0.554	0.086	0.657	0.257	1.002	1.800	1.237
49	355.40	0.225	0.136	0.639	0.281	0.448	0.271	1.055	2.823	0.987
50	348.72	0.079	0.817	0.104	0.125	0.769	0.106	1.640	1.039	2.979
51	346.77	0.662	0.247	0.091	0.612	0.354	0.034	1.024	1.702	1.166
52	357.35	0.163	0.122	0.715	0.210	0.462	0.328	1.027	3.020	1.002
53	349.51	0.037	0.889	0.074	0.066	0.839	0.095	1.806	1.010	3.656
54	349.48	0.052	0.924	0.024	0.102	0.864	0.034	1.990	1.001	4.043
55	348.63	0.091	0.898	0.011	0.171	0.815	0.014	1.959	1.004	3.739
56	347.54	0.145	0.837	0.018	0.240	0.741	0.019	1.785	1.022	3.219
57	346.81	0.197	0.791	0.012	0.303	0.686	0.011	1.699	1.030	2.867
58	346.22	0.264	0.715	0.021	0.359	0.625	0.016	1.532	1.062	2.432
59	345.54	0.353	0.634	0.013	0.422	0.569	0.008_7	1.378	1.120	2.187
60	345.39	0.421	0.556	0.023	0.461	0.526	0.013	1.268	1.187	1.857
61	345.11	0.508	0.477	0.015	0.516	0.477	0.007_5	1.187	1.268	1.658
62	345.33	0.599	0.375	0.026	0.570	0.419	0.011	1.104	1.406	1.391
63	345.79	0.721	0.263	0.016	0.657	0.336	0.006_5	1.043	1.578	1.313
64	347.21	0.831	0.140	0.029	0.758	0.231	0.011	0.997	1.923	1.165

Table 2. (Continued)

Run No.	T/K	Mole fraction								
		x_1	x_2	x_3	y_1	y_2	y_3	γ_1	γ_2	γ_3
65	348.90	0.905	0.063	0.032	0.871	0.117	0.012	0.997	2.024	1.084
66	350.19	0.868	0.051	0.081	0.870	0.094	0.036	0.996	1.915	1.230
67	351.79	0.810	0.030	0.160	0.868	0.070	0.062	1.013	2.279	1.015
68	352.40	0.719	0.050	0.231	0.783	0.120	0.097	1.010	2.292	1.078
69	355.12	0.653	0.027	0.320	0.784	0.075	0.141	1.025	2.400	1.033
70	355.83	0.557	0.044	0.399	0.696	0.133	0.171	1.044	2.543	0.982
71	358.68	0.491	0.026	0.483	0.683	0.092	0.225	1.067	2.681	0.972
72	359.64	0.402	0.040	0.558	0.566	0.157	0.277	1.050	2.875	1.005
73	363.72	0.327	0.023	0.650	0.543	0.104	0.353	1.101	2.866	0.966
74	364.38	0.243	0.036	0.721	0.417	0.183	0.400	1.116	3.154	0.968
75	369.47	0.165	0.021	0.814	0.338	0.133	0.529	1.156	3.303	0.971
76	370.47	0.091	0.030	0.879	0.185	0.221	0.594	1.115	3.718	0.980
77	355.29	0.020	0.199	0.781	0.022	0.633	0.345	0.932	2.736	1.032
78	352.41	0.030	0.317	0.653	0.031	0.678	0.291	0.956	2.049	1.147
79	351.39	0.018	0.425	0.557	0.019	0.700	0.281	1.007	1.641	1.344
80	350.51	0.026	0.545	0.429	0.029	0.719	0.252	1.093	1.359	1.612
81	350.16	0.015	0.623	0.362	0.018	0.744	0.238	1.190	1.246	1.827
82	349.75	0.024	0.691	0.285	0.030	0.753	0.217	1.253	1.156	2.145
83	349.73	0.014	0.757	0.229	0.019	0.777	0.204	1.362	1.089	2.512
84	349.66	0.021	0.874	0.105	0.036	0.837	0.127	1.724	1.019	3.422
85	350.05	0.020	0.932	0.048	0.039	0.890	0.071	1.938	1.001	4.134

provided with a flame ionization detector and an integrator. The column in the unit was 4 m in length and 3 mm in inner diameter and was packed with Porapak-S. Calibration curves with benzene as an internal standard were made by the gravimetric technique.

Each sample of both phases was analyzed twice; it was found that the accuracy of the unit was 0.0004 mole fraction. However, because the reproducibility of the equilibrium apparatus during operation might be less than 0.0004, the compositions were determined to the third decimal places (Table 2).

