Vapor−Liquid Equilibrium Data for Acetone + Methanol + Benzene, Chloroform + Methanol + Benzene, and Constituent Binary Systems at 101.3 KPa

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Isobaric vapor−liquid equilibria were measured for the ternary systems of acetone + methanol + benzene and chloroform + methanol + benzene and their constituent binary systems of acetone + benzene and methanol + benzene at atmospheric pressure. The pressure control system was the only modification of the apparatus described previously. Parameters of the Wilson and NRTL equations were determined from binary data, and the predictions for the two ternary systems were compared with experiments. The NRTL equation gave better results for the acetone + methanol + benzene system, and the Wilson equation yielded a better prediction for the chloroform + methanol + benzene system.

Introduction

This paper reports the experimental vapor−liquid equilibrium (VLE) data for the ternary systems acetone + methanol + benzene and chloroform + methanol + benzene and their constituent binary systems of acetone + benzene and methanol + benzene at 101.3 kPa. For the acetone + benzene system, we previously reported the isobaric VLE data at 101.3 kPa (Kojima et al., 1991), but the VLE measurement was performed again to check the new isobaric VLE measuring apparatus reported in this paper. Results for the constituent binary systems acetone + methanol, chloroform + methanol, and chloroform + benzene were reported in our previous publications (Kojima et al., 1991; Hiaki et al., 1994). The VLE data for the acetone + methanol + benzene system are not available in the literature. For the chloroform + methanol + benzene system, two data sets of isobaric VLE at 101.3 kPa were reported previously (Shishkin and Kotsyuba, 1955; Wisniak and Tamir, 1978). These experimental data, however, indicate that some tie lines cross. It was accordingly felt that the VLE data for the system chloroform + methanol + benzene at 101.3 kPa should be measured anew.

We also confirm whether these ternary systems exhibit an azeotrope and a valley in the liquid composition vs bubble point temperature surface from the behavior of the experimental vapor−liquid tie lines. The term “valley” has been defined as the curves that divide the patterns of vapor-liquid tie lines by Naka et al. (Naka et al., 1975, 1983). It is important to discuss the existence of the valley in addition to the azeotrope because the composition profiles of distillation columns are restricted by the valley.

Experimental Section

Apparatus and Procedure. In this VLE measurement, we have used a modified Rogalski−Malanowski equilibrium still combined with an isobaric VLE measuring apparatus by modifying the pressure-controlling system that was used in previous work (Kurihara et al., 1995). The apparatus contained an ebulliometer for a reference substance (water) in addition to an equilibrium still for samples. In this work, the apparatus was equipped with a pressure pump and the pressure in the still was controlled by a personal computer until the bubble temperature of water was equal to (373.124 ± 0.005) K ((99.974 ± 0.005) °C). A tube filled with silica gel was connected to the inlet pipe of the pressure pump to remove the moisture in the air. The modifications allow the measurement of VLE at 101.325 kPa to within ±0.036 kPa. The equilibrium temperature was measured with a calibrated platinum resistance thermometer with an accuracy of ±0.01 K.

Table 1. Densities, ρ, and Normal Boiling Points, T_b, of the Components

component	ρ (298.15 K)/(g cm^{-3}) exptl	ρ (298.15 K)/(g cm^{-3}) lit.[a]	T_b/K exptl	T_b/K lit.[a]
acetone	0.7842	0.784 40	329.26	329.217
chloroform	1.4797	1.479 70	334.33	334.328
methanol	0.7865	0.786 37	337.70	337.696
benzene	0.8736	0.873 60	353.24	353.244

[a] Riddick et al., 1986.

Analysis. Vapor and liquid samples were analyzed with a Simazu gas chromatograph type GC-8AIT equipped with a thermal conductivity cell. PEG 20M was used as column packing and helium as the carrier gas. The compositions were determined by the relative area method with an accuracy of ±0.001 mole fraction.

Materials. Acetone, methanol, and benzene were special grade pure reagents (Wako Pure Chemical Industry, Ltd., Japan) and were used after removing traces of water with molecular sieves. Water was used after ion exchange and distillation. The purity of the materials was checked by gas chromatography and found to be better than 99.9 mol %. In Table 1, some measured properties of the purified reagents are shown together with the literature values.

