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Phase Equilibria at Superatmospheric Pressures for Systems Containing Halohydrocarbon, Aromatic Hydrocarbon, and Alcohol

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The vapor−liquid equilibrium (VLE) data for four binary and two ternary systems concerning chloroform, benzene, ethanol, and 1-butanol are determined at pressures from 101.3 to 303.0 kPa. The experimental VLE data of binary systems are correlated with the Wilson equation, and those at relevant pressures for ternary systems are predicted with the three-component Wilson equation in which the parameters are taken from the corresponding binary systems. Minimum boiling azeotropes are found for chloroform + ethanol, ethanol + benzene, and benzene + 1-butanol only at 303.0 kPa. In the presence of alcohols, chloroform decomposes at $T > 400$ K, so the experimental investigation cannot be completed for chloroform + alcohol containing systems at higher pressures.

Introduction

The hydrocarbon + alcohol mixtures are asymmetrical systems with very highly nonideal behavior. They are also typical systems in petrochemical industry and engineering. It is of great interest and practical importance to investigate their phase equilibrium behavior and the other thermodynamic properties. The vapor−liquid equilibria at superatmospheric pressures for the chloroform + benzene + alcohol systems are not reported in the literature. As representatives, the vapor−liquid equilibria at superatmospheric pressures for chloroform + ethanol, + benzene, and + 1-butanol, benzene + 1-butanol, chloroform + ethanol + benzene, and chloroform + benzene + 1-butanol binary and ternary systems are determined and calculated in this work. Vijayaraghavan et al. (*1*) determined the vapor−liquid equilibrium data of benzene + 1-butanol at 192.7 and 294.0 kPa and correlated the data with Chao's modified Redlich−Kister equation and van Laar equation. The vapor−liquid equilibrium data for the above binary systems at 101.3 kPa have also been reported in the literature (*2*−*5*).

Experimental Section

Apparatus. A stainless steel dual circulating VLE apparatus at superatmospheric pressures (*6*), see Figure 1, is used to determine VLE at pressures up to 303 kPa. The temperature is measured by a standard platinum resistance thermometer equipped with a Keithley 195A six-digital multimeter; its accuracy is ±0.001 Ω, equivalent to ±0.01 K. The system pressure is measured and controlled by a digital pressure transducer with an accuracy of ±0.1 kPa.

Chemicals. Chloroform, benzene, ethanol, and 1-butanol used in this work are of analytical reagent grade and further purified in a rectifying column, and the fraction with a fixed boiling point and refractive index was used in the experiment. The physical properties are listed in Table 1.

Composition Analysis. The density of chloroform is substantially different from those of ethanol, benzene, and 1-butanol, and the refractive index of benzene also differs from those of chloroform, ethanol, and 1-butanol. Therefore, the compositions of the three binary mixtures which contain chloroform are analyzed by the density measurement, and those of benzene + 1-butanol mixtures by the refractive index method. The compositions of the ternary mixtures can be analyzed by measuring the densities and the refractive indices of the mixtures and interpolating them in diagrams of density and refractive index as functions of composition with the computerized interpolation technique (*8*). An Abbe refractometer and a Paar DMA45 digital densimeter were used in the experimental work. The analytical methods are examined by a series of compounded sample mixtures, and the average absolute deviations are ±0.001 mole fraction for binary mixtures and ±0.002 mole fraction for ternary mixtures.

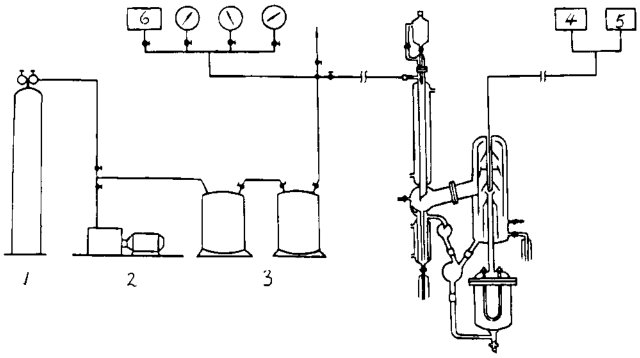

Figure 1. Scheme of the dual circulation VLE apparatus at superatmospheric pressures: (1) cylinder, (2) vacuum pump, (3) pressure buffer, (4) multimeter, (5) recorder, (6) pressure transducer.

Determination and Calculation of Vapor−Liquid Equilibria

Vapor Pressures. The vapor pressures up to 1000 kPa for chloroform were determined and correlated by the Antoine equation with a linearization algorithm (*9*):

$$\ln(p^\circ/\mathrm{kPa}) = 14.15983 - 2782.156/(T/\mathrm{K} - 42.691) \quad (306-427\ \mathrm{K})$$

The average relative deviation for the correlation is 0.11%.

