Vapor−Liquid Equilibrium Data for the Quaternary System Acetone + Chloroform + Methanol + Benzene at 101.3 kPa

Kiyofumi Kurihara,* Yoshitaka Takimoto, Kenji Ochi, and Kazuo Kojima

Department of Materials and Applied Chemistry, Nihon University, 1-8 Kanda Surugadai, Chiyoda-ku,
Tokyo 101-8308, Japan

Isobaric vapor−liquid equilibria were measured for the quaternary system acetone + chloroform + methanol + benzene at atmospheric pressure. No literature VLE data were available for this system. The parameters of the Wilson, NRTL, and UNIQUAC equations were determined from the vapor−liquid equilibrium data of the constituent six binary systems, and the predictions for this quaternary system were compared with experiments.

Introduction

In previous studies,[1−3] the experimental vapor−liquid equilibrium (VLE) data have been presented for the four ternary systems acetone + chloroform + methanol, acetone + chloroform + benzene, acetone + methanol + benzene, and chloroform + methanol + benzene. These ternary systems exhibit a valley and/or a ridge in the liquid composition versus bubble point temperature surface from the behavior of the experimental vapor−liquid tie lines. The terms “valley” and “ridge” have been defined as the curves which divide the patterns of vapor−liquid tie lines by Naka et al.[4,5] It is important to discuss the existence of the valley and ridge, because the composition profiles of the distillation columns are restricted for them. The VLE data for the constituent six binary systems of the ternary systems previously described have also been reported in the same paper.[1−3]

In this work, the experimental target was extended to the system of acetone + chloroform + methanol + benzene. The VLE data for the quaternary system were determined at 101.3 kPa in order to elucidate its phase behavior including the formation of an azeotrope.

Experimental Section

Apparatus and Procedure. In this VLE measurement, a modified Rogalski−Malanowski equilibrium still has been used by combining it with the isobaric controlling equipment reported in previous work.[3] The equipment contains an ebulliometer for a reference substance (water) in addition to an equilibrium still for the samples. In this work, 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). This apparatus allowed the measurement of the 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.

Analysis. The 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 the 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.

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

	ρ (298.15 K)/(g cm^{-3})		T_b/K	
component	exptl	lit.[a]	exptl	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.[6]

Materials. Acetone, chloroform, methanol, and benzene were special grade pure chemicals (Wako Pure Chemical Industry, Ltd., Japan). 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 and benzene were used after removing any 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 chemicals are shown together with the literature values.

Experimental Results

Table 2 shows the experimental VLE data for the quaternary system of acetone + chloroform + methanol + benzene at 101.3 kPa. The continuous vapor−liquid tie lines were measured as the quaternary VLE data, because the purpose of this paper was to clarify the behavior of its tie lines. The number of data points was 145.

The activity coefficients, γ_i, in Table 2 were calculated by the following equation:

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

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

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* Corresponding author. E-mail: kurihara@chem.cst.nihon-u.ac.jp.

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Table 2. 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) + Benzene (4) System at 101.3 kPa