Experimental Results

The activity coefficients γ_i were calculated by the following equation

$$\varphi_i P y_i = x_i \gamma_i P_i^S \varphi_i^S \exp[\nu_i^L (P - P_i^S)/RT] \qquad (1)$$

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Table 2. Parameters, *a*, *b*, of the Polar Contribution Term in the Tsonopoulos Method and Antoine Constants of Components[a]

component	*a*	*b*	*A*	*B*	*C*
acetone	-3.45×10^{-2}[b]	0	6.242 00	1210.595	−43.486
chloroform	1.45×10^{-4}[b]	0	6.079 60	1170.966	−46.918
methanol	8.78×10^{-2}[c]	6.40×10^{-2}[d]	7.205 87	1582.271	−33.424
benzene	0	0	6.017 60	1203.531	−53.262

[a] $\log(P/\mathrm{kPa}) = A - B/[(T/\mathrm{K}) + C]$ (Boublik et al., 1973). [b] Dymond and Smith, 1969. [c] Tsonopoulos, 1974. [d] Tsonopoulos et al., 1989.

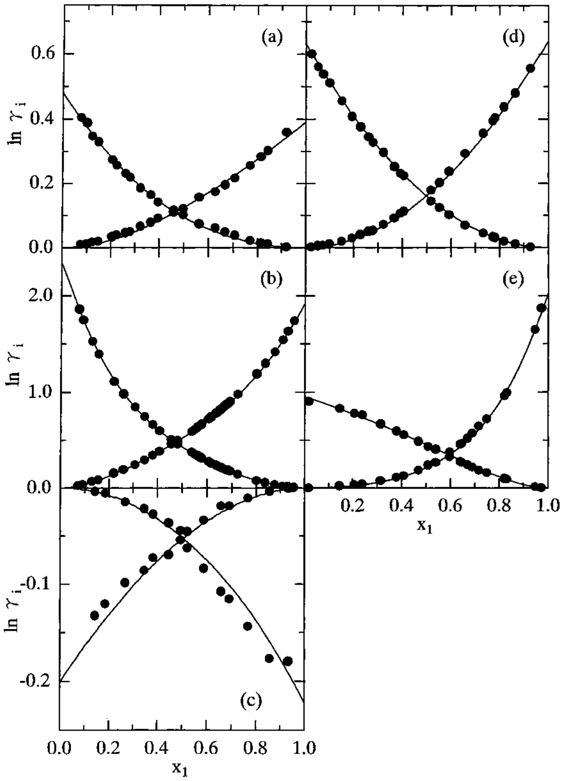

Figure 1. Activity coefficient−liquid composition diagram for the binary systems (a) acetone (1) + benzene (2), (b) methanol (1) + benzene (2), (c) chloroform (1) + benzene (2), (d) acetone (1) + methanol (2), and (e) chloroform (1) + methanol (2): (●) experimental; (—) NRTL equation.

where φ_i and φ_i^{S} are the fugacity coefficients of component *i* in the mixture and the pure vapor, respectively. They were calculated using the second virial coefficients obtained by the Tsonopoulos method (Tsonopoulos, 1974). The parameters, a_i, b_i, of pure components in the polar contribution term of the Tsonopoulos method are shown in Table 2, and the binary constants, k_{ij}, were set as 0.05 for acetone + methanol, 0.12 for acetone + benzene, 0.20 for methanol + benzene, −0.03 for chloroform + methanol, and zero for chloroform + benzene as recommended by Tsonopoulos (Tsonopoulos, 1974, 1975) except for the value of k_{ij} for chloroform + methanol, which was determined from the second virial coefficients of chloroform + ethanol reported by Markuzin and Baindin (1973) because the second virial coefficient data for this system were not available. The liquid molar volumes, v_i^{L}, were calculated by the modified Rackett equation (Spencer and Adler, 1978). The vapor pressures of the pure components, P_i^{S}, were calculated from the Antoine equation constants (Boublik et al., 1973) shown in Table 2.