Determination of Vapor−Liquid Equilibria. The vapor−liquid equilibrium data of chloroform (1) + ethanol (2) at 101.3 and 303.3 kPa, chloroform + ethanol + benzene (3) at 101.3 and 302.5 kPa, and chloroform + benzene, chloroform + 1-butanol (4), benzene + 1-butanol, and

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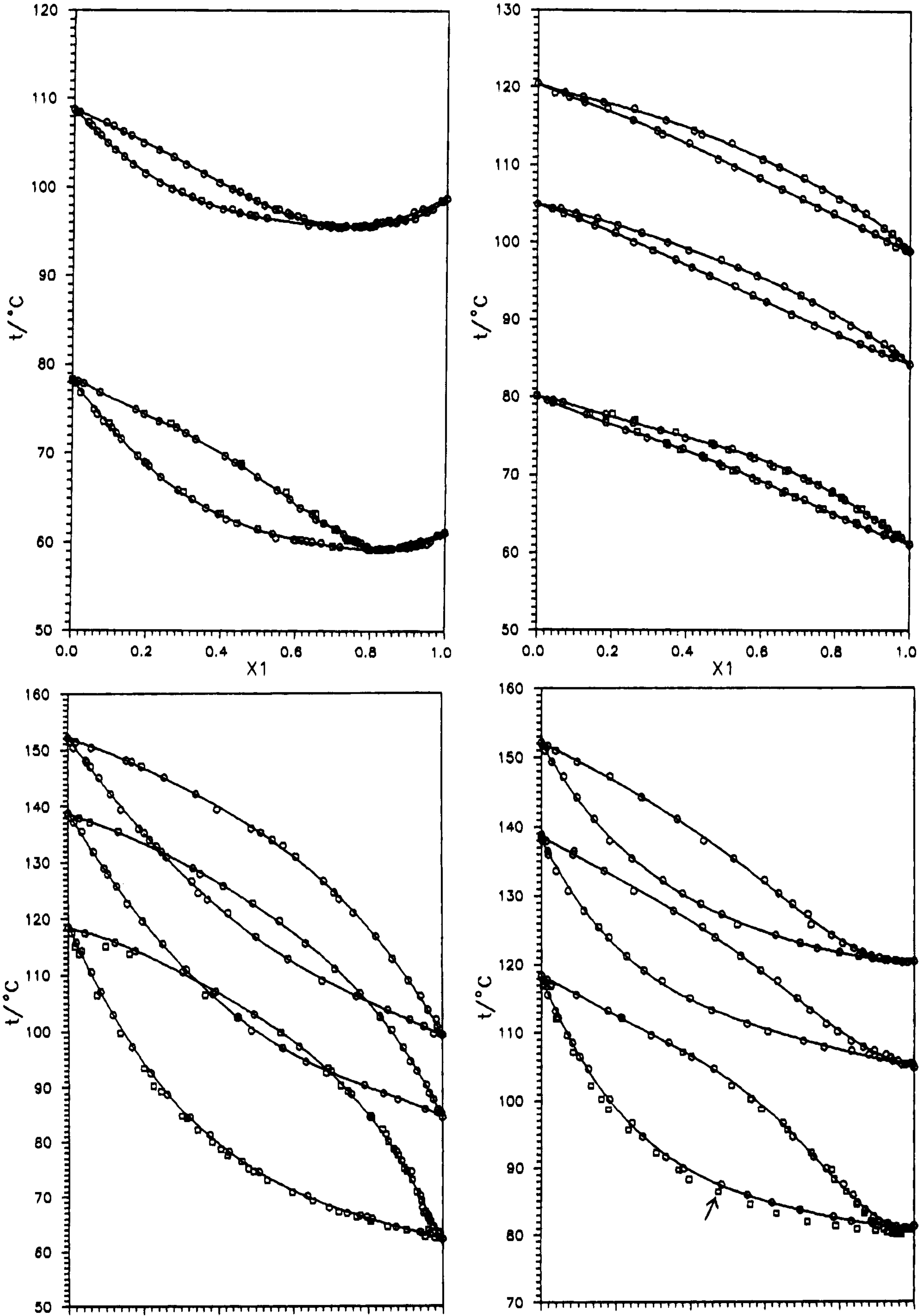

Figure 2. Temperature–composition diagrams at various pressures: (a, top left) chloroform + ethanol, (b, top right) chloroform + benzene, (c, bottom left) chloroform + 1-butanol, (d, bottom right) benzene + 1-butanol, (○) experimental, (—) fitted, (□) literature. Pressure (kPa): (a) top, 303.0; bottom, 101.3; (b) top, 303.0; middle, 205.0; bottom, 105.0; (c) top, 303.0; middle, 205.0; bottom, 105.0; (d) top, 303.0; middle, 205.0; bottom, 105.0; arrow indicates literature value at 101.3 kPa.

