Vapor–Liquid Equilibria for Acetone + Chloroform + Methanol and Constituent Binary Systems at 101.3 kPa

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Isobaric vapor–liquid equilibria for acetone + chloroform + methanol and for the constituent binary systems chloroform + methanol and chloroform + acetone were measured at 101.3 kPa using a liquid–vapor ebullition-type equilibrium still (*1*). The experimental data were correlated with the extended Redlich–Kister and Wilson equations. The data were best correlated and completely calculated for the ternary and three binary azeotropic data using the extended Redlich–Kister equation.

Introduction

Vapor–liquid equilibria (VLE) and azeotropic data, which are useful for the design and operation of separation processes, have been observed for many systems. For the same system and under the same conditions, however, detailed studies on azeotropic data often reveal differences with respect to the equilibrium values. The example in Figure 1 involving literature azeotropic data, at 101.3 kPa, for three binary systems, acetone + chloroform, chloroform + methanol, and methanol + acetone, shows how azeotropic compositions and temperatures tend to be scattered. The object of our study is accurate measurement of VLE and determination of azeotropic data for the isobaric binary and ternary systems.

In previous studies, some consistent data (*2–4*) for the isothermal system of acetone + chloroform + methanol were reported. The knowledge of the isothermal VLE is thermodynamically interesting. On the other hand, the accurate isobaric VLE is of theoretical as well as practical importance from the standpoint of the technology of separation processes.

In the present study, VLE were measured for the ternary system acetone + chloroform + methanol and the two constituent binary systems chloroform + methanol and chloroform + acetone at 101.3 kPa using a liquid–vapor ebullition-type equilibrium still (*1*) which was proposed for accurate measurement of azeotropic data. Another constituent binary system of acetone + chloroform was reported in our previous study (*5*). The experimental data were correlated with the extended Redlich–Kister equation (*1, 6, 7*) in order to coincide with the experimental three binary and ternary azeotropic data perfectly at the isobaric condition. For comparison, those data were also correlated using the Wilson equation (*8*).

Experimental Section

Materials. Acetone, chloroform, and methanol were special grade reagents, supplied by Wako Pure Chemical Co. Acetone was used after its minute water content was removed with calcium sulfate. Chloroform was treated with sulfuric acid, neutralized with sodium hydroxide, washed with water, dried overnight on potassium carbonate, and then distilled. Chloroform should be purified just before measurements, because it reacts with oxygen when exposed to the air and light. Methanol was used after its minute water content was removed with molecular sieves 3A. A gas-chromatographic analysis on all three materials indicated that each had a purity of at least 99.9 mol %. Table 1 gives a comparison between some of the measured properties and literature data.

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

	T_b/K		ϱ(298.15 K)/(g cm^{-3})	
material	obsd	lit. (*17*)	obsd	lit. (*17*)
acetone	329.95	329.217	0.784 13	0.784 40
chloroform	334.36	334.328	1.479 76	1.479 70
methanol	337.70	337.696	0.786 56	0.786 37

Table 2. Antoine Constants of the Materials Used[a] **(*18*)**

material	*A*	*B*	*C*
acetone	6.242 00	1210.595	−43.486
chloroform	6.079 60	1170.966	−46.918
methanol	7.205 87	1582.271	−33.424

[a] $\log(P/\text{kPa}) = A - B/[(T/\text{K}) + C]$.

Procedure. A liquid–vapor ebullition-type equilibrium still, described in detail in ref 1, was used for measuring VLE. The pressure, *P*, in the still was measured by means of a Fortin-type mercury barometer. Since the barometric pressure changed slightly, the experimental temperatures were corrected to 101.3 kPa. The equilibrium temperature, *T*, was measured using a Hewlett-Packard quartz thermometer, model 2804A, with an accuracy of 0.01 K, calibrated at the triple point of water.

Analysis. The equilibrium composition of the samples was determined using a Shimadzu gas chromatograph, type GC-4CT, equipped with a thermal conductivity cell. PEG-1500 (15% polyethylene glycol on chromosorb W-AW 60/80) was used as the column packing and helium as the carrier gas. The relationship between peak area and composition was determined from analysis of samples of known composition. The accuracy of liquid, x_i, and vapor, y_i, composition measurements is estimated to be 0.002 in mole fraction.