Table 3. Isobaric Vapor−Liquid Equilibrium Data, Liquid Phase, x_1, and Vapor Phase, y_1, Mole Fractions, Temperature, *T*, and Activity Coefficients, γ_i, for the Two Binary Systems at 101.3 kPa

x_1	y_1	*T*/K	γ_1	γ_2
		Acetone (1) + Benzene (2)		
0.076	0.198	348.30	1.498	1.009
0.101	0.250	347.01	1.473	1.010
0.124	0.287	346.03	1.414	1.016
0.149	0.329	344.98	1.388	1.018
0.207	0.408	342.88	1.313	1.032
0.226	0.430	342.28	1.289	1.039
0.262	0.472	341.22	1.257	1.046
0.281	0.493	340.66	1.244	1.050
0.325	0.534	339.56	1.202	1.067
0.367	0.573	338.54	1.177	1.080
0.398	0.597	337.93	1.151	1.095
0.462	0.650	336.64	1.121	1.114
0.501	0.680	335.90	1.106	1.127
0.565	0.722	334.84	1.074	1.167
0.629	0.768	333.74	1.061	1.189
0.669	0.793	333.17	1.049	1.215
0.709	0.818	332.62	1.038	1.240
0.772	0.856	331.86	1.021	1.289
0.816	0.883	331.32	1.014	1.325
0.845	0.901	330.97	1.010	1.350
0.922	0.949	330.08	1.002	1.431
		Benzene (1) + Methanol (2)		
0.075	0.449	336.31	6.400	1.025
0.092	0.474	335.36	5.706	1.030
0.129	0.503	333.90	4.564	1.068
0.155	0.521	333.35	4.016	1.082
0.221	0.541	332.41	3.032	1.164
0.260	0.552	332.09	2.661	1.210
0.308	0.565	331.82	2.323	1.269
0.347	0.571	331.67	2.095	1.334
0.381	0.575	331.54	1.931	1.400
0.409	0.578	331.45	1.815	1.461
0.458	0.586	331.30	1.652	1.572
0.483	0.590	331.25	1.580	1.636
0.540	0.602	331.17	1.446	1.791
0.552	0.602	331.14	1.416	1.841
0.564	0.605	331.12	1.394	1.879
0.575	0.607	331.12	1.372	1.918
0.580	0.607	331.11	1.360	1.941
0.608	0.613	331.10	1.311	2.050
0.615	0.615	331.11	1.300	2.076
0.618	0.615	331.11	1.293	2.092
0.636	0.620	331.12	1.266	2.167
0.639	0.620	331.11	1.261	2.186
0.642	0.622	331.12	1.258	2.192
0.654	0.624	331.12	1.239	2.256
0.655	0.624	331.14	1.236	2.261
0.658	0.625	331.13	1.233	2.276
0.669	0.629	331.13	1.220	2.327
0.676	0.630	331.14	1.209	2.370
0.684	0.634	331.16	1.201	2.403
0.691	0.635	331.17	1.190	2.450
0.695	0.638	331.18	1.189	2.461
0.725	0.647	331.26	1.151	2.656
0.803	0.684	331.71	1.078	3.275
0.838	0.708	332.06	1.054	3.642
0.877	0.745	332.67	1.034	4.111
0.911	0.786	333.46	1.017	4.654
0.932	0.818	334.07	1.010	5.084
0.956	0.865	335.01	1.003	5.663

Binary Systems. The binary VLE data of acetone + benzene and methanol + benzene are reported in Table 3 and Figure 1 along with the activity coefficients calculated by eq 1. Figure 1 also shows the activity coefficients for the constituent binary systems chloroform + benzene, acetone + methanol, and chloroform + methanol, which were reported in our previous work (Kojima et al., 1991; Hiaki et al., 1994). The experimental VLE data were examined by the thermodynamic consistency test proposed in our previous paper (Kojima et al., 1990; Moon et al.,