x_1	x_2	x_3	y_1	y_2	y_3	T/K	γ_1	γ_2	γ_3	γ_4
0.027	0.019	0.773	0.036	0.027	0.658	331.55	1.283	1.586	1.085	3.163
0.041	0.029	0.644	0.045	0.034	0.599	330.97	1.073	1.328	1.216	2.349
0.051	0.034	0.587	0.054	0.036	0.580	330.92	1.036	1.199	1.295	2.101
0.059	0.037	0.565	0.062	0.038	0.571	330.91	1.027	1.163	1.326	2.027
0.073	0.041	0.551	0.076	0.041	0.563	330.89	1.017	1.131	1.342	1.996
0.084	0.040	0.568	0.088	0.041	0.558	330.86	1.024	1.160	1.292	2.126
0.094	0.042	0.554	0.100	0.042	0.556	330.85	1.039	1.131	1.320	2.039
0.102	0.040	0.554	0.108	0.040	0.554	330.83	1.035	1.131	1.316	2.053
0.117	0.041	0.543	0.124	0.039	0.546	330.80	1.036	1.076	1.326	2.041
0.127	0.040	0.551	0.136	0.039	0.545	330.77	1.047	1.103	1.306	2.085
0.138	0.040	0.543	0.148	0.038	0.540	330.71	1.050	1.076	1.316	2.067
0.154	0.039	0.539	0.164	0.036	0.533	330.70	1.042	1.045	1.309	2.098
0.161	0.034	0.537	0.175	0.032	0.529	330.68	1.064	1.065	1.306	2.076
0.170	0.026	0.534	0.184	0.024	0.527	330.62	1.062	1.046	1.311	2.073
0.196	0.025	0.520	0.214	0.023	0.514	330.52	1.073	1.044	1.319	2.038
0.217	0.020	0.515	0.238	0.017	0.505	330.44	1.079	0.965	1.313	2.058
0.242	0.016	0.491	0.263	0.015	0.489	330.35	1.071	1.065	1.340	1.980
0.258	0.014	0.494	0.282	0.012	0.485	330.27	1.080	0.976	1.325	2.021
0.284	0.008	0.484	0.310	0.007	0.473	330.14	1.081	0.998	1.327	2.016
0.308	0.007	0.473	0.327	0.006	0.464	330.08	1.053	0.979	1.336	2.064
0.327	0.006	0.463	0.354	0.004	0.451	329.96	1.077	0.763	1.334	2.027
0.038	0.028	0.261	0.039	0.022	0.516	332.02	0.969	0.856	2.488	1.258
0.042	0.020	0.512	0.043	0.022	0.568	331.02	0.999	1.242	1.449	1.791
0.045	0.022	0.565	0.047	0.023	0.578	330.96	1.021	1.183	1.339	1.994
0.049	0.024	0.575	0.052	0.026	0.579	330.94	1.038	1.226	1.319	2.033
0.053	0.024	0.580	0.056	0.024	0.579	330.93	1.034	1.132	1.308	2.075
0.058	0.024	0.580	0.061	0.022	0.578	330.92	1.029	1.038	1.306	2.094
0.065	0.022	0.575	0.069	0.022	0.575	330.91	1.039	1.132	1.311	2.064
0.070	0.026	0.571	0.074	0.026	0.572	330.89	1.034	1.132	1.315	2.059
0.085	0.023	0.565	0.091	0.023	0.566	330.85	1.048	1.132	1.317	2.049
0.092	0.024	0.564	0.099	0.024	0.562	330.85	1.053	1.131	1.310	2.061
0.094	0.023	0.561	0.101	0.022	0.561	330.84	1.052	1.082	1.315	2.055
0.099	0.022	0.564	0.108	0.022	0.563	330.82	1.068	1.132	1.314	2.043
0.109	0.020	0.563	0.119	0.020	0.555	330.81	1.069	1.131	1.298	2.083
0.120	0.021	0.547	0.129	0.021	0.548	330.78	1.052	1.131	1.321	2.031
0.172	0.018	0.512	0.186	0.017	0.522	330.62	1.061	1.070	1.355	1.948