Experimental Results

The activity coefficients γ_i were calculated using the

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0021-9568/94/1739-0714$04.50/0

Table 3. Isobaric Vapor–Liquid Equilibrium Data, Liquid Phase, x_i, and Vapor Phase, y_i, Mole Fractions, Temperature, T, and Activity Coefficients, γ_i, for Two Binary Systems at 101.3 kPa

x_1	y_1	T/K	γ_1	γ_2	x_1	y_1	T/K	γ_1	γ_2
	Chloroform (1) + Methanol (2)					Methanol (1) + Acetone (2)			
0.018	0.046	336.92	2.446	1.001	0.070	0.082	328.82	1.735	1.001
0.147	0.305	332.03	2.282	1.019	0.133	0.144	328.58	1.610	1.010
0.208	0.391	330.36	2.173	1.030	0.181	0.188	328.46	1.546	1.019
0.241	0.433	329.54	2.129	1.036	0.217	0.218	328.39	1.495	1.030
0.316	0.498	328.30	1.939	1.074	0.227	0.226	328.40	1.480	1.032
0.379	0.544	327.59	1.804	1.108	0.265	0.255	328.45	1.424	1.044
0.410	0.563	327.32	1.740	1.132	0.340	0.311	328.54	1.337	1.071
0.470	0.593	326.89	1.620	1.196	0.406	0.356	328.89	1.265	1.105
0.509	0.605	326.72	1.534	1.263	0.446	0.382	329.11	1.222	1.130
0.540	0.621	326.61	1.489	1.301	0.481	0.406	329.30	1.194	1.153
0.599	0.635	326.51	1.376	1.444	0.593	0.486	330.05	1.119	1.246
0.641	0.645	326.48	1.307	1.572	0.606	0.496	330.20	1.110	1.257
0.647	0.648	326.48	1.301	1.586	0.631	0.515	330.44	1.095	1.283
0.672	0.655	326.48	1.266	1.673	0.676	0.550	330.84	1.073	1.341
0.691	0.657	326.50	1.234	1.765	0.719	0.590	331.47	1.053	1.384
0.718	0.663	326.53	1.197	1.898	0.737	0.608	331.64	1.051	1.407
0.751	0.679	326.60	1.168	2.044	0.771	0.643	332.12	1.041	1.452
0.823	0.707	326.92	1.097	2.595	0.805	0.681	332.72	1.030	1.499
0.834	0.715	326.93	1.094	2.692	0.849	0.735	333.56	1.018	1.571
0.949	0.815	329.54	1.004	5.148	0.900	0.809	334.68	1.011	1.659
0.974	0.875	330.98	1.001	6.465	0.926	0.852	335.36	1.007	1.706
					0.947	0.890	335.94	1.006	1.743
					0.976	0.947	336.84	1.003	1.811