Table 4. Isobaric Vapor−Liquid Equilibrium Data, Liquid Phase, x_i, and Vapor Phase, y_i, Mole Fractions, Temperature, T, and Activity Coefficients, γ_i, for the Two Ternary Systems at 101.3 kPa

x_1	x_2	y_1	y_2	T/K	γ_1	γ_2	γ_3	x_1	x_2	y_1	y_2	T/K	γ_1	γ_2	γ_3
Acetone (1) + Methanol (2) + Benzene (3)															
0.023	0.511	0.023	0.584	331.14	0.975	1.485	1.746	0.400	0.513	0.455	0.452	329.64	1.140	1.223	2.353
0.024	0.904	0.041	0.784	333.60	1.548	1.017	4.686	0.405	0.224	0.428	0.328	330.89	1.015	1.944	1.373
0.060	0.831	0.091	0.703	332.27	1.427	1.046	3.799	0.413	0.434	0.442	0.417	329.61	1.073	1.337	2.025
0.066	0.103	0.091	0.419	335.04	1.179	4.568	1.060	0.426	0.067	0.523	0.160	333.93	1.067	2.842	1.172
0.066	0.876	0.113	0.755	333.28	1.561	1.024	4.437	0.439	0.380	0.461	0.387	329.61	1.051	1.420	1.844
0.094	0.623	0.108	0.585	330.87	1.125	1.232	2.273	0.447	0.207	0.472	0.301	330.81	1.015	1.941	1.375
0.118	0.210	0.132	0.456	332.54	1.034	2.682	1.204	0.467	0.041	0.591	0.100	334.48	1.079	2.854	1.157
0.136	0.533	0.148	0.543	330.73	1.068	1.346	1.963	0.478	0.395	0.506	0.382	329.35	1.067	1.364	1.958
0.146	0.133	0.182	0.387	333.95	1.098	3.412	1.116	0.489	0.192	0.514	0.276	330.72	1.012	1.930	1.385
0.149	0.727	0.199	0.616	331.20	1.290	1.096	3.106	0.492	0.342	0.511	0.355	329.47	1.042	1.459	1.782
0.154	0.584	0.174	0.553	330.65	1.110	1.255	2.200	0.498	0.038	0.620	0.089	334.16	1.071	2.778	1.169
0.175	0.508	0.191	0.521	330.60	1.072	1.363	1.919	0.504	0.275	0.518	0.319	329.79	1.020	1.613	1.608
0.191	0.434	0.203	0.494	330.71	1.039	1.508	1.698	0.508	0.420	0.548	0.384	329.18	1.092	1.299	2.115
0.201	0.546	0.225	0.524	330.45	1.104	1.283	2.110	0.523	0.148	0.559	0.228	331.07	1.016	2.046	1.346
0.209	0.257	0.225	0.427	331.65	1.019	2.128	1.321	0.532	0.108	0.586	0.186	331.73	1.024	2.235	1.286
0.214	0.735	0.304	0.612	331.36	1.360	1.071	3.423	0.537	0.261	0.550	0.302	329.69	1.018	1.618	1.604
0.218	0.668	0.278	0.569	330.72	1.245	1.125	2.841	0.553	0.033	0.669	0.070	333.66	1.056	2.572	1.198
0.219	0.164	0.255	0.368	332.96	1.055	2.737	1.181	0.562	0.245	0.573	0.287	329.66	1.014	1.642	1.591
0.229	0.569	0.264	0.522	330.35	1.138	1.232	2.264	0.579	0.156	0.605	0.219	330.50	1.010	1.911	1.412
0.250	0.142	0.296	0.333	333.23	1.061	2.835	1.169	0.587	0.331	0.607	0.324	328.98	1.051	1.409	1.898
0.254	0.459	0.272	0.477	330.34	1.056	1.399	1.865	0.610	0.351	0.637	0.328	328.82	1.067	1.354	2.040