Table 1. Physical Properties of Pure Components

compound	T_b/K exptl	T_b/K lit (7)	d^{20}/(g cm^{-3}) exptl	d^{20}/(g cm^{-3}) lit. (7)	n_D^{20} exptl	n_D^{20} lit. (7)	A	B	C
chloroform	334.28	334.85	1.4832	1.4832	1.4458	1.4459	14.159 83	2782.156	−42.691
ethanol	351.30	351.65	0.7892	0.7893	1.3611	1.3611	15.898 89	3204.372	−67.295
benzene	353.26	353.25	0.8765	0.8765	1.5010	1.5011	13.885 80	2788.510	−52.360
1-butanol	390.50	390.35	0.8095	0.8098	1.3993	1.3993	14.311 18	2635.384	−118.725

Table 2. VLE for Chloroform (1) + Ethanol (2)

101.3 kPa						302.5 kPa					
T/K	x_1	y_1	T/K	x_1	y_1	T/K	x_1	y_1	T/K	x_1	y_1
351.30	0.0000	0.0000	334.15	0.5392	0.7291	381.93	0.0000	0.0000	369.93	0.4874	0.6001
351.22	0.0052	0.0159	333.64	0.5476	0.7357	381.62	0.0064	0.0136	370.05	0.4720	0.5813
350.98	0.0102	0.0301	333.50	0.5965	0.7468	380.48	0.0383	0.0866	369.72	0.5182	0.6160
349.96	0.0221	0.0745	333.45	0.6160	0.7553	380.11	0.0475	0.1055	368.91	0.6295	0.6785
348.05	0.0580	0.1710	333.35	0.6304	0.7612	379.45	0.0609	0.1324	368.88	0.6622	0.6927
347.54	0.0672	0.1940	333.24	0.6448	0.7669	379.03	0.0725	0.1542	368.70	0.6890	0.7086
346.70	0.0838	0.2331	333.12	0.6690	0.7774	378.16	0.0910	0.1874	368.67	0.7113	0.7189
346.00	0.1057	0.2805	332.69	0.7201	0.7933	377.39	0.1108	0.2288	368.80	0.7299	0.7300
345.39	0.1180	0.3052	332.47	0.7907	0.8262	376.58	0.1346	0.2679	368.76	0.7681	0.7534
344.73	0.1318	0.3313	332.41	0.8299	0.8359	375.72	0.1588	0.3012	368.78	0.7941	0.7723
342.87	0.1765	0.4100	332.43	0.8497	0.8469	374.70	0.1922	0.3472	368.86	0.8039	0.7791
342.10	0.1962	0.4366	332.46	0.8596	0.8524	373.68	0.2310	0.3914	368.88	0.8089	0.7800
341.73	0.2071	0.4543	332.61	0.8992	0.8793	372.97	0.2631	0.4247	369.20	0.8492	0.8113
340.50	0.2386	0.4977	332.72	0.9110	0.8873	372.66	0.2897	0.4447	369.23	0.8652	0.8269
339.04	0.2854	0.5509	332.85	0.9244	0.8979	372.10	0.3172	0.4681	369.49	0.8881	0.8455
338.02	0.3235	0.5848	332.99	0.9390	0.9102	371.66	0.3413	0.4912	369.66	0.9142	0.8734
337.03	0.3607	0.6127	333.06	0.9526	0.9256	371.16	0.3629	0.5113	370.43	0.9463	0.9121
336.38	0.3934	0.6450	333.33	0.9613	0.9358	370.71	0.4000	0.5405	370.78	0.9628	0.9355
335.76	0.4138	0.6549	334.03	0.9889	0.9793	370.27	0.4445	0.5736	371.74	0.9923	0.9864
335.32	0.4441	0.6757	334.28	1.0000	1.0000	370.69	0.4240	0.5500	371.97	1.0000	1.0000
334.63	0.4997	0.7111									

Table 3. VLE for Chloroform (1) + Ethanol (2) + Benzene (3)