Ethyl acetate, ethanol and toluene of all commercial grades were used without further purification after being dehydrated by Molecular Sieves-3A. Their purities were confirmed to exceed 99.9% using the gas chromatograph mentioned above. Table 1 shows the densities, refractive indices and boiling points of the reagents, which have been compared with published values.[2-4)]

Results

The atmospheric pressure changed daily and fluctuated from 99.52 to 101.76 kPa during the experiment. Since a constant pressure was conveinent, it was represented by the mean pressure, 100.61 kPa; consequently, the temperatures during each run number were slightly adjusted. The results are given in Table 2 and Fig. 1. In Table 2, the activity coefficients, γ_i, were calculated using

$$\gamma_i = P y_i \phi_i / x_i f^0_i, \tag{1}$$

where P is the total pressure, x_i the liquid mole fraction of component i, y_i the vapor mole fraction of component i, and ϕ_i the fugacity coefficient of component i in a vapor mixture. The fugacity of a pure component i is given by f_i^0,

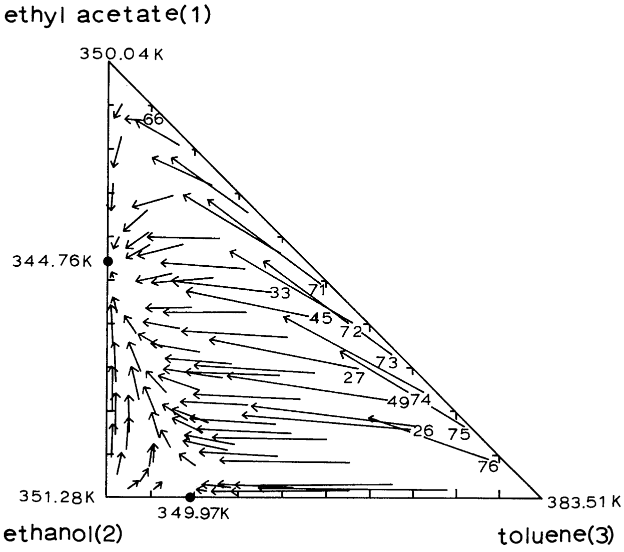

Fig. 1. Phase diagram of the ethyl acetate (1)–ethanol (2)–toluene (3) ternary system at 100.61 kPa. ●: azeotropic point. Arrows are drawn in the direction of liquid composition to vapor composition. All the boiling points of pure and azeotropic components are of 100.61 kPa. Run Nos. 66, 72—75 and 76 give the temperature differences of more than 0.5 K by the calculations with the constituent binary constants, but they give the differences of less than 0.5 K by those with the ternary constants. Run Nos. 26, 27, 33, 45, 49, and 71 give the temperature differences of more than 0.5 K by the calculations with the ternary constants, but they do the differences of less than 0.5 K by those with the constituent binary constants.

$$f^0{}_i = p^S{}_i \phi^S{}_i \exp[v^L{}_i(P - p^S{}_i)/RT] \tag{2}$$

where $p^S{}_i$ is the saturated vapor pressure of a pure component i at temperature T, $v^L{}_i$ the molar volume of liquid for a pure component, $\phi^S{}_i$ is the fugacity of a pure component at $p^S{}_i$ and T, and R is the gas constant.

ϕ_i was calculated as follows:

$$\ln \phi_i = \frac{2}{v}\sum_j^N y_i B_{ij} - \ln z, \tag{3}$$

where

$$z = \frac{Pv}{RT} = 1 + \frac{B}{v} \tag{4}$$

and

$$B = \sum_i^N \sum_j^N y_i y_j B_{ij}, \tag{5}$$

Here, v is the molar volume of a vapor mixture, z the compressibility factor of a vapor mixture, B the second virial coefficient of a vapor mixture, $B_{ij}(i \neq j)$ is cross-second virial coefficient between components of i and j, and B_{ii} the second virial coefficient of a pure component i.