0.274	0.085	0.357	0.249	334.78	1.109	3.350	1.115	0.617	0.297	0.631	0.300	328.96	1.039	1.458	1.811
0.274	0.555	0.314	0.503	330.18	1.135	1.227	2.303	0.621	0.140	0.646	0.196	330.40	1.007	1.918	1.412
0.275	0.619	0.337	0.532	330.34	1.208	1.155	2.652	0.646	0.263	0.656	0.274	328.96	1.031	1.507	1.737
0.297	0.457	0.321	0.461	330.13	1.071	1.371	1.906	0.658	0.125	0.681	0.176	330.31	1.004	1.940	1.414
0.310	0.316	0.323	0.407	330.67	1.013	1.717	1.519	0.669	0.292	0.682	0.286	328.66	1.045	1.434	1.877
0.320	0.204	0.348	0.345	331.71	1.021	2.170	1.305	0.682	0.222	0.686	0.243	329.01	1.019	1.584	1.667
0.323	0.578	0.386	0.499	330.04	1.186	1.176	2.519	0.707	0.105	0.730	0.147	330.20	1.004	1.944	1.412
0.327	0.468	0.355	0.456	329.98	1.079	1.332	1.995	0.728	0.240	0.731	0.244	328.60	1.030	1.498	1.793
0.350	0.499	0.389	0.460	329.82	1.110	1.269	2.181	0.750	0.220	0.749	0.228	328.60	1.024	1.529	1.760
0.351	0.077	0.444	0.201	334.41	1.085	3.038	1.142	0.765	0.122	0.770	0.153	329.47	1.002	1.795	1.513
0.361	0.415	0.383	0.425	329.92	1.055	1.406	1.858	0.816	0.110	0.817	0.132	329.21	1.004	1.742	1.549
0.372	0.378	0.391	0.405	330.05	1.040	1.465	1.759	0.844	0.092	0.844	0.112	329.24	1.002	1.769	1.545
0.398	0.352	0.416	0.388	329.97	1.036	1.514	1.696								
Chloroform (1) + Methanol (2) + Benzene (3)															
0.008	0.815	0.012	0.689	331.79	1.668	1.067	3.441	0.219	0.576	0.269	0.534	329.90	1.439	1.269	2.072
0.011	0.733	0.015	0.646	331.25	1.539	1.138	2.741	0.237	0.609	0.312	0.531	329.64	1.555	1.206	2.218
0.016	0.618	0.018	0.610	331.05	1.275	1.286	2.114	0.240	0.691	0.365	0.546	329.53	1.804	1.097	2.819
0.028	0.919	0.060	0.802	333.97	2.238	1.008	4.957	0.251	0.449	0.268	0.503	330.11	1.240	1.523	1.631
0.036	0.800	0.057	0.674	331.66	1.766	1.069	3.353	0.259	0.546	0.312	0.513	329.62	1.422	1.302	1.952
0.044	0.452	0.042	0.571	331.18	1.075	1.640	1.586	0.262	0.068	0.240	0.373	335.42	0.892	6.094	1.021
0.053	0.824	0.091	0.687	331.90	1.902	1.048	3.662	0.280	0.575	0.360	0.508	329.30	1.533	1.241	2.002
0.053	0.702	0.071	0.622	331.03	1.520	1.155	2.610	0.283	0.373	0.282	0.483	330.15	1.154	1.760	1.456
0.062	0.564	0.067	0.585	330.92	1.228	1.360	1.941	0.302	0.136	0.261	0.429	332.48	0.926	3.919	1.081
0.064	0.886	0.130	0.752	333.12	2.173	1.015	4.610	0.318	0.547	0.391	0.489	328.99	1.480	1.272	1.974
0.065	0.598	0.074	0.591	330.89	1.295	1.297	2.076	0.325	0.431	0.348	0.474	329.49	1.267	1.535	1.591