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 Acetone (1) + Chloroform (2) + Methanol (3) System 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
0.229	0.175	0.250	0.211	331.42	1.027	1.328	1.168	0.346	0.222	0.350	0.216	331.03	0.959	1.077	1.327
0.257	0.210	0.274	0.219	330.90	1.018	1.166	1.257	0.353	0.292	0.332	0.264	331.00	0.890	1.002	1.508
0.260	0.276	0.256	0.294	330.59	0.944	1.202	1.302	0.356	0.242	0.354	0.230	330.79	0.949	1.059	1.381
0.262	0.305	0.242	0.327	330.80	0.878	1.201	1.327	0.360	0.230	0.362	0.226	330.79	0.960	1.094	1.342
0.269	0.304	0.248	0.326	330.88	0.874	1.198	1.326	0.361	0.241	0.360	0.240	331.01	0.944	1.101	1.331
0.271	0.278	0.260	0.301	330.94	0.909	1.207	1.290	0.367	0.283	0.346	0.266	331.17	0.887	1.034	1.460
0.272	0.269	0.262	0.292	330.92	0.914	1.211	1.288	0.371	0.233	0.366	0.221	330.98	0.936	1.050	1.382
0.278	0.277	0.265	0.299	330.97	0.902	1.202	1.297	0.372	0.234	0.372	0.223	331.00	0.948	1.054	1.362
0.279	0.188	0.307	0.204	331.07	1.045	1.204	1.205	0.372	0.223	0.375	0.220	331.10	0.952	1.087	1.319
0.279	0.278	0.268	0.299	330.94	0.910	1.198	1.295	0.379	0.318	0.351	0.288	331.23	0.868	0.994	1.569
0.279	0.284	0.264	0.304	330.84	0.899	1.197	1.316	0.410	0.234	0.408	0.216	330.81	0.948	1.024	1.413
0.281	0.294	0.262	0.311	330.90	0.884	1.180	1.334	0.414	0.304	0.391	0.263	331.29	0.884	0.946	1.614
0.282	0.313	0.255	0.324	330.85	0.858	1.157	1.384	0.526	0.266	0.520	0.204	331.50	0.920	0.826	1.740
0.292	0.294	0.270	0.304	330.94	0.876	1.152	1.364	0.756	0.125	0.769	0.071	330.39	0.981	0.624	1.858
0.292	0.204	0.301	0.223	331.11	0.976	1.211	1.240	0.388	0.119	0.438	0.116	330.79	1.083	1.082	1.204
0.296	0.205	0.311	0.227	330.84	1.003	1.236	1.230	0.378	0.125	0.428	0.116	330.89	1.083	1.027	1.216
0.297	0.274	0.286	0.289	331.00	0.911	1.172	1.311	0.523	0.450	0.555	0.371	335.17	0.875	0.792	3.166
0.307	0.203	0.324	0.220	331.17	0.997	1.196	1.220	0.521	0.444	0.546	0.364	334.86	0.872	0.795	3.002
0.313	0.216	0.319	0.223	331.16	0.963	1.140	1.275	0.343	0.399	0.294	0.361	330.83	0.811	1.008	1.792
0.315	0.214	0.326	0.226	331.02	0.982	1.171	1.255	0.331	0.357	0.291	0.334	330.66	0.838	1.049	1.618
0.316	0.218	0.321	0.215	331.04	0.964	1.093	1.312	0.788	0.184	0.846	0.106	331.91	0.986	0.601	2.254
0.318	0.210	0.328	0.216	331.09	0.977	1.138	1.271	0.732	0.188	0.761	0.113	331.43	0.969	0.639	2.095
0.318	0.252	0.318	0.241	330.82	0.954	1.067	1.365	0.411	0.471	0.368	0.401	332.78	0.794	0.888	2.449
0.318	0.242	0.318	0.240	330.81	0.954	1.107	1.338	0.152	0.072	0.222	0.112	332.57	1.338	1.663	1.053
0.319	0.252	0.314	0.241	330.81	0.939	1.068	1.381	0.147	0.076	0.215	0.122	332.62	1.337	1.714	1.045
0.320	0.245	0.318	0.244	331.05	0.941	1.103	1.328	0.221	0.648	0.145	0.592	330.93	0.610	1.019	2.690
0.332	0.246	0.327	0.246	331.06	0.932	1.106	1.335	0.250	0.599	0.173	0.548	331.05	0.643	1.016	2.462
0.335	0.228	0.337	0.219	331.10	0.952	1.061	1.337	0.142	0.170	0.165	0.248	331.00	1.108	1.639	1.118
0.336	0.247	0.328	0.247	331.15	0.921	1.103	1.340	0.162	0.293	0.144	0.366	329.65	0.876	1.462	1.249
0.338	0.244	0.331	0.235	331.15	0.924	1.062	1.364	0.224	0.732	0.161	0.697	333.49	0.613	0.977	3.941
0.338	0.247	0.329	0.247	331.17	0.917	1.102	1.342	0.230	0.620	0.153	0.568	330.81	0.622	1.026	2.501
0.339	0.247	0.330	0.247	331.17	0.917	1.102	1.343	0.738	0.133	0.751	0.077	330.46	0.980	0.635	1.835
0.340	0.248	0.330	0.247	331.13	0.916	1.099	1.351	0.608	0.109	0.626	0.073	330.03	1.008	0.751	1.474
0.340	0.241	0.333	0.248	330.98	0.928	1.141	1.325	0.528	0.100	0.563	0.074	330.11	1.043	0.831	1.341
0.343	0.251	0.336	0.248	331.12	0.924	1.090	1.350	0.088	0.142	0.112	0.241	331.89	1.184	1.862	1.059
0.346	0.241	0.344	0.230	331.00	0.943	1.057	1.364								