0.185	0.019	0.521	0.201	0.017	0.520	330.55	1.068	1.015	1.330	2.017
0.203	0.016	0.518	0.221	0.015	0.513	330.48	1.071	1.064	1.324	2.026
0.221	0.017	0.510	0.241	0.015	0.504	330.42	1.074	1.002	1.325	2.026
0.241	0.018	0.501	0.263	0.016	0.494	330.34	1.076	1.011	1.327	2.019
0.039	0.077	0.247	0.040	0.062	0.505	332.06	0.964	0.876	2.571	1.232
0.047	0.062	0.495	0.046	0.060	0.556	330.96	0.954	1.094	1.472	1.777
0.051	0.056	0.553	0.051	0.059	0.569	330.90	0.977	1.194	1.350	1.971
0.056	0.057	0.567	0.057	0.060	0.571	330.87	0.995	1.194	1.323	2.039
0.073	0.056	0.564	0.076	0.058	0.565	330.86	1.017	1.173	1.317	2.051
0.082	0.053	0.563	0.085	0.054	0.563	330.85	1.013	1.154	1.315	2.065
0.088	0.051	0.558	0.091	0.052	0.558	330.83	1.011	1.155	1.316	2.067
0.094	0.048	0.562	0.099	0.049	0.560	330.83	1.029	1.156	1.312	2.067
0.098	0.048	0.562	0.104	0.049	0.557	330.82	1.037	1.156	1.305	2.081
0.109	0.047	0.554	0.116	0.047	0.553	330.80	1.040	1.132	1.316	2.054
0.118	0.045	0.550	0.126	0.045	0.549	330.79	1.043	1.131	1.316	2.047
0.145	0.040	0.540	0.157	0.038	0.537	330.70	1.060	1.076	1.317	2.052
0.158	0.038	0.532	0.170	0.036	0.530	330.66	1.054	1.073	1.321	2.046
0.170	0.033	0.531	0.184	0.030	0.526	330.62	1.061	1.030	1.316	2.064
0.181	0.032	0.534	0.197	0.030	0.525	330.59	1.068	1.063	1.308	2.073
0.199	0.030	0.521	0.217	0.027	0.515	330.52	1.071	1.021	1.319	2.044
0.218	0.026	0.514	0.237	0.024	0.504	330.45	1.069	1.048	1.313	2.064
0.233	0.025	0.499	0.253	0.021	0.497	330.40	1.069	0.954	1.337	2.007
0.251	0.022	0.496	0.274	0.019	0.489	330.32	1.076	0.982	1.328	2.016
0.273	0.023	0.486	0.296	0.020	0.478	330.24	1.071	0.990	1.330	2.025
0.292	0.020	0.480	0.318	0.016	0.470	330.16	1.077	0.912	1.329	2.026
0.319	0.014	0.466	0.338	0.012	0.464	330.06	1.051	0.979	1.357	1.997
0.256	0.236	0.251	0.242	0.194	0.378	331.72	0.881	0.892	1.935	1.466
0.245	0.186	0.378	0.235	0.162	0.443	330.89	0.921	0.974	1.550	1.751
0.235	0.150	0.452	0.235	0.138	0.474	330.67	0.969	1.037	1.397	1.980
0.240	0.131	0.475	0.248	0.122	0.481	330.63	1.003	1.051	1.350	2.046
0.250	0.115	0.484	0.262	0.107	0.483	330.59	1.019	1.051	1.332	2.076
0.262	0.102	0.481	0.276	0.091	0.481	330.51	1.028	1.009	1.339	2.083
0.276	0.086	0.485	0.295	0.077	0.478	330.43	1.046	1.014	1.324	2.090
0.292	0.075	0.485	0.314	0.066	0.473	330.35	1.055	0.998	1.315	2.124
0.312	0.063	0.475	0.337	0.054	0.463	330.23	1.063	0.975	1.321	2.090
0.335	0.053	0.465	0.363	0.044	0.452	330.12	1.070	0.946	1.324	2.069