0.066	0.484	0.066	0.570	331.02	1.132	1.539	1.680	0.344	0.171	0.301	0.432	331.57	0.965	3.253	1.114
0.066	0.181	0.054	0.512	332.73	0.873	3.464	1.124	0.345	0.389	0.355	0.463	329.63	1.211	1.653	1.484
0.069	0.632	0.082	0.597	330.87	1.354	1.240	2.245	0.359	0.470	0.405	0.465	328.94	1.358	1.413	1.690
0.078	0.581	0.088	0.583	330.83	1.286	1.320	2.019	0.370	0.481	0.428	0.459	328.68	1.404	1.378	1.701
0.084	0.537	0.090	0.575	330.86	1.219	1.408	1.846	0.381	0.092	0.340	0.375	333.35	0.928	4.909	1.026
0.091	0.584	0.104	0.580	330.77	1.305	1.310	2.038	0.397	0.507	0.475	0.448	328.16	1.477	1.304	1.831
0.100	0.671	0.131	0.597	330.75	1.498	1.174	2.494	0.410	0.382	0.425	0.442	329.02	1.243	1.649	1.415
0.101	0.176	0.083	0.501	332.68	0.878	3.495	1.123	0.414	0.098	0.371	0.368	332.68	0.951	4.646	1.038
0.110	0.521	0.118	0.565	330.77	1.223	1.432	1.799	0.415	0.223	0.374	0.426	330.34	1.034	2.585	1.166
0.121	0.563	0.138	0.567	330.64	1.306	1.336	1.964	0.443	0.115	0.394	0.374	331.93	0.967	4.143	1.046
0.136	0.612	0.167	0.572	330.47	1.415	1.248	2.193	0.453	0.489	0.521	0.436	327.60	1.446	1.347	1.726
0.142	0.639	0.184	0.574	330.44	1.495	1.201	2.343	0.472	0.357	0.478	0.418	328.56	1.232	1.703	1.367
0.148	0.299	0.130	0.519	331.36	0.980	2.243	1.299	0.482	0.279	0.457	0.410	329.19	1.129	2.085	1.223
0.149	0.670	0.204	0.579	330.38	1.583	1.158	2.548	0.503	0.144	0.447	0.372	330.71	1.006	3.456	1.066
0.156	0.701	0.228	0.586	330.38	1.690	1.120	2.765	0.510	0.437	0.566	0.399	327.32	1.406	1.399	1.550
0.157	0.494	0.167	0.544	330.57	1.220	1.467	1.744	0.539	0.267	0.507	0.391	328.74	1.136	2.118	1.173
0.163	0.734	0.257	0.596	330.42	1.822	1.086	3.032	0.550	0.070	0.505	0.303	332.85	0.967	5.342	0.973
0.165	0.343	0.150	0.522	331.05	1.025	1.991	1.379	0.590	0.300	0.570	0.374	327.82	1.202	1.875	1.173
0.172	0.764	0.292	0.607	330.55	1.955	1.056	3.340	0.608	0.188	0.545	0.358	328.97	1.073	2.735	1.051
0.173	0.582	0.209	0.552	330.28	1.399	1.278	2.077	0.647	0.069	0.591	0.275	331.86	0.993	5.127	0.940
0.177	0.794	0.326	0.619	330.72	2.110	1.029	3.993	0.693	0.219	0.622	0.339	327.73	1.118	2.342	1.023
0.198	0.466	0.207	0.528	330.40	1.204	1.521	1.670	0.695	0.079	0.621	0.277	330.79	1.005	4.708	0.933
0.202	0.087	0.179	0.406	335.08	0.873	5.243	1.045	0.729	0.043	0.689	0.209	332.64	1.000	6.092	0.866
0.212	0.305	0.192	0.501	331.04	1.020	2.152	1.314	0.829	0.055	0.737	0.217	330.41	1.011	5.405	0.830