following rigorous equation:

$$\phi_i P y_i = \gamma_i P_i^{\mathrm{s}} x_i \phi_i^{\mathrm{s}} \exp[v_i^{\mathrm{L}}(P - P_i^{\mathrm{s}})/RT] \qquad (1)$$

where ϕ_i and ϕ_i^{s}, the fugacity coefficients of component i in the mixture and pure vapor, respectively, were evaluated using the second virial coefficients obtained by the Tsonopoulos method (*9*). The vapor pressures of the pure component, P_i^{s}, were obtained using the Antoine equation constants (Table 2). The liquid molar volumes v_i^{L} were calculated by the Rackett equation (*10*).

Binary System. The two binary VLE data for chloroform (1) + methanol (2) and methanol (1) + acetone (2) are reported in Table 3 along with the activity coefficients calculated using eq 1. Both chloroform (1) + methanol (2) and methanol (1) + acetone (2) systems form a minimum boiling azeotrope. The system of acetone (1) + chloroform (2), reported in our previous paper (*5*), forms a maximum

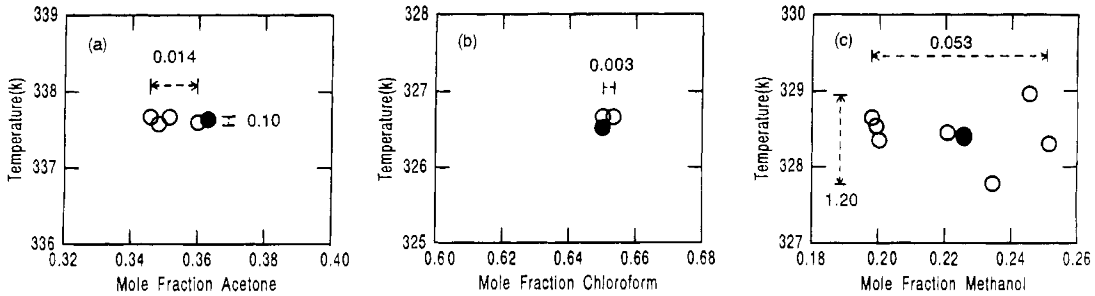

Figure 1. Azeotropic data at 101.3 kPa: (a) acetone + chloroform, (b) chloroform + methanol, (c) methanol + acetone, (●) this work, (○) literature.

Table 5. Azeotropic Data for the Three Binary Systems and the Ternary System at 101.3 kPa

	exptl values			lit. values			
system	x_1	x_2	T/K	x_1	x_2	T/K	ref
acetone (1) + chloroform (2)	0.363	0.637	337.62	0.346	0.654	337.65	*19*
				0.360	0.640	337.58	*20*
				0.349	0.651	337.55	*21*
				0.352	0.648	337.65	*22*
chloroform (1) + methanol (2)	0.650	0.350	326.48	0.653	0.347	326.65	*19*
				0.650	0.350	326.65	*22*
				0.650	0.350	326.65	*23*
methanol (1) + acetone (2)	0.225	0.775	328.39	0.198	0.802	328.65	*19*
				0.234	0.766	337.75	*22*
				0.199	0.801	328.55	*24*
				0.245	0.755	328.95	*25*
				0.200	0.800	328.35	*26*
				0.225	0.775	328.40	*27*
				0.251	0.749	328.31	*28*
				0.220	0.780	328.45	*7*
acetone (1) + chloroform (2) + methanol (3)	0.381	0.241	330.82	0.319	0.243	330.65	*19*
				0.316	0.238	331.02	*23*

Table 6. Extended Redlich–Kister Constants

system	B_{12} a_{12}	C_{12} b_{12}	D_{12} c_{12}	E_{12} d_{12}	F_{12} e_{12}
acetone (1) + chloroform (2)	−0.709 711	0.088 894	0.000 808	−0.107 501	−0.052 285
	0.038 844	−0.801 954	0.058 600	0.040 766	−0.038 363
chloroform (1) + methanol (2)	1.330 500	0.373 929	0.137 042	0.211 090	−0.007 554
	−0.013 246	1.329 470	0.446 754	0.130 514	0.125 018
methanol (1) + acetone (2)	0.632 705	0.020 944	0.125 240	−0.018 062	−0.141 667
	0.010 275	0.634 960	0.001 305	−0.018 682	0.011 851

system	B b	C_1 c_1	C_2 c_2	C_3 c_3
acetone (1) + chloroform (2) + methanol (3)	−0.893 219		−0.151 646	−0.382 173
	−0.642 452		−0.712 480	0.180 508