$\phi^S{}_i$ was also given by

$$\ln \phi^S{}_i = \frac{2}{v^S{}_i} B_{ii} - \ln z_i, \tag{6}$$

where

$$z_i = \frac{p^S{}_i v^S{}_i}{RT} = 1 + \frac{B_{ii}}{v^S{}_i}, \tag{7}$$

Here, $v^S{}_i$ is the molar volume of satureted vapor for a pure component i, and z_i is the compressibility factor of a pure component. In Eqs 4 and 7, the quadratic equations for v and $v^S{}_i$, respectively, were solved. $p^S{}_i$ kPa was calculated from the Antoine equation with the constants of Gmehling et al.,[5]

$$\log p^S{}_i = a_{ai} - b_{ai}/(c_{ai} + T), \tag{8}$$

where the constants are reported in Table 3. The differences in temperatures for pure ethyl acetate, ethanol and toluene between the experimental and calculated values from Eq. 8, $\Delta T(=T_{\text{exptl}} - T_{\text{calcd}})$, are 0.02, 0.08, and −0.06 K, respectively, at the atmospheric pressures given in Table 1. $v^L{}_i$ cm^3 mol^{-1} was correlated as the quadratic equation of the temperature,

$$v^L{}_i = a_{mi} + b_{mi}T + c_{mi}T^2, \tag{9}$$

where the constants are listed in Table 4. The second virial coefficients, B_{ij}, were calculated by a method of Tsonopoulos.[7] Because of the small error and simple use, $\phi_i = 1$ and $f^0{}_i = p^S{}_i$ are assumed, and Eq. 1 is frequently represented as

$$Py_i = \gamma_i x_i p^S{}_i. \tag{10}$$

Table 3. Antoine Constants[a)]

Compound	a_{ai}	b_{ai}	c_{ai}
Ethyl acetate	6.22669	1244.951	−55.269
Ethanol	7.23710	1592.864	−46.966
Toluene	6.08295	1346.773	−53.457

a) Ref. 5.

Table 4. Constants of Liquid Molar Volumes[a)]

Compound	a_{mi}	b_{mi}	c_{mi}
Ethyl acetate	123.861	−0.27328	0.0006366
Ethanol	53.7004	−0.031108	0.000160
Toluene	98.8647	−0.0557782	0.000277

a) Made from the values of liquid molar volumes in the table of Ref. 6.

Discussion

The results were examined by the Wilson equation. The activity coefficient of the liquid phase for component i, γ_i, is expressed by Wilson as

$$\ln \gamma_i = 1 - \ln(\sum x_i \Lambda_{ij}) - \sum x_k \Lambda_{ki}/(\sum x_j \Lambda_{kj}), \tag{11}$$

where

$$\Lambda_{ij} = \frac{v^L{}_j}{v^L{}_i} \exp[-(\lambda_{ij} - \lambda_{ii})/RT] \tag{12}$$

$$(i \neq j)$$
$$i,j = 1, 2, \text{ or } 3$$
$$\Lambda_{11} = \Lambda_{22} = \Lambda_{33} = 1.0.$$

$\lambda_{ij} - \lambda_{ii}$ is called the Wilson constant for components i and j. The Q-function$(=g^E/RT)$ is also given as

$$Q = -\sum_{i=1}^N x_i \ln \left(\sum_{j=1}^N x_j \Lambda_{ij} \right) \tag{13}$$

where the Q-function is defined as $\sum x_i \ln \gamma_i$, and g^E is the excess molar Gibbs free energy.

Three pairs of binary constants, $\lambda_{12} - \lambda_{11}$ and $\lambda_{21} - \lambda_{22}$, for the ethyl acetate(1)–ethanol(2) system were selected from the literature of Gmehling et al.[5,8] Three paris of the ethanol(1)–toluene(2) system were extracted from the literature of Gmehling et al.[5,8] (each one pair) and our previous work[10] (one pair). For the ethyl acetate(1)–toluene(2) system, three pairs of Gmehling et al.[9] and one pair of Hirata et al.[11] (four pairs in total) were used.

Thirty six combinations of the pairs were applied to the calculations of VLE of the ethyl acetate(1)–ethanol(2)–toluene(3) system by the use of both Eqs 1 and 10 separately for the given experimental liquid compositions, and pressures. The vapor compositions and temperatures were obtaned.

All the three pairs of the ethyl acetate(1)-ethanol(2) system gave good correlations to almost the same extent. One pair of Gmehling et al.,[5] and that of our work for the ethanol(2)-toluene(3) system gave almost the same good correlations; another pair of Gmehling et al.,[8] however, provided a poor correlation. One pair of Gmehling et al. and that of Hirata et al. for the ethyl acetate(1)-toluene(3) system gave good correlations, though another two pairs of Gmehling et al. gave worse correlations. The three pairs of Gmehling et al.,[5,9] which are listed in the left side of Table 5, gave the best correlation.