1991), which permits overall evaluation of the data by combining three tests, namely, a point test, an area test, and an infinite dilution test. The results indicate that the reported data for both systems are thermodynamically consistent. For the acetone + benzene and methanol + benzene systems at 101.3 kPa, there are 6 and 15 data sets,

Table 5. Parameters and Deviations between the Calculated and Experimental Vapor-Phase Mole Fractions, Δy_1, and Temperature, ΔT, for the Five Binary Systems Using the Wilson and NRTL Equations[a]

parameter	acetone (1) + methanol (2)	methanol (1) + benzene (2)	acetone (1) + benzene (2)	chloroform (1) + methanol (2)	chloroform (1) + benzene (2)
			Wilson Equation		
$\lambda_{12} - \lambda_{11}$[b]	−767.72	7476.31	1991.5	−1492.36	−181.72
$\lambda_{12} - \lambda_{22}$[b]	2692.40	730.83	−569.94	7509.93	−401.78
			NRTL Equation		
$g_{12} - g_{22}$[b]	770.15	3352.10	−156.80	5942.88	−86.75
$g_{21} - g_{11}$[b]	1023.18	5003.95	1572.56	−308.55	−501.44
α_{12}	0.1099	0.5020	0.4307	0.3253	0.3000

	$\Delta y_1 \times 100$	ΔT/K	$\Delta y_1 \times 100$	ΔT/K	$\Delta y_1 \times 100$	ΔT/K	$\Delta y_1 \times 100$	ΔT/K	$\Delta y_1 \times 100$	ΔT/K
					Wilson Equation					
avg.	0.2	0.04	0.2	0.06	0.2	0.09	0.7	0.13	0.2	0.07
max.	0.4	0.09	0.4	0.16	0.4	0.20	1.3	0.24	0.4	0.15
					NRTL Equation					
avg.	0.2	0.04	0.2	0.02	0.2	0.09	0.5	0.15	0.2	0.07
max.	0.3	0.07	0.5	0.17	0.4	0.21	1.1	0.30	0.4	0.15

[a] $\Delta y_1 = \sum_k |y_{1,\mathrm{exp}} - y_{1,\mathrm{calc}}|_k/N$, $\Delta T = 100 \sum_k |T_{\mathrm{exp}} - T_{\mathrm{calc}}|_k/N$, N = number of data points. [b] J mol^{-1}.

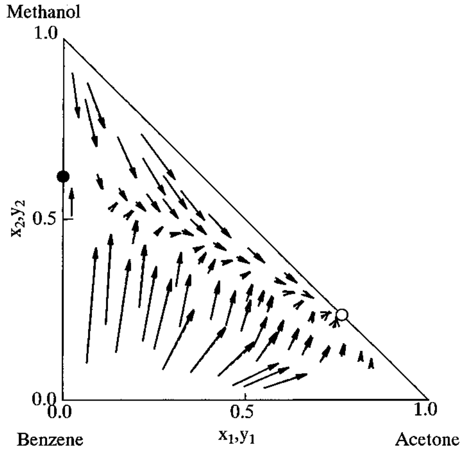

Figure 2. Vapor−liquid equilibrium tie lines (tails of arrows represent liquid-phase mole fractions x_1, x_2, and heads of arrows represent vapor-phase mole fractions y_1, y_2) for acetone (1) + methanol (2) + benzene (3) at 101.3 kPa: (○) azeotropic point of acetone (1) + methanol (2) (x_1(AZ) = 0.775, T(AZ) = 328.39 K reported by Hiaki et al. (1994)); (●) azeotropic point of methanol (2) + benzene (3); (→) experimental values; (- - ->) NRTL equation.

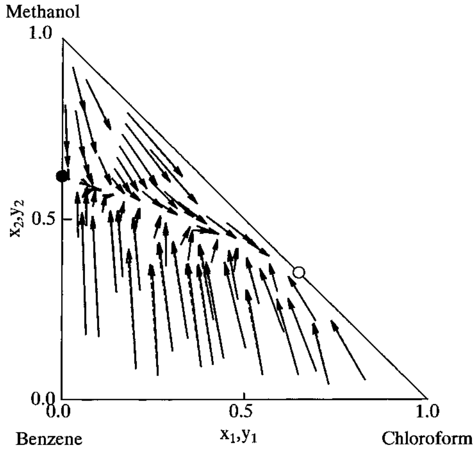

Figure 3. Vapor−liquid equilibrium tie lines (tails of arrows represent liquid-phase mole fractions x_1, x_2, and heads of arrows represent vapor-phase mole fractions y_1, y_2) for chloroform (1) + methanol (2) + benzene (3) at 101.3 kPa: (○) azeotropic point of chloroform (1) + methanol (2) (x_1(AZ) = 0.650, T(AZ) = 326.48 K reported by Hiaki et al. (1994)); (●) azeotropic point of methanol (2) + benzene (3); (→) experimental values; (- - ->) Wilson equation.

containing pressure, liquid composition, and vapor composition, available in the literature (Gmehling and Onken, 1977−1982), respectively. However, only seven data sets [Müller and Stage (1961), Free and Hutchison (1959); and Kojima et al., (1991) (our previous work) for acetone + benzene; Hudson and Van Winkle (1969); Nagata (1969); Triday et al. (1978); and Coca and Pis (1979) for methanol + benzene] are consistent with our proposed test.

The methanol (1) + benzene (2) system forms a minimum boiling azeotrope. The binary azeotropic point was determined by a graphical method (Hiaki et al., 1986) on the basis of experimental VLE data and is x_1(AZ) = 0.615 and T(AZ) = 331.11 K. The agreement between literature [x_1(AZ) = 0.616 and T(AZ) = 331.11 K] reported by Tochigi et al. (1985) and experimental azeotropic data was good.