Table 7. Deviations between Calculated and Experimental Vapor-Phase Mole Fractions Δy_i and Temperatures ΔT for the Extended Redlich–Kister Equation[a]

	acetone (1) + chloroform (2)		chloroform (1) + methanol (2)		methanol (1) + acetone (2)		acetone (1) + chloroform (2) + ethanol (3)			
	Δy_1	ΔT/K	Δy_1	ΔT/K	Δy_1	ΔT/K	Δy_1	Δy_2	Δy_3	ΔT/K
average	0.001	0.04	0.003	0.04	0.001	0.04	0.002	0.005	0.005	0.16
maximum	0.003	0.13	0.010	0.23	0.002	0.12	0.009	0.018	0.015	0.40
azeotropic point	0	0	0	0	0	0	0	0	0	0

[a] $\Delta y_1 = \sum^N |y_{1,\mathrm{obsd}} - y_{1,\mathrm{calcd}})|/N$, $\Delta T = \sum^N |(T_{\mathrm{obsd}} - T_{\mathrm{calcd}})|/N$, N = number of data points.

boiling azeotrope.

The experimental data were tested for thermodynamic consistency using the point test of Fredenslund et al. (*11*) and Van Ness et al. (*12*) and the area test of Herington (*13*) and Redlich and Kister (*14*) as described by Gmehling and Onken (*15*). In addition, the data were checked by our previous method (*16*), which permits the overall check of the data by combining three tests, namely, a point test, area test, and infinite dilution test. Those results indicate that the experimental data for the three binary systems are thermodynamically consistent.

Ternary System. The experimental VLE data for the ternary system acetone (1) + chloroform (2) + methanol (3) at 101.3 kPa are reported in Table 4. This ternary system forms a saddle azeotropic mixture.

Azeotropic Data. Ternary and binary azeotropic data were determined by a graphical method (see ref 1) on the basis of experimental VLE data. The azeotropic composition and temperature for the ternary system acetone + chloroform + methanol and the three constituent binary systems are shown in Table 5. Table 5 also shows literature azeotropic data.

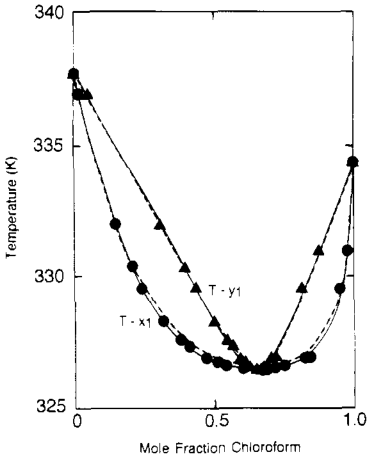

Figure 2. Temperature–composition diagram for the chloroform + methanol system: (●, ▲) this work, (—) extended Redlich–Kister equation, (- - -) Wilson equation.

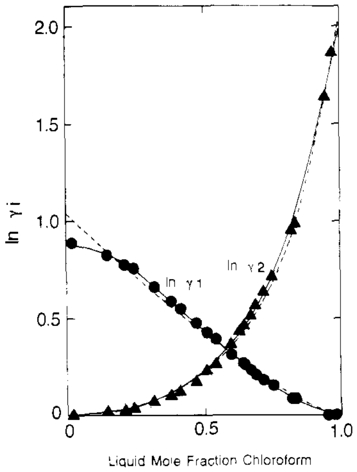

Figure 3. Activity coefficient–liquid composition diagram for the chloroform + methanol system: (●, ▲) this work, (—) extended Redlich–Kister equation, (- - -) Wilson equation.

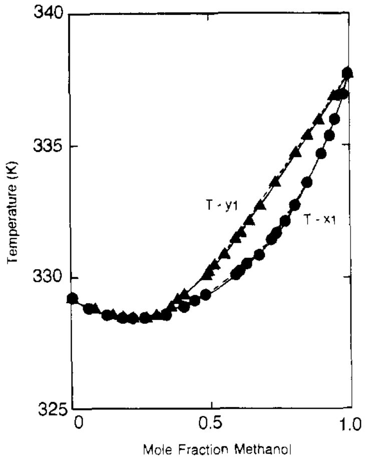

Figure 4. Temperature–composition diagram for the methanol + acetone system: (●, ▲) this work, (—) extended Redlich–Kister equation, (- - -) Wilson equation.

