Vapor−Liquid Equilibria for the Ternary Systems of Methyl *tert*-Butyl Ether + Methanol + Methylcyclohexane and Methyl *tert*-Butyl Ether + Methanol + *n*-Heptane and Constituent Binary Systems at 313.15 K

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Isothermal vapor−liquid equilibrium (VLE) data are measured for the ternary systems of methyl *tert*-butyl ether (MTBE) + methanol + methylcyclohexane (MCH) and MTBE + methanol + *n*-heptane and constituent four binary systems, MTBE + MCH, MTBE + *n*-heptane, methanol + MCH, and methanol + *n*-heptane, at 313.15 K. The experimental binary VLE data were correlated with common g^E model equations. The correlated Wilson and NRTL parameters of the constituent binary systems were used to calculate the phase behavior of the ternary mixtures. The calculated ternary VLE data using Wilson and NRTL parameters and the predicted data using modified UNIFAC (Dortmund) model were compared with experimental ternary data.

Introduction

Studies on phase equilibria of liquid mixtures are considerably important for the design of thermal separation processes and theoretical understanding the nature of molecular behavior.[1,2] Many investigations of vapor−liquid equilibria (VLE) and excess properties have already been carried out for binary mixtures, while that of ternary mixtures are relatively rare in the literature.

Oxygenated compounds such as methyl *tert*-butyl ether (MTBE), ethyl *tert*-butyl ether (ETBE), and *tert*-amyl methyl ether (TAME) can all be used as gasoline additives because of their good anti-knocking properties. The accurate VLE data of these additives with alcohols and hydrocarbons are used to develop calculational models for gasoline reformulation and also in the design of systems that reduce evaporative emissions in the fuel tank and avoid vapor lock formation in automobile fuel-injection systems.[3] The phase equilibrium and excess properties for systems containing MTBE, alcohols, and hydrocarbons have been the subject of numerous investigations in the recent years. Nevertheless, more data are required to develop solution models and to design separation processes.

In this paper, experimental results of isothermal VLE are reported for the four binary systems MTBE (1) + methylcyclohexane(MCH) (2), MTBE (1) + *n*-heptane (2), methanol (1) + MCH (2), and methanol (1) + *n*-heptane (2) at 313.15 K and ternary systems MTBE (1) + methanol (2) + MCH (3) and MTBE (1) + methanol (2) + *n*-heptane (3) at the same temperature by using the headspace gas chromatography (HSGC) method. For measured binary systems, some experimental values are already presented in some literature, but most of them are not at the same experimental condition. Experimental data at various temperatures are needed to the process modeling and development of thermodynamic parameters.

The experimental binary VLE data were correlated using common g^E model equations; Margules, van Laar, Wilson, NRTL, and UNIQUAC. Besides, experimental ternary VLE data were compared with the estimated ternary VLE data using constituent binary Wilson and NRTL parameters and the predicted data using a modified UNIFAC (Dortmund) model.

Experimental Section

Materials. MTBE and MCH were from Aldrich Chemical Co., and methanol and *n*-heptane were from Merck Co. MTBE had a declared purity of better than 99.8 wt % and was used without further purification. Others were used after water has been removed using molecular sieves with a pore diameter of 0.4 nm. The purity of all chemicals was checked by gas chromatography and by measuring densities and comparing with the values reported in the literature. The water content of all the chemicals by using a Karl-Fisher titrator (Metrohm 684 KF-Coulometer) was less than 50 ppm. The purities, densities, Antoine constants, and calculated vapor pressures at 313.15K are summarized in Table 1.

Apparatus and Procedure. Isothermal VLE data have been measured by using headspace gas chromatography (HSGC) for all the binary and ternary systems. The HSGC system consists of a commercial gas chromatograph (HP 5890 series II) and a headspace sampler (HP19395A), which has an electro-pneumatic sampling system and a precision thermostat, having an accuracy of ±0.1 K. A HP-FFAP (Hewlett-Packard, poly(ethylene glycol)-TPA modified, 50 m × 0.2 mm × 0.3 μm) capillary column and a thermal conductivity detector were used for the analysis. By the HSGC method, only the equilibrated vapor phase is automatically analyzed with the help of an electro-pneumatic sampling system, while the equilibrium liquid compositions and total pressures are calculated with thermodynamic relations and mass balance from the feed compositions. All the sample mixtures samples (ca. 3 cm^3)

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10.1021/je050029o CCC: $30.25