101.3 kPa					303.0 kPa				
T/K	x_1	y_1	x_2	y_2	T/K	x_1	y_1	x_2	y_2
336.32	0.5348	0.6021	0.2330	0.2472	369.82	0.4811	0.5601	0.4598	0.3912
336.45	0.5824	0.6298	0.1674	0.2140	370.22	0.4982	0.5428	0.3767	0.3611
336.74	0.4459	0.5616	0.3614	0.2941	370.46	0.4337	0.5048	0.4647	0.4089
336.94	0.3689	0.5811	0.5633	0.3479	370.72	0.5119	0.5363	0.3075	0.3356
337.05	0.3974	0.5303	0.4308	0.3258	371.68	0.3310	0.4019	0.5078	0.4520
337.22	0.3621	0.5346	0.5263	0.3485	371.83	0.3214	0.4039	0.5539	0.4754
337.45	0.6681	0.7249	0.0514	0.1092	372.51	0.2543	0.3161	0.5587	0.5000
338.23	0.3034	0.4863	0.6007	0.3943	372.74	0.2278	0.2875	0.5850	0.5168
338.99	0.6946	0.7917	0.0145	0.0374	372.87	0.4016	0.4152	0.2792	0.3543
339.74	0.6493	0.7523	0.0154	0.0448	372.99	0.3485	0.3485	0.3459	0.3959
340.12	0.2687	0.3107	0.2945	0.3352	373.01	0.2315	0.3225	0.6659	0.5515
340.20	0.6163	0.7226	0.0173	0.0501	373.37	0.1721	0.2190	0.6033	0.5418
340.90	0.0466	0.0556	0.4175	0.4279	373.54	0.8866	0.9102	0.0175	0.0349
341.08	0.0354	0.0486	0.5644	0.4766	373.82	0.1347	0.1536	0.4991	0.5073
341.13	0.0571	0.0637	0.2870	0.3934	373.90	0.8217	0.8540	0.0297	0.0617
341.77	0.0640	0.0700	0.1939	0.3482	374.09	0.1032	0.1287	0.6131	0.5648
341.70	0.0267	0.0426	0.6798	0.5209	374.30	0.1320	0.1438	0.4490	0.4896
342.29	0.1611	0.3324	0.7905	0.5724	374.79	0.0773	0.1051	0.7115	0.6303
342.54	0.4224	0.5111	0.0329	0.0965	374.80	0.0706	0.0751	0.4487	0.5037
342.57	0.0199	0.0356	0.7554	0.5686	374.97	0.2632	0.2824	0.3578	0.4222
342.79	0.0710	0.0672	0.1182	0.2908	374.97	0.6374	0.6709	0.0660	0.1412
343.44	0.3218	0.3919	0.0408	0.1270	375.00	0.4785	0.5139	0.1871	0.2624
343.60	0.0159	0.0311	0.8127	0.6162	375.23	0.1273	0.2027	0.7846	0.6678
344.61	0.0760	0.0881	0.0626	0.2191	376.05	0.0501	0.0791	0.8125	0.7119
344.73	0.0117	0.0264	0.8568	0.6648	377.10	0.0356	0.0692	0.8681	0.7669
344.78	0.2747	0.3419	0.0441	0.1344	378.46	0.0236	0.0429	0.9144	0.8334
345.39	0.0424	0.1024	0.8836	0.7128	379.62	0.1909	0.1944	0.1563	0.3171
345.84	0.0076	0.0211	0.8940	0.7157	381.83	0.1217	0.1344	0.0803	0.2287
347.06	0.0399	0.0498	0.0377	0.1799					
348.93	0.0599	0.0832	0.0142	0.0838					

chloroform + benzene + 1-butanol systems at 105.0, 205.0, and 303.0 kPa were determined with the dual circulating VLE apparatus and presented in Tables 2–7 and in Figure 2 for the binary systems. The literature data (*2–5*) of the binary systems at 101.3 kPa are also presented in the figure for comparison. The experimental results of binary systems are thermodynamically consistent by the Herington (*10*) method.

Correlation and Prediction. The fugacities for vapor and liquid phases must be equal to each other when equilibrium is achieved:

$$\phi_i y_i p = \gamma_i x_i \phi_i^\circ p_i^\circ \exp\left[\int_{p_i^\circ}^{p} \frac{V_i^L}{RT}\,dp\right] \qquad (1)$$

where ϕ and ϕ° are the fugacity coefficients for the mixture

Table 4. VLE for Chloroform (1) + Benzene (3)

101.3 kPa			205.0 kPa			303.0 kPa		
T/K	x_1	y_1	*T*/K	x_1	y_1	*T*/K	x_1	y_1
353.26	0.0000	0.0000	378.01	0.0000	0.0000	393.58	0.0000	0.0000
352.67	0.0269	0.0437	377.46	0.0399	0.0627	392.40	0.0457	0.0723
352.36	0.0417	0.0692	376.83	0.0709	0.1037	391.87	0.0847	0.1225
349.80	0.1855	0.2581	376.20	0.1113	0.1619	391.18	0.1259	0.1768
350.87	0.1332	0.1849	375.30	0.1544	0.2153	390.34	0.1879	0.2588
348.85	0.2372	0.3316	374.33	0.2093	0.2798	388.87	0.2553	0.3436
347.87	0.2948	0.3980	373.13	0.2579	0.3494	387.56	0.3207	0.4201
347.04	0.3506	0.4749	372.10	0.3094	0.4061	387.06	0.3349	0.4406
346.51	0.3921	0.5245	370.92	0.3707	0.4939	385.94	0.4070	0.5215
345.58	0.4427	0.5714	369.92	0.4141	0.5381	383.87	0.4851	0.6043
344.57	0.4897	0.6257	368.82	0.4621	0.5897	382.90	0.5279	0.6495
343.78	0.5347	0.6742	367.51	0.5303	0.6613	381.53	0.5961	0.7151
342.77	0.5781	0.7164	366.33	0.5781	0.7067	380.03	0.6555	0.7642
341.95	0.6209	0.7553	365.47	0.6141	0.7376	378.80	0.7115	0.8109
341.07	0.6654	0.7936	363.84	0.6819	0.7923	377.69	0.7515	0.8503
340.02	0.7181	0.8257	362.48	0.7440	0.8405	376.91	0.7961	0.8817
338.87	0.7579	0.8595	361.28	0.8091	0.8886	375.06	0.8715	0.9303
338.13	0.7954	0.8851	360.10	0.8667	0.9313	374.33	0.9063	0.9527
337.49	0.8278	0.9057	359.55	0.8973	0.9516	373.36	0.9380	0.9701
336.86	0.8603	0.9262	358.92	0.9248	0.9614	372.65	0.9620	0.9847
336.31	0.8892	0.9427	358.32	0.9521	0.9763	372.27	0.9880	0.9957
335.53	0.9308	0.9648	357.45	1.0000	1.0000	372.09	1.0000	1.0000
335.07	0.9571	0.9792						
334.28	1.0000	1.0000						