0.361	0.044	0.454	0.391	0.035	0.440	329.98	1.073	0.908	1.328	2.061
0.386	0.034	0.437	0.416	0.026	0.426	329.83	1.072	0.876	1.345	2.012
0.412	0.026	0.429	0.443	0.019	0.415	329.68	1.074	0.840	1.344	2.028
0.442	0.019	0.420	0.473	0.013	0.404	329.54	1.073	0.789	1.345	2.039
0.140	0.454	0.150	0.107	0.406	0.331	332.09	0.697	0.963	2.805	1.212
0.117	0.388	0.331	0.083	0.378	0.423	330.21	0.689	1.120	1.740	1.506
0.090	0.356	0.431	0.063	0.384	0.455	329.68	0.692	1.264	1.465	1.729
0.069	0.363	0.464	0.046	0.408	0.459	329.33	0.666	1.334	1.392	1.837
0.056	0.386	0.466	0.036	0.439	0.451	329.00	0.648	1.364	1.381	1.786
0.038	0.442	0.447	0.021	0.497	0.427	328.36	0.566	1.377	1.401	1.708
0.020	0.506	0.425	0.010	0.558	0.402	327.61	0.522	1.383	1.432	1.423
0.587	0.108	0.067	0.652	0.067	0.119	332.71	0.997	0.636	2.236	1.342
0.643	0.065	0.131	0.668	0.037	0.183	330.67	0.996	0.623	1.899	1.476
0.661	0.039	0.191	0.673	0.022	0.227	329.63	1.010	0.639	1.680	1.577
0.664	0.020	0.238	0.671	0.012	0.258	329.12	1.020	0.692	1.560	1.700
0.033	0.126	0.816	0.043	0.232	0.664	331.86	1.222	2.036	1.025	4.959
0.046	0.214	0.680	0.044	0.315	0.561	330.22	0.937	1.706	1.114	2.852
0.050	0.296	0.574	0.038	0.378	0.501	329.46	0.758	1.513	1.219	2.272
0.045	0.364	0.504	0.026	0.434	0.463	328.95	0.584	1.434	1.312	1.969
0.491	0.427	0.042	0.524	0.357	0.089	335.19	0.881	0.804	2.445	1.363
0.531	0.350	0.089	0.546	0.270	0.161	333.43	0.898	0.783	2.221	1.480
0.553	0.257	0.166	0.558	0.185	0.238	331.66	0.935	0.772	1.874	1.626
0.561	0.176	0.243	0.567	0.124	0.295	330.55	0.973	0.783	1.650	1.496
0.387	0.090	0.185	0.408	0.061	0.302	331.74	0.983	0.726	2.102	1.373
0.395	0.059	0.300	0.405	0.041	0.367	330.47	0.998	0.778	1.650	1.615
0.402	0.043	0.367	0.419	0.032	0.392	330.06	1.028	0.845	1.463	1.803
0.415	0.031	0.397	0.436	0.023	0.401	329.81	1.045	0.849	1.397	1.944
0.432	0.021	0.409	0.459	0.016	0.401	329.64	1.062	0.876	1.365	1.973
0.461	0.013	0.400	0.486	0.011	0.387	329.49	1.058	0.975	1.357	2.033
0.114	0.275	0.161	0.105	0.234	0.380	332.52	0.839	0.905	2.936	1.224
0.118	0.228	0.370	0.100	0.218	0.456	330.93	0.814	1.074	1.626	1.654
0.111	0.209	0.441	0.095	0.213	0.487	330.74	0.828	1.154	1.466	1.797
0.114	0.201	0.469	0.100	0.213	0.490	330.72	0.849	1.200	1.387	1.913
0.113	0.206	0.478	0.097	0.220	0.495	330.68	0.832	1.212	1.377	1.946
0.108	0.207	0.488	0.094	0.224	0.497	330.65	0.844	1.229	1.356	1.975
0.105	0.211	0.495	0.089	0.237	0.502	330.61	0.822	1.278	1.352	1.917
0.090	0.238	0.494	0.081	0.250	0.501	330.51	0.875	1.200	1.358	1.994