The results of calculated VLE by the use of the above three pairs are summarized in Table 6. Though the correlation from Eq. 1 is almost identical with that from Eq. 10, the latter is slightly better than the former. The temperature differences between the experimental and calculated values exceed 0.5 K at the six points of Run Nos. 66, 72—75, and 76, and in all cases the calculated values are smaller than the experimental ones. All of the points, except No. 66, lie near the binary line of the ethyl acetate(1)-toluene(3) system of richer than 0.6 mole fraction of toluene in liquid (Fig. 1). The results regarding the other eleven combinations which gave good correlations show almost similar tendencies.

Table 5. Wilson Constants

System	Constants of binary system		Constants obtained directly from the ternary data	
	$\lambda_{ij}-\lambda_{ii}$/J mol^{-1}	$\lambda_{ji}-\lambda_{ii}$/J mol^{-1}	$\lambda_{ij}-\lambda_{ii}$/J mol^{-1}	$\lambda_{ji}-\lambda_{ii}$/J mol^{-1}
i=1, j=2	37.630[a)]	2636.72[a)]	−75.438	2775.18
i=2, j=3	5317.32[a)]	972.78[a)]	4478.10	1687.15
i=3, j=1	2850.39[b)]	−1474.19[b)]	3374.54	−1952.21

1: Ethyl acetate, 2: Ethanol, 3: Toluene. a) Ref. 5. b) Ref. 9.

Table 6. Capability of Predicting Vapor Compositions and the Temperatures for Ethyl Acetate(1)-Ethanol(2)-Toluene(3) System at 100.61 kPa by Use of the Wilson Equation with the Constants of the Three Binary Systems Described in Table 5

Used Eqs.	Differences of vapor-phase composition and temperature							
	Δy_1		Δy_2		Δy_3		ΔT/K	
	Av[a)]	Max[b)]	Av[a)]	Max[b)]	Av[a)]	Max[b)]	Av[a)]	Max[b)]
Eq. 1	0.006	0.035[c)]	0.007	−0.031[c)]	0.007	−0.023[d)]	0.21	1.49[e)]
Eq. 10	0.005	0.027[c)]	0.007	−0.034[c)]	0.005	−0.018[d)]	0.20	1.56[e)]

a) Average difference: $\Delta y_i=\Sigma|y_{i,\text{exptl}}-y_{i,\text{calcd}}|/n$, $\Delta T=\Sigma|T_{\text{exptl}}-T_{\text{calcd}}|/n$, n: number of data (=85). b) Maximum difference: $\Delta y_i=y_{i,\text{exptl}}-y_{i,\text{calcd}}$, $\Delta T=T_{\text{exptl}}-T_{\text{calcd}}$. c) Run. No. 75. d) Run. No. 45. e) Run No. 76.

Table 7. Capability of Predicting Vapor Compositions and the Temperatures for Each Binary System at Atmospheric Pressure by Use of the Wilson Equation with the Respective Constants Described in Table 5

Used Eqs.	Ethyl acetate(1)-ethanol(2) system[a)]				
	Δy_1		ΔT/K		
	Av	Max	Av	Max	
Eq. 1	0.002	−0.010	0.44	0.59	Pressure; 101.3 kPa
Eq. 10	0.002	−0.011	0.17	0.17	No. of data; 9
Used Eqs.	Ethanol(1)-toluene(2) system[b)]				
	Δy_1		ΔT/K		
	Av	Max	Av	Max	
Eq. 1	0.004	0.010	0.28	0.53	Pressure; 100.8 kPa
Eq. 10	0.010	0.017	0.23	−0.45	No. of data; 16
Used Eqs.	Ethyl acetate(1)-toluene(2) system[c)]				
	Δy_1		ΔT/K		
	Av	Max	Av	Max	
Eq. 1	0.006	−0.016	0.23	−0.58	Pressure; 101.3 kPa,
Eq. 10	0.004	0.010	0.27	−0.60	No. of data; 18

a) Ref. 12. b) Ref. 13. c) Ref. 14. The sysmols are the same as those of Table 6.

Table 8. Capability of Predicting Vapor Compositions and the Temperatures for Ethyl Acetate(1)–Ethanol(2)–Toluene(3) System at 100.61 kPa by Use of the Wilson Equation with the Constants, from the Ternary Data, Described in Table 5

Used Eqs.	Differences of vapor-phase composition and temperature							
	Δy_1		Δy_2		Δy_3		ΔT/K	
	Av	Max	Av	Max	Av	Max	Av	Max
Eq. 1	0.009	0.041[a)]	0.006	−0.022[a)]	0.006	−0.023[b)]	0.25	−0.74[c)]
Eq. 10	0.008	0.032[a)]	0.008	−0.024[a)]	0.004	−0.016[b)]	0.19	−0.82[c)]

a) Run. No. 73. b) Run No. 49. c) Run No. 45. The symbols are the same as those of Table 6.