Table 5. VLE for Chloroform (1) + 1-Butanol (4)

105.0 kPa			205.0 kPa			303.0 kPa		
T/K	x_1	y_1	*T*/K	x_1	y_1	*T*/K	x_1	y_1
391.61	0.0000	0.0000	411.93	0.0000	0.0000	425.25	0.0000	0.0000
390.62	0.0091	0.0449	411.07	0.0087	0.0300	424.54	0.0073	0.0213
388.96	0.0213	0.1255	410.30	0.0157	0.0583	423.54	0.0145	0.0623
387.43	0.0357	0.1801	408.68	0.0316	0.1348	421.35	0.0471	0.1560
383.69	0.0612	0.3066	405.03	0.0677	0.2509	421.05	0.0501	0.1709
380.17	0.0865	0.3937	401.06	0.1053	0.3525	420.29	0.0602	0.1970
376.14	0.1195	0.4974	398.92	0.1293	0.4149	418.27	0.0833	0.2583
370.37	0.1707	0.6171	402.09	0.0967	0.3336	415.33	0.1140	0.3422
365.64	0.2203	0.6899	395.84	0.1580	0.4940	412.51	0.1420	0.3981
361.90	0.2644	0.7575	392.70	0.1993	0.5650	409.16	0.1900	0.4901
357.72	0.3247	0.8065	388.69	0.2532	0.6345	408.39	0.2041	0.5163
354.43	0.3773	0.8499	384.13	0.3160	0.7129	407.12	0.2187	0.5462
351.34	0.4278	0.8767	379.79	0.3866	0.7805	406.10	0.2365	0.5756
349.62	0.4624	0.8909	375.70	0.4539	0.8343	404.14	0.2633	0.6087
347.67	0.5091	0.9166	373.25	0.4895	0.8650	399.76	0.3310	0.6834
343.31	0.6386	0.9405	375.54	0.4522	0.8342	397.69	0.3480	0.7111
341.13	0.6967	0.9461	370.13	0.5728	0.8967	396.56	0.3723	0.7249
340.09	0.7445	0.9497	367.67	0.6357	0.9151	394.10	0.4275	0.7630
339.67	0.7798	0.9608	365.94	0.7025	0.9329	389.90	0.5019	0.8226
339.09	0.8113	0.9635	363.50	0.7925	0.9580	385.93	0.5879	0.8676
339.36	0.7981	0.9633	362.03	0.8435	0.9653	382.06	0.6789	0.9096
337.54	0.8755	0.9762	360.93	0.8815	0.9763	379.32	0.7705	0.9419
336.60	0.9400	0.9893	359.13	0.9545	0.9885	376.85	0.8548	0.9617
336.34	0.9661	0.9893	358.42	0.9887	0.9981	375.09	0.9131	0.9840
335.56	0.9804	0.9921	357.53	1.0000	1.0000	373.91	0.9513	0.9871
335.37	1.0000	1.0000				372.58	0.9771	0.9947
						372.35	1.0000	1.0000

and the pure component, γ is the activity coefficient in the liquid phase, x and y are the mole fractions for liquid and vapor, p is the total pressure, T is the equilibrium temperature, and V is the molar volume. This equation will be simplified using the second virial coefficient and neglecting the pressure dependence of the molar volume of the pure components:

$$\exp\left[\frac{(B_i - V_i^{\mathrm{L}})\,(p - p_i{}^{\circ})}{RT}\right] y_i p = \gamma_i x_i p_i{}^{\circ} \tag{2}$$

The second virial coefficient B_i can be calculated by the Tsonopoulos (*11*) method. The vapor pressure $p_i{}^{\circ}$ is calculated by the Antoine equation; the constants of ethanol and benzene are taken from ref 12 and those of 1-butanol from ref 13, and also listed in Table 1.