Ternary System. Table 4 and Figures 2 and 3 show the experimental VLE data for the ternary systems of acetone + methanol + benzene and chloroform + methanol + benzene at 101.3 kPa. The tails of the solid arrows in Figures 2 and 3 represent experimental liquid compositions, and the heads of the arrows show experimental vapor compositions on the same tie line. The valleys were observed from the behavior of those tie lines in both figures. For the acetone + methanol + benzene system, the valley connected the two binary minimum boiling azeotropes of methanol + benzene and acetone + methanol. Similarly, the chloroform + methanol + benzene system has a valley from the binary minimum boiling azeotrope of methanol + benzene to that of chloroform + methanol. The vapor−

Table 6. Deviations between the Calculated and Experimental Vapor-Phase Mole Fractions, Δy_i, and Temperature, ΔT, for the Two Ternary Systems Using the Wilson and NRTL Equations[a]

	acetone (1) + methanol (2) + benzene (3)			chloroform (1) + methanol (2) + benzene (3)		
deviation	$\Delta y_1 \times$ 100	$\Delta y_2 \times$ 100	ΔT/K	$\Delta y_1 \times$ 100	$\Delta y_2 \times$ 100	ΔT/K
			Wilson Equation			
avg.	0.2	0.4	0.12	0.2	0.3	0.07
max.	0.7	0.8	0.43	0.9	1.2	0.40
			NRTL Equation			
avg.	0.2	0.2	0.13	0.4	0.6	0.20
max.	0.5	0.7	0.21	2.0	2.2	0.72

[a] $\Delta y_i = \sum_k |y_{i,\mathrm{exp}} - y_{i,\mathrm{calc}}|_k/N$, $\Delta T = 100 \sum_k |T_{\mathrm{exp}} - T_{\mathrm{calc}}|_k/N$, N = number of data points.

liquid tie lines of both systems near each valley turn toward the valleys.

For the chloroform + methanol + benzene system at 101.3 kPa, Wisniak and Tamir (1978) indicated that the system probably exhibits azeotrope behavior. We, however, conclude that both ternary systems in this work do not have an azeotropic point at atmospheric pressure on the basis of the behavior of the experimental tie lines in Figures 2 and 3.

Correlation and Prediction

The activity coefficients of the binary systems were correlated by the Wilson (Wilson, 1964) and NRTL equations (Renon and Prausnitz, 1968). The following objective function was minimized during optimization of the parameters in each of the two equations:

$$\mathrm{OF} = \sum_{k=1}^{N}\left[\left(\frac{\gamma_{1,\mathrm{calc}} - \gamma_{1,\mathrm{exp}}}{\gamma_{1,\mathrm{exp}}}\right)_k^2 + \left(\frac{\gamma_{2,\mathrm{calc}} - \gamma_{2,\mathrm{exp}}}{\gamma_{2,\mathrm{exp}}}\right)_k^2\right] \quad (2)$$

Table 5 lists the estimated parameters of five binary systems and the deviations between experimental and calculated vapor-phase compositions and bubble point temperatures. In Table 5, the parameters for the constituent binary systems of acetone + methanol, chloroform + methanol, and chloroform + benzene were determined from the VLE data at 101.3 kPa presented in our previous work (Kojima et al., 1991; Hiaki et al., 1994). The liquid molar volumes, v_i^{L}, in the Wilson equation were predicted by the modified Rackett equation, since the influence of pressure on the v_i^{L} is small at the temperature range in this work. The Wilson and NRTL equations yielded similar results. The solid lines in Figure 1 show the correlated results by the NRTL equation.

The predictions of the VLE of the two ternary systems acetone + methanol + benzene and chloroform + methanol + benzene using the binary Wilson and NRTL parameters are shown in Table 5. The results are summarized in Table 6. The NRTL equation gave the lower deviations for the acetone + methanol + benzene system. On the other hand, the results for the Wilson equation were better than those for the NRTL equation for the chloroform + methanol + benzene system, which occur mainly at the higher concentrations of chloroform. The results given by each of the activity coefficient equations are illustrated by the broken lines in Figures 2 and 3.

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