0.090	0.240	0.495	0.072	0.269	0.494	330.37	0.781	1.286	1.344	2.001
0.079	0.255	0.493	0.062	0.289	0.491	330.22	0.769	1.307	1.350	1.947
0.071	0.274	0.489	0.052	0.312	0.487	330.08	0.720	1.320	1.357	1.922
0.065	0.295	0.485	0.046	0.336	0.480	329.88	0.699	1.329	1.360	1.919
0.056	0.318	0.486	0.038	0.366	0.474	329.63	0.674	1.354	1.355	1.894
0.730	0.051	0.065	0.774	0.029	0.092	331.08	1.001	0.611	1.909	1.430
0.773	0.030	0.088	0.794	0.017	0.113	330.10	1.001	0.628	1.800	1.516
0.777	0.020	0.125	0.786	0.011	0.147	329.56	1.003	0.621	1.680	1.592
0.769	0.013	0.157	0.772	0.007	0.178	329.09	1.012	0.618	1.647	1.590
0.285	0.527	0.069	0.262	0.486	0.170	334.68	0.768	0.909	2.871	1.260
0.279	0.476	0.156	0.228	0.428	0.282	332.26	0.738	0.959	2.296	1.385
0.256	0.412	0.275	0.195	0.392	0.364	330.99	0.719	1.061	1.757	1.787
0.207	0.372	0.364	0.161	0.383	0.409	330.47	0.748	1.171	1.518	1.746
0.173	0.365	0.410	0.127	0.394	0.430	330.19	0.712	1.241	1.430	2.013
0.142	0.367	0.437	0.103	0.414	0.434	329.93	0.709	1.309	1.368	1.955
0.111	0.388	0.449	0.077	0.436	0.442	329.41	0.689	1.328	1.383	1.897
0.089	0.420	0.441	0.055	0.481	0.423	329.03	0.619	1.370	1.370	1.819
0.067	0.460	0.429	0.036	0.518	0.412	328.49	0.547	1.372	1.403	1.744
0.056	0.493	0.415	0.028	0.545	0.401	328.12	0.514	1.363	1.434	1.650
0.035	0.519	0.418	0.019	0.558	0.402	327.60	0.567	1.349	1.457	1.745
0.058	0.104	0.553	0.051	0.137	0.530	330.92	0.853	1.488	1.260	2.061
0.057	0.134	0.529	0.049	0.158	0.533	330.80	0.836	1.338	1.330	1.942
0.054	0.151	0.534	0.048	0.164	0.536	330.73	0.866	1.235	1.329	2.025
0.052	0.158	0.535	0.048	0.171	0.548	330.57	0.903	1.238	1.364	1.929
0.051	0.168	0.544	0.046	0.181	0.542	330.54	0.883	1.234	1.329	2.059
0.048	0.179	0.540	0.039	0.204	0.527	330.57	0.793	1.303	1.301	2.080
0.044	0.198	0.524	0.036	0.219	0.527	330.47	0.800	1.269	1.346	1.970
0.195	0.036	0.040	0.308	0.031	0.167	338.35	1.205	0.750	4.183	1.087
0.285	0.024	0.152	0.329	0.024	0.317	332.67	1.050	1.043	2.582	1.197
0.314	0.017	0.329	0.333	0.013	0.407	330.60	1.032	0.856	1.654	1.533
0.324	0.011	0.415	0.335	0.006	0.452	330.12	1.024	0.621	1.481	1.782
0.323	0.004	0.459	0.351	0.004	0.452	329.93	1.082	1.145	1.350	1.955
0.328	0.052	0.567	0.368	0.051	0.512	330.78	1.085	1.098	1.195	2.755
0.372	0.052	0.504	0.405	0.049	0.467	330.39	1.064	1.064	1.249	2.351
0.423	0.049	0.438	0.452	0.040	0.420	330.19	1.049	0.924	1.306	2.109
0.466	0.042	0.401	0.497	0.032	0.389	329.94	1.054	0.866	1.337	1.962