The activity coefficients in the the liquid phase are correlated by the Wilson (*14*) equation:

$$\ln \gamma_i = 1 - \ln\left(\sum_{j=1}^{c} \Lambda_{ij} x_j\right) - \sum_{k=1}^{c} \frac{\Lambda_{ki} x_k}{\sum_{j=1}^{c} \Lambda_{kj} x_j} \tag{3}$$

$$\Lambda_{ij} = \frac{V_j^{\mathrm{L}}}{V_i^{\mathrm{L}}} \exp\left[-\frac{\lambda_{ij} - \lambda_{ii}}{RT}\right]$$

The Wilson energy parameters, $\lambda_{ij} - \lambda_{ii}$, are optimized by a nonlinear least-squares technique employing the summation of the squares of the vapor composition deviation as an objective function for binary systems. The energy

Table 6. VLE for Benzene (3) + 1-Butanol (4)

105.0 kPa						205.0 kPa						303.0 kPa					
T/K	x_3	y_3	*T*/K	x_3	y_3	*T*/K	x_3	y_3	*T*/K	x_3	y_3	*T*/K	x_3	y_3	*T*/K	x_3	y_3
391.61	0.0000	0.0000	364.78	0.3339	0.7312	411.93	0.0000	0.0000	388.20	0.3983	0.6865	425.26	0.0000	0.0000	398.93	0.5252	0.7236
390.97	0.0042	0.0153	363.00	0.3810	0.7659	411.47	0.0001	0.0009	386.40	0.4572	0.7217	424.78	0.0042	0.0175	397.38	0.6284	0.7788
390.28	0.0065	0.0274	360.64	0.4837	0.8112	411.07	0.0030	0.0130	384.38	0.5523	0.7651	424.09	0.0098	0.0384	396.25	0.6942	0.8094
388.69	0.0164	0.0944	359.08	0.5533	0.8369	409.11	0.0186	0.0853	383.24	0.6079	0.7956	422.49	0.0285	0.0967	395.48	0.7407	0.8387
386.35	0.0373	0.1793	357.95	0.6186	0.8497	409.56	0.0174	0.0878	381.85	0.7037	0.8315	420.35	0.0593	0.1841	394.85	0.8003	0.8633
385.38	0.0499	0.2137	356.83	0.6941	0.8704	406.72	0.0395	0.1685	380.98	0.7594	0.8641	417.36	0.0955	0.2687	394.32	0.8515	0.8857
382.74	0.0692	0.2942	355.81	0.7846	0.8919	403.83	0.0725	0.2474	380.43	0.8324	0.8939	414.25	0.1424	0.3644	394.03	0.8884	0.9070
381.66	0.0834	0.3418	355.15	0.8324	0.9079	400.95	0.1141	0.3544	379.87	0.8794	0.9252	411.12	0.1837	0.4352	393.81	0.9221	0.9299
379.59	0.1037	0.4037	354.82	0.8883	0.9291	398.61	0.1543	0.4318	379.43	0.9079	0.9373	408.47	0.2434	0.5157	393.66	0.9492	0.9518
377.82	0.1271	0.4635	354.32	0.9396	0.9536	397.03	0.1815	0.4663	378.95	0.9431	0.9574	405.35	0.3259	0.5983	393.49	0.9683	0.9675
373.38	0.1837	0.5636	354.19	0.9738	0.9761	394.34	0.2290	0.5343	378.43	0.9674	0.9766	403.47	0.3785	0.6362	393.47	0.9839	0.9821
369.79	0.2440	0.6489	354.03	0.9833	0.9916	392.29	0.2750	0.5881	378.56	0.9899	0.9964	401.96	0.4273	0.6737	393.58	1.0000	1.0000
367.77	0.2718	0.6749	354.41	1.0000	1.0000	390.75	0.3239	0.6333	378.01	1.0000	1.0000	400.43	0.4837	0.7151			

Table 7. VLE for Chloroform (1) + Benzene (3) + 1-Butanol (4)