In addition, the three pairs were also applied to the VLE calculations of the respective binary systems. The results were shown as the differences in the vapor compositions and the tempepratures between the experimental values from the literature[12–14)] and the calculated values given in Table 7. For the ethyl acetate–ethanol system though both Eqs 1 and 10 show good correlations, the latter is better than the former. For the ethanol–toluene system the correlation of Eq. 1 is better than that of Eq. 10. For the ethyl acetate–toluene system Eq. 10 gives a slightly better value than Eq. 1 does.

The other constants, $\lambda_{ij}-\lambda_{ii}$ and $\lambda_{ji}-\lambda_{jj}$, were directly determined by means of least-squares fit of Eq. 13 from all the ternary data of Table 2. The constants are listed in the right side of Table 5. Similar ternary VLE calculations with the constants were carried out; the results are given in Table 8. The correlation of Eq. 10 is better than that of Eq. 1. The temperature differences of the six points of Run Nos. 26, 27, 33, 45, 49, and 71, exceed 0.5 K and all of the calculated values are larger than the experimental ones. All of the points, except Run No. 71, form almost a straight line in Fig. 1.

The above eleven points of Run Nos. 72—76 and Nos. 26, 27, 33, 45, 49, and 71 (except No. 66) make one area, which has a large difference between vapor and liquid compositions and, consequently, is characterized by a large temperature slope against the liquid composition. Tables 6 and 7 show a correlation from the three binary systems is slightly better than that from the ternary data. Both, however, have almost the same accuracies.

Conclusion

(1) VLE data of 85 points for the ethyl acetate–ethanol–toluene system under atmospheric pressure were obtained.

(2) It was found that the Wilson equation did not necessarily give accurate predictions of the system over the entire area of the compositions. There is the certain part of the area in which the equation gives inaccurate predictions.

(3) The correlation using Eq. 1 is generally believed to be more correct than that using a convenient equation, Eq. 10. Inversely, the former was inferior to the latter; that is, the former showed no superiority against the latter.

References

1) H. Katayama and I. Watanabe, *J. Chem. Eng. Data,* **25**, 107 (1980).

2) J. Timmermans, "Physico-Chemical Constants of Pure Organic Compounds," Elsevier, Amsterdam (1950), Vol. 1, pp. 151, 417.

3) J. Timmermans, "Physico-Chemical Constants of Pure Organic Compounds," Elsevier, Amsterdam (1965), Vol. 2, pp. 100, 253, and 286.

4) T. Boublik, V. Fried, and E. Hala, "The Vapour Pressures of Pure Substances," 2nd revised ed, Elsevier, Amsterdam (1984), pp. 141, 260, and 546.

5) J. Gmehling and U. Onken, "Vapor-Liquid Equilibrium Data Collection," 1st ed, DECHEMA, Frankfurt (1977), Vol. 1, Part 2a, pp. 352, 354, and 470.

6) J. Prausnitz, C. Eckert, R. Orye, and J. O'Connell, "Computer Calculations for Multicomponent Vapor-Liquid Equilibria," Prentice-Hall Inc., Englewood Cliffs, N. J. (1967), pp. 214 and 215.

7) C. Tsonopoulos, *AIChE J,* **20**, 263 (1974).

8) J. Gmehling, U. Onken, and W. Art, "Vapor-Liquid Equilibrium Data Collection," 1st ed, DECHEMA, Frankfult (1982), Vol. 1, Part 2c, pp. 338, 444.

9) J. Gmehling, U. Onken, and P. Grenzheuser, "Vapor-Liquid Equilibrium Data Collection," 1st ed, DECHEMA, Frankfurt (1982), Vol. 1, Part 5, pp. 516, 520, and 529.

10) H. Katayama, unpublished paper.

11) M. Hirata, S. Ohe, and K. Nagahama, "Denshikeisanki ni yoru Kiekiheikou Data," Koudanshya Scientific, Tokyo (1975), p. 247.

12) J. Griswold, P. L. Chu, and W. O. Winsauer, *Ind. Eng. Chem.,* **41**, 2352 (1949).

13) J. C. Landwehr, S. Yerazunis, and H. H. Steinhauser, *J. Chem. Eng. Data,* **3**, 231(1985).

14) A. D. Carr and H. W. Kropholler, *J. Chem. Eng. Data,* **7**, 26 (1962).