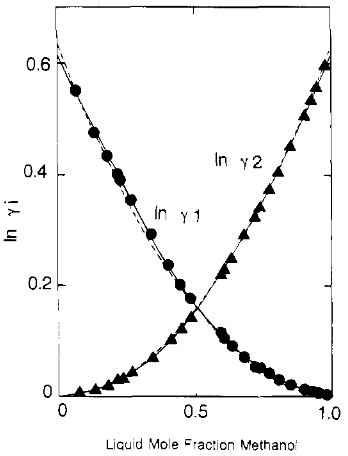

Figure 5. Activity coefficient–liquid composition diagram for the methanol + equation system: (●, ▲) this work, (—) extended Redlich–Kister equation, (- - -) Wilson equation.

Table 8. Wilson Parameters

system	$(\lambda_{12} - \lambda_{11})$/J mol^{-1}	$(\lambda_{12} - \lambda_{22})$/J mol^{-1}
acetone (1) + chloroform (2)	−349.3	−1586.4
chloroform (1) + methanol (2)	−1489.3	7528.4
methanol (1) + acetone (2)	2716.4	−810.7
acetone (1) + chloroform (1) + methanol (3)	no ternary parameters	

Correlation and Prediction

Most of the large number of activity-coefficient equations proposed are derived under conditions of constant temperature and pressure. In this work, the activity coefficients γ_i were correlated using the extended Redlich–Kister equation (*1, 6, 7*) in order to coincide with the experimental three binary and ternary azeotropic data perfectly and calculate the VLE accurately at the isobaric condition. For comparison, those data were also correlated using the Wilson equation (*8*).

For activity coefficient equations applicable to the condition of constant pressure, the modified Redlich–Kister equations have been proposed by Chao and Hougen (*6*) and by Ochi and Lu (*7*) for a binary system.

In these equations the Q function and $\ln(\gamma_1/\gamma_2)$ are given by eqs 2 and 3, respectively. Activity coefficients are then obtained for components 1 and 2 by using Q_{12} and $\ln(\gamma_1/\gamma_2)$ as eqs 4 and 5. Between Q_{12} and $\ln(\gamma_1/\gamma_2)$, eq 6 must be

$$Q_{12} = G^E/RT = x_1x_2[B_{12} + C_{12}(x_1 - x_2) + D_{12}(x_1 - x_2)^2 + E_{12}(x_1 - x_2)^3 + F_{12}(x_1 - x_2)^4 + ...] \quad (2)$$

$$\ln(\gamma_1/\gamma_2) = a_{12} + b_{12}(x_2 - x_1) + c_{12}(6x_1x_2 - 1) + d_{12}(x_2 - x_1)(1 - 8x_1x_2) + e_{12}(x_2 - x_1)^2(10x_1x_2 - 1) + ... \quad (3)$$

$$\ln \gamma_1 = Q_{12} + x_2 \ln(\gamma_1/\gamma_2) \quad (4)$$

$$\ln \gamma_2 = Q_{12} - x_1 \ln(\gamma_1/\gamma_2) \quad (5)$$

fulfilled. The binary constants B_{12}, C_{12}, D_{12} , E_{12} and F_{12} in equation 2 are determined using the Q function data, and a_{12}, b_{12}, c_{12} , d_{12}, and e_{12} in eq 3 are determined using the $\ln(\gamma_1/\gamma_2)$ data.

$$\left.\begin{aligned}[Q_{12}/x_1x_2]_{x_1=0} &= \ln(\gamma_1/\gamma_2)_{x_1=0} = \ln(\gamma_1)_{x_1=0}\\ [Q_{12}/x_1x_2]_{x_2=0} &= \ln(\gamma_2/\gamma_1)_{x_2=0} = \ln(\gamma_2)_{x_2=0}\end{aligned}\right\} \quad (6)$$