105.0 kPa					205.0 kPa					303.0 kPa				
T/K	x_1	y_1	x_3	y_3	*T*/K	x_1	y_1	x_3	y_3	*T*/K	x_1	y_1	x_3	y_3
348.60	0.3983	0.5812	0.4265	0.4011	369.26	0.4811	0.6097	0.4942	0.3697	380.80	0.6836	0.7823	0.3089	0.2153
349.75	0.3598	0.5517	0.4342	0.4066	370.68	0.4463	0.6096	0.4107	0.3427	382.32	0.6344	0.7454	0.2936	0.2174
350.97	0.3286	0.4911	0.3986	0.4158	372.15	0.4936	0.7876	0.1228	0.0933	384.21	0.5807	0.7603	0.2743	0.2053
351.76	0.3094	0.4968	0.3468	0.4166	372.41	0.3951	0.5859	0.3875	0.3439	385.80	0.5324	0.7383	0.2563	0.2163
352.08	0.3503	0.6643	0.1867	0.2364	372.86	0.4660	0.7361	0.1873	0.1504	387.35	0.4865	0.7056	0.2347	0.2110
352.72	0.2852	0.5230	0.3030	0.3767	373.57	0.4095	0.6596	0.2598	0.2434	389.51	0.4305	0.6631	0.2126	0.2128
352.80	0.2865	0.5100	0.3509	0.4070	374.04	0.4502	0.7405	0.1472	0.1464	393.08	0.3820	0.6037	0.1905	0.2184
353.14	0.3672	0.6924	0.1424	0.1851	374.49	0.3805	0.5955	0.3225	0.3180	395.19	0.2783	0.4510	0.3378	0.3804
353.30	0.3395	0.6816	0.1529	0.2138	374.83	0.3556	0.5179	0.3463	0.3580	397.48	0.2450	0.3866	0.3028	0.3828
353.62	0.3089	0.5816	0.2570	0.3167	375.12	0.3468	0.5447	0.3780	0.3731	400.75	0.1890	0.3435	0.2595	0.3718
354.42	0.2661	0.4781	0.3295	0.4104	375.43	0.3419	0.5268	0.4315	0.4158	401.93	0.2159	0.4473	0.1549	0.2385
355.00	0.3056	0.6500	0.1634	0.2296	376.20	0.2710	0.3845	0.4866	0.4983	402.99	0.1627	0.3018	0.2220	0.3495
355.18	0.2252	0.3909	0.3793	0.4840	376.35	0.3212	0.5362	0.3163	0.3480	403.02	0.2301	0.4966	0.0925	0.1570
355.21	0.1738	0.2850	0.4757	0.5900	376.43	0.2408	0.3400	0.5358	0.5437	405.08	0.1421	0.2682	0.1693	0.3017
355.26	0.2571	0.4562	0.3419	0.4336	376.77	0.3955	0.6700	0.1697	0.1631	405.10	0.1854	0.4014	0.0935	0.1968
356.30	0.2360	0.4375	0.3132	0.4171	378.19	0.3486	0.6584	0.1927	0.1934	406.45	0.1210	0.2285	0.1671	0.3260
356.72	0.2022	0.3474	0.4104	0.5235	379.21	0.2883	0.5021	0.2832	0.3463	408.15	0.1710	0.4186	0.0327	0.0972
357.56	0.2232	0.4350	0.2800	0.4192	379.30	0.3080	0.5498	0.2086	0.2586	408.76	0.0954	0.2163	0.1344	0.2708
358.05	0.2592	0.5525	0.1754	0.2789	380.43	0.2533	0.4738	0.2325	0.3100	410.70	0.0821	0.2046	0.1153	0.2553
361.09	0.1882	0.4369	0.1971	0.3532	381.06	0.2564	0.4766	0.2539	0.3402	413.99	0.0609	0.1644	0.0844	0.2126
362.45	0.1364	0.3442	0.2141	0.4141	382.90	0.2088	0.4071	0.2617	0.3659	416.51	0.0444	0.1290	0.0634	0.1732
363.05	0.1652	0.3655	0.2219	0.4171	383.14	0.2256	0.4541	0.2221	0.3341	418.50	0.0338	0.0987	0.0484	0.1284
364.91	0.0945	0.2519	0.2408	0.4893	385.22	0.1976	0.3961	0.1970	0.3257					
366.09	0.1261	0.3255	0.1746	0.3991	385.48	0.1470	0.2877	0.2836	0.4534					
366.75	0.0610	0.1657	0.2402	0.5516	386.17	0.1250	0.2751	0.2591	0.4354					
369.63	0.0990	0.3203	0.1404	0.3603	387.38	0.1586	0.3737	0.1577	0.2970					
371.81	0.0824	0.2798	0.1207	0.3411	388.22	0.0781	0.1646	0.2642	0.4939					
					389.73	0.1227	0.3254	0.1363	0.2899					
					392.34	0.1141	0.3156	0.1142	0.2579					
					394.95	0.0954	0.2777	0.0987	0.2271					

parameters of the chloroform (1) + ethanol (2), chloroform (1) + benzene (3), and ethanol (2) + benzene (3) (*12*) binary mixtures at 101.3 kPa are as follows:

$$(\lambda_{12} - \lambda_{11})/(\mathrm{J\ mol^{-1}}) = -834.1$$

$$(\lambda_{21} - \lambda_{22})/(\mathrm{J\ mol^{-1}}) = 4550$$

$$(\lambda_{13} - \lambda_{11})/(\mathrm{J\ mol^{-1}}) = 5623$$

$$(\lambda_{31} - \lambda_{33})/(\mathrm{J\ mol^{-1}}) = -3163$$

$$(\lambda_{23} - \lambda_{22})/(\mathrm{J\ mol^{-1}}) = 6129$$

$$(\lambda_{32} - \lambda_{33})/(\mathrm{J\ mol^{-1}}) = 571.4$$

The equilibrium temperatures and vapor compositions at the experimental pressures and liquid compositions for these three binary systems at superatmospheric pressure of 303.0 kPa and for chloroform + ethanol + benzene at 101.3 and 302.5 kPa are predicted from the above energy parameters. The deviations of the predicted results from the experimental and the literature (*2*) data are listed in Table 8. It shows that the predicted results are in good agreement with experiment and the literature. As to the binary systems concerning chloroform (1), benzene (3), and 1-butanol (4), the optimized Wilson energy parameters are correlated with the pressure:

$$(\lambda_{13} - \lambda_{11})/(\mathrm{J\ mol^{-1}}) = 5581 + 0.4225P/\mathrm{kPa}$$

$$(\lambda_{31} - \lambda_{33})/(\mathrm{J\ mol^{-1}}) = -3042 - 1.201P/\mathrm{kPa}$$

$$(\lambda_{14} - \lambda_{11})/(\mathrm{J\ mol^{-1}}) = -1408 + 2.287P/\mathrm{kPa}$$

$$(\lambda_{41} - \lambda_{44})/(\mathrm{J\ mol^{-1}}) = 6177 - 13.58P/\mathrm{kPa}$$

$$(\lambda_{34} - \lambda_{33})/(\mathrm{J\ mol^{-1}}) = -159.7 + 2.118P/\mathrm{kPa}$$

$$(\lambda_{43} - \lambda_{44})/(\mathrm{J\ mol^{-1}}) = 5294 - 9.711P/\mathrm{kPa}$$

The vapor–liquid equilibria for the corresponding binary and chloroform + benzene + 1-butanol ternary systems at

Table 8. Comparison of Calculated and Experimental Results for the Systems Concerning Chloroform (1), Ethanol (2), and Benzene (3)

1 + 2			1 + 2 + 3				
P/kPa	Δ*T*/K	Δy_1	*P*/kPa	Δ*T*/K	Δy_1	Δy_2	Δy_3
101.3	0.46	0.0060	101.3	0.51	0.0080	0.0092	0.0068
303.0	0.44	0.0065	302.5	0.48	0.0089	0.0069	0.0095
101.3	0.50	0.0087 (*2*)					

Table 9. Comparison of Calculated and Experimental Results for the Systems Concerning Chloroform (1), Benzene (3), and 1-Butanol (4)

	1 + 3		1 + 4		3 + 4		1 + 3 + 4			
P/kPa	ΔT/K	Δy_1	ΔT/K	Δy_1	ΔT/K	Δy_3	ΔT/K	Δy_1	Δy_3	Δy_4
105.0	0.39	0.0038	0.46	0.0069	0.56	0.0069	0.76	0.0115	0.0108	0.0100
205.0	0.36	0.0038	0.61	0.0115	0.64	0.0104	0.49	0.0113	0.0083	0.0119
303.0	0.45	0.0026	0.46	0.0059	0.42	0.0053	0.48	0.0128	0.0095	0.0115
101.3	0.46	0.0021 (*3*)	0.50	0.0067 (*4*)	0.62	0.0085 (*5*)				
192.7					0.76	0.0077 (*1*)				
294.0					0.32	0.0052 (*1*)				

experimental and literature pressures are also predicted on the basis of the above correlations, and compared with the experimental and literature (*1*, *3–5*) data. The deviations are presented in Table 9. The predicted results agree with the experimental and literature data.

Results and Discussion

(1) Vapor–liquid equilibria of chloroform + ethanol, + benzene, and + 1-butanol, benzene + 1-butanol, chloroform + ethanol + benzene, and chloroform + benzene + 1-butanol have been measured with a dual circulating vapor–liquid equilibrium apparatus at pressures from 101.3 to 303.3 kPa. Binary VLE results are correlated with the Wilson activity coefficient model for the liquid phase and second virial equation for the vapor phase. The calculated results are in good agreement with the experimental values. The ternary results are predicted from the corresponding binary parameters with the multicomponent Wilson equation. The Wilson activity coefficient model can be well used to correlate and predict the VLE behavior at superatmospheric pressures for the asymmetric systems containing halohydrocarbon, aromatic hydrocarbon, and low molecular weight alcohols.

(2) Chloroform + ethanol forms a minimum boiling azeotrope at the experimental pressures, but chloroform + 1-butanol does not.

(3) Ethanol + benzene exhibits a minimum boiling azeotrope over a wide range of pressures from subatmospheric to superatmospheric pressures of 911.9 kPa (*12*), but benzene + 1-butanol does so only at a pressure of 303.0 kPa. However, toluene + 1-butanol also forms an azeotrope at pressures up to 911.9 kPa.

(4) The molecules of alcohol associate in the liquid phase because of the hydrogen bonding. When nonpolar or weakly polar hydrocarbons are added to the alcohol, the degree of association for the alcohol is decreased, the amount of monomer of the alcohol in solution increases, and the vapor pressure of the solution goes up. Thus, the boiling point goes down. Therefore, a minimum boiling azeotrope often appears in the temperature–composition diagram for hydrocarbon + alcohol systems.

(5) The amount of alcohol in the azeotropic mixture increases as the pressure goes up, but the amount of alcohol in the azeotropic mixture decreases as the number of carbons in the alcohol is increased at the same pressure.

(6) In the presence of alcohol, chloroform appears to decompose when the temperature is over 400 K. Cl^- ions can be detected by $AgNO_3$ reagent. It might be caused by a nucleophilic substitution reaction on the saturated carbon atom of chloroform.

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