by the Tsonopoulos method.[7] The parameters, a_i and b_i of the pure components in the polar contribution term of the Tsonopoulos method are shown in Table 3. The binary constants, k_{ij}, for the Tsonopoulos method are also listed in Table 4. The k_{ij} value was set as the value recommended by Tsonopoulos[7,8] except for the acetone + chloroform and chloroform + methanol systems. The k_{ij} value for acetone + chloroform was evaluated from the second virial coefficients of this mixture reported by Zaalishvili and Kolysko.[9] For the chloroform + methanol system, the value of k_{ij} was also determined from the second virial coefficients of chloroform + ethanol reported by Markuzin and Bain-

Table 3. Parameters, *a* and *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.[12] [b] These values were determined in this paper from the second virial coefficients reported by Dymond and Smith.[13] [c] Tsonopoulos.[7] [d] Tsonopoulos et al.[14]

Table 4. Characteristic Binary Constants, k_{ij}, for the Tsonopoulos Method

	acetone	chloroform	methanol	benzene
acetone	0	−0.10[a]	0.05[b]	0.12[b]
chloroform	−0.10[a]	0	−0.03[a]	0[c]
methanol	0.05[b]	−0.03[a]	0	0.20[b]
benzene	0.12[b]	0[c]	0.20[b]	0

[a] These values were determined in this paper. [b] Tsonopoulos.[7] [c] Tsonopoulos.[8]

din,[10] 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.[11] The vapor pressures of the pure components, P_i^{S}, were calculated from the Antoine equation constants[12] shown in Table 3.

Prediction

Due to predicting the VLE of the quaternary acetone + chloroform + methanol + benzene system, the activity coefficients of these constituent six binary systems were correlated by the Wilson,[15] NRTL,[16] and UNIQUAC[17] equations. The following objective function was minimized during optimization of the parameters in each of the three equations on the basis of the experimental binary VLE data at 101.3 kPa presented in previous studies.[1−3]

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

These binary VLE data have been examined using the thermodynamic consistency test proposed in previous papers,[18,19] 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 all six binary systems were thermodynamically consistent.

Table 5 lists the estimated parameters of the six binary systems and the deviations between the experimental and calculated vapor-phase compositions and bubble point temperatures. The liquid molar volumes, v_i^{L}, in the Wilson equation were predicted by the modified Rackett equation, since the influence of pressure on v_i^{L} is small in the temperature range used in this study. Table 5 indicates that all three activity coefficient equations give good correlations for the six binary systems.

Table 6. Deviations between the Calculated and Experimental Vapor-Phase Mole Fractions, Δy_i, and Temperature, ΔT, for the Acetone (1) + Chloroform (2) + Methanol (3) + Benzene (4) System at 101.3 kPa Using the Wilson, NRTL, and UNIQUAC Equations[a]

deviation	$\Delta y_1 \times 100$	$\Delta y_2 \times 100$	$\Delta y_3 \times 100$	ΔT/K
		Wilson Equation		
avg	0.4	0.3	0.5	0.18
max.	1.8	2.3	2.8	0.54
		NRTL Equation		
avg	0.4	0.3	0.4	0.17
max.	1.9	2.0	2.7	0.57
		UNIQUAC Equation		
avg	0.3	0.3	0.6	0.16
max.	2.0	2.2	2.9	0.61

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

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

parameter	acetone (1) + chloroform (2)[c]	acetone (1) + methanol (2)[d]	acetone (1) + benzene (2)[e]	chloroform(1) + methanol (2)[d]	chloroform(1) + benzene (2)[c]	methanol (1) + benzene (2)[e]
			Wilson Equation			
$\lambda_{12} - \lambda_{11}$[b]	−250.04	−767.72	1991.5	−1492.36	−181.72	7476.31
$\lambda_{12} - \lambda_{22}$[b]	−1670.35	2692.40	−569.94	7509.93	−401.78	730.83
			NRTL Equation			
$g_{12} - g_{22}$[b]	−1409.81	770.15	−156.80	5942.88	−86.75	3352.10
$g_{21} - g_{11}$[b]	−520.99	1023.18	1572.56	−308.55	−501.44	5003.95
α_{12}	0.4199	0.1099	0.4307	0.3253	0.3000	0.5020
			UNIQUAC Equation			
$u_{12} - u_{11}$[b]	−986.50	1916.30	−926.43	5578.84	−63.66	−265.88
$u_{12} - u_{22}$[b]	158.97	−443.46	1497.38	−1147.19	−260.28	4671.15