For the ternary system, an extended Redlich–Kister equation applicable to the condition of constant pressure has been presented in our previous study (*1*). The Q function was obtained for the ternary system as follows:

$$Q_{123} = Q_{12} + Q_{23} + Q_{31} + x_1x_2x_3[B + C_1(x_2 - x_3) + C_2(x_3 - x_1) + C_3(x_1 - x_2) + ...] \quad (7)$$

where B, C_1,C_2, and C_3 are ternary constants. The equa-

Table 9. Deviations between Calculated and Experimental Vapor-Phase Mole Fractions Δy_i and Temperatures ΔT for the Wilson Equation[a]

	acetone (1) + chloroform (2)		chloroform (1) + methanol (2)		methanol (1) + acetone (2)		acetone (1) + chloroform (2) + methanol (3)			
	Δy_1	ΔT/K	Δy_1	ΔT/K	Δy_1	ΔT/K	Δy_1	Δy_2	Δy_3	ΔT/K
average	0.005	0.40	0.007	0.14	0.002	0.04	0.007	0.005	0.007	0.46
maximum	0.012	0.67	0.014	0.27	0.004	0.11	0.014	0.025	0.018	0.74
azeotropic point	0.002	0.36	0.006	0.10	0.003	0.05	0.009	0.007	0.002	0.41

[a] $\Delta y_1 = \sum^N |(y_{1,\mathrm{obsd}} - y_{1,\mathrm{calcd}})|/N$, $\Delta T = \sum^N |(T_{\mathrm{obsd}} - T_{\mathrm{calcd}})|/N$, N = number of data points.

tions giving $\ln(\gamma_1/\gamma_2)$ and $\ln(\gamma_3/\gamma_1)$ must fulfill the following conditions:

$$[\{\ln(\gamma_1/\gamma_2)\}_{\text{ternary system}}]_{x_3=0} = \{\ln(\gamma_1/\gamma_2)\}_{\text{binary system}} \tag{8}$$

$$[\{\ln(\gamma_3/\gamma_1)\}_{\text{ternary system}}]_{x_2=0} = \{\ln(\gamma_3/\gamma_1)\}_{\text{binary system}} \tag{9}$$

$$\{(\ln \gamma_1)_{\text{ternary system}}\}_{x_3=0} = (\ln \gamma_1)_{\text{binary system}} \tag{10}$$

$$\{(\ln \gamma_2)_{\text{ternary system}}\}_{x_1=0} = (\ln \gamma_2)_{\text{binary system}} \tag{11}$$

$$\{(\ln \gamma_3)_{\text{ternary system}}\}_{x_2=0} = (\ln \gamma_3)_{\text{binary system}} \tag{12}$$

The equations for $\ln(\gamma_1/\gamma_2)$ and $\ln(\gamma_3/\gamma_1)$ were derived as follows:

$$\begin{aligned} \ln(\gamma_1/\gamma_2) = {} & [\{a_{12}(1 - x_3) - (a_{23} + a_{31})x_3\} - \\ & (x_1 - x_2)b_{12} + (4x_1x_2 - x_1^2 - x_2^2)c_{12} + \\ & (x_1 - x_2)(6x_1x_2 - x_1^2 - x_2^2)d_{12} + \\ & (x_1 - x_2)^2(8x_1x_2 - x_1^2 - x_2^2)e_{12} + ...] + \\ & [-x_3b_{23} + (x_3^2 - 2x_2x_3)c_{23} + (x_2 - x_3)(x_3^2 - 3x_2x_3)c_{23} + \\ & (x_2 - x_3)^2(x_3^2 - 4x_2x_3)e_{23} + ...] + [x_3b_{31} + \\ & (x_3^2 - 2x_1x_3)c_{31} + (x_3 - x_1)(x_3^2 - 3x_1x_3)d_{31} + \\ & (x_3 - x_1)^2(x_3^2 - 4x_1x_3)e_{31} + ...] + [x_3(x_2 - x_1)b + \\ & \{x_2x_3(x_2 - x_3) - x_1x_3(x_2 - x_3) - x_1x_2x_3\}c_1 + \\ & \{x_2x_3(x_3 - x_1) - x_1x_3(x_3 - x_1) - x_1x_2x_3\}c_2 + \\ & \{x_2x_3(x_1 - x_2) - x_1x_3(x_1 - x_2) + 2x_1x_2x_3\}c_3 + ...] \end{aligned} \tag{13}$$

$$\begin{aligned} \ln(\gamma_3/\gamma_1) = {} & [\{a_{31}(1 - x_2) - (a_{12} + a_{23})x_2\} - \\ & (x_3 - x_1)b_{31} + (4x_3x_1 - x_3^2 - x_1^2)c_{31} + \\ & (x_3 - x_1)(6x_3x_1 - x_3^2 - x_1^2)d_{31} + (x_3 - x_1)^2(8x_3x_1 - \\ & x_3^2 - x_1^2)e_{31} + ...] + [-x_2b_{21} + (x_2^2 - 2x_1x_2)c_{12} + \\ & (x_1 - x_2)(x_2^2 - 3x_1x_2)d_{12} + (x_1 - x_2)^2(x_1^2 - \\ & 4x_1x_2)e_{12} + ...] + [x_2b_{23} + (x_2^2 - 2x_2x_3)c_{23} + (x_2 - \\ & x_3)(x_2^2 - 3x_2x_3)d_{23} + (x_2 - x_3)^2(x_2^2 - 4x_2x_3)e_{23} + ...] + \\ & [x_2(x_1 - x_3)b + \{x_1x_2(x_2 - x_3) - x_2x_3(x_2 - x_3) - \\ & x_1x_2x_3\}c_1 + \{x_1x_2(x_3 - x_1) - x_2x_3(x_3 - x_1) - 2x_1x_2x_3\}c_2 + \\ & \{x_1x_2(x_1 - x_2) - x_2x_3(x_1 - x_2) - x_1x_2x_3\}c_3 + ...] \end{aligned} \tag{14}$$

where ternary constants b, c_1, c_2, and c_3 are determined from the ternary $\ln(\gamma_1/\gamma_2)$ and $\ln(\gamma_3/\gamma_1)$ data. The activity coefficients of components 1–3 for the ternary system are then obtained from ternary Q_{123}, $\ln(\gamma_1/\gamma_2)$, and $\ln(\gamma_3/\gamma_1)$.

$$\ln \gamma_1 = Q_{123} + x_2 \ln(\gamma_1/\gamma_2) - x_3 \ln(\gamma_3/\gamma_1) \tag{15}$$

$$\ln \gamma_2 = \ln \gamma_1 - \ln(\gamma_1/\gamma_2) \tag{16}$$

$$\ln \gamma_3 = \ln \gamma_1 + \ln(\gamma_3/\gamma_1) \tag{17}$$

Table 6 shows the extended Redlich–Kister equation constants of the three binary systems and the ternary system on the basis of the experimental data. The deviations between the experimental and calculated vapor-phase compositions and bubble point temperatures for three binary and ternary systems are shown in Table 7. The calculated results using the extended Redlich–Kister equation are shown by solid lines in Figures 2–5.

For comparison, the activity coefficients were correlated using the Wilson equation (*8*). Table 8 shows the Wilson parameters $\lambda_{ij} - \lambda_{ii}$ and $\lambda_{ij} - \lambda_{jj}$ of binary systems $i + j$ determined on the basis of the experimental data. The deviations between the experimental and calculated vapor-phase compositions and bubble point temperatures are shown in Table 9. The calculated results using the Wilson equation are shown by broken lines in Figures 2–5.

The prediction of ternary VLE was carried out with the Wilson parameters in Table 8. Overall deviations between the experimental and calculated vapor-phase compositions and bubble point temperatures for the three binary systems and the ternary system are shown in Table 9. Table 9 also shows deviations at experimental binary and ternary azeotropic points. At the azeotropic point, the correlated and predicted results using the Wilson parameters are not in perfect agreement with those experimental values. The experimental VLE data were best correlated and completely calculated for the ternary and three binary azeotropic data using the modified Redlich–Kister equation.

Glossary

P	total pressure
R	molar gas constant, 8.3144 J mol^{-1} K^{-1}
T	equilibrium temperature
x	mole fraction in the liquid phase
y	mole fraction in the vapor phase
Greek Letters	
γ	activity coefficient
ϕ	fugacity coefficient
Subscripts	
i, j, k, 1, 2, 3	components

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Received for review November 1, 1993. Accepted May 9, 1994.[⊗]

[⊗] Abstract published in *Advance ACS Abstracts,* August 15, 1994.