deviation	$\Delta y_1 \times 100$	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	$\Delta y_1 \times 100$	ΔT/K
						Wilson Equation						
avg	0.5	0.40	0.2	0.04	0.2	0.09	0.7	0.12	0.2	0.07	0.2	0.06
max.	1.2	0.68	0.4	0.09	0.4	0.20	1.3	0.24	0.4	0.15	0.4	0.16
						NRTL Equation						
avg	0.6	0.35	0.2	0.04	0.2	0.09	0.5	0.15	0.2	0.07	0.2	0.02
max.	1.3	0.66	0.4	0.07	0.4	0.21	1.1	0.30	0.4	0.15	0.5	0.17
						UNIQUAC Equation						
avg	0.5	0.34	0.2	0.04	0.2	0.08	0.5	0.11	0.2	0.07	0.7	0.15
max.	1.1	0.60	0.4	0.08	0.4	0.16	1.3	0.33	0.4	0.16	1.6	0.94

[a] $\Delta y_1 = \sum_k |y_{1,\mathrm{exp}} - y_{1,\mathrm{calc}}|_k/N$, $\Delta T = \sum_k |T_{\mathrm{exp}} - T_{\mathrm{calc}}|_k/N$; N = number of data points. [b] $\mathrm{J \cdot mol^{-1}}$. [c] Kojima et al.[1] [d] Hiaki et al.[2] [e] Kurihara et al.[3]

Table 7. Predicted Azeotropic Composition, $x_{i(\mathrm{az})}$, in Mole Fractions, and Temperature, $T_{(\mathrm{az})}$, for the Acetone (1) + Chloroform (2) + Methanol (3) + Benzene (4) System at 101.3 kPa Using the Wilson, NRTL, and UNIQUAC Equations

equation	$x_{1(\mathrm{az})}$	$x_{2(\mathrm{az})}$	$x_{3(\mathrm{az})}$	$T_{(\mathrm{az})}$/K
Wilson	0.287	0.180	0.461	330.39
NRTL	0.350	0.212	0.436	330.45
UNIQUAC	0.315	0.194	0.447	330.37

The prediction of the VLE of the quaternary acetone + chloroform + methanol + benzene system was performed using the binary Wilson, NRTL, and UNIQUAC parameters shown in Table 5. The results are summarized in Table 6. The three equations yielded similar results for this quaternary system. The average deviations given from these equations became $100\Delta y \leq 0.6$ and $\Delta T \leq 0.18$ K.

On the basis of the predicted results from all three equations, an attempt was made to predict the quaternary azeotropic point. The azeotropic temperatures and compositions are shown in Tables 7. For this quaternary system at 101.3 kPa, Styazhkin et al.[20] has presented the quaternary azeotropic point ($x_{1(\mathrm{az})} = 0.182$, $x_{2(\mathrm{az})} = 0.120$, $x_{3(\mathrm{az})} = 0.500$ in mole fractions and $T_{(\mathrm{az})} = 331.05$ K) which was estimated by the Wilson equations. Although the predicted results are different from the values of Styazhkin et al., it is concluded that the acetone + chloroform + methanol + benzene system has an azeotropic point at atmospheric pressure on the basis of the behavior of the experimental vapor−liquid tie lines in addition to the predicted results given by the three activity coefficient equations.

Conclusion

The isobaric vapor−liquid equilibrium data were measured for the quaternary system acetone + chloroform + methanol + benzene at 101.3 kPa. The number of measured data points was 145, and the other VLE data for this system could not be found in the literature. These experimental data were compared with those predicted by the Wilson, NRTL, and UNIQUAC equations. The parameters in each of the three equations were fitted on the basis of the VLE data for the constituent six binary systems at 101.3 kPa presented in previous studies. The results of VLE predicted by those parameters showed good agreement with the experimental data for the quaternary system. All three equations provided generally similar results and exhibited the existence of a quaternary azeotropic point at 101.3 kPa.

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