Table 1. Purities, Measured Densities at 298.15 K and Antoine Constants of Pure Components

	GC analysis	density/g cm^{-3}		Antoine constants^a			vapor pressure^b at 313.15 K
chemicals	wt %	present study	lit. value^a	A	B	C	kPa
MTBE	99.9	0.7406	0.7405	6.25487	1265.40	242.571	59.68
methanol	99.8	0.7868	0.7866	7.20587	1582.27	239.726	35.43
MCH	99.9	0.7652	0.7651	5.96390	1278.57	222.168	12.22
n-heptane	99.9	0.6795	0.6795	6.01876	1264.37	216.640	12.36

[a] Data from Dortmund Data Bank (DDB, version 1998). [b] $\log_{10} P_i^{\text{sat}}$ (kPa) $= A - [B/(t(°\text{C}) + C)]$.

Table 2. Isothermal VLE for Binary Systems of MTBE (1) + MCH (2), MTBE (1) + *n*-Heptane (2), Methanol (1) + MCH (2), and Methanol (1) + *n*-Heptane (2) at 313.15 K

P (calcd) kPa	x_1	y_1	γ_1	γ_2	P (calcd) kPa	x_1	y_1	γ_1	γ_2
				MTBE (1) + MCH (2)					
13.81	0.0202	0.1326	1.5180	1.0005	43.34	0.5489	0.8574	1.1344	1.1215
15.94	0.0504	0.2704	1.4340	1.0024	45.87	0.5992	0.8794	1.1279	1.1301
17.61	0.0737	0.3556	1.4231	1.0029	47.29	0.6479	0.8912	1.0898	1.1959
19.19	0.1000	0.4227	1.3588	1.0074	49.91	0.6976	0.9123	1.0936	1.1855
22.55	0.1492	0.5359	1.3573	1.0070	52.11	0.7486	0.9280	1.0823	1.2214
25.92	0.1988	0.6193	1.3531	1.0079	52.84	0.8000	0.9339	1.0336	1.4286
28.55	0.2487	0.6716	1.2921	1.0215	54.75	0.8504	0.9504	1.0252	1.4858
31.09	0.2989	0.7148	1.2456	1.0354	56.26	0.9006	0.9648	1.0098	1.6284
34.22	0.3496	0.7598	1.2464	1.0348	57.60	0.9239	0.9762	1.0198	1.4745
36.71	0.3976	0.7900	1.2219	1.0474	58.07	0.9476	0.9802	1.0066	1.7909
38.84	0.4488	0.8138	1.1802	1.0739	59.06	0.9800	0.9916	1.0012	2.0396
41.69	0.4986	0.8421	1.1797	1.0743					
				MTBE (1) + n-Heptane (2)					
13.53	0.0198	0.1038	1.1902	1.0004	40.35	0.5487	0.8563	1.0550	1.0393
15.15	0.0497	0.2232	1.1397	1.0018	42.25	0.5992	0.8747	1.0333	1.0685
16.58	0.0756	0.3096	1.1377	1.0019	44.83	0.6499	0.8976	1.0375	1.0601
18.00	0.1007	0.3814	1.1428	1.0014	47.29	0.6998	0.9169	1.0382	1.0592
20.54	0.1492	0.4858	1.1203	1.0041	49.12	0.7476	0.9303	1.0242	1.0968
23.52	0.1993	0.5793	1.1453	0.9998	51.55	0.7988	0.9470	1.0239	1.0988
25.28	0.2509	0.6251	1.0554	1.0236	52.91	0.8493	0.9565	0.9984	1.2362
28.40	0.3002	0.6930	1.0984	1.0078	55.12	0.8997	0.9723	0.9980	1.2310
30.53	0.3492	0.7310	1.0706	1.0205	56.22	0.9221	0.9795	1.0005	1.2001
33.37	0.3986	0.7747	1.0864	1.0111	57.35	0.9481	0.9864	0.9997	1.2127
35.95	0.4500	0.8081	1.0818	1.0146	58.70	0.9782	0.9945	0.9999	1.1990
38.06	0.4989	0.8324	1.0642	1.0294					
				Methanol (1) + MCH (2)					
27.37	0.0166	0.5596	25.9721	1.0033	42.89	0.5503	0.7299	1.6056	2.1082
35.65	0.0471	0.6660	14.2206	1.0229	43.08	0.6021	0.7355	1.4852	2.3439
37.79	0.0757	0.6866	9.6745	1.0486	43.16	0.6496	0.7391	1.3862	2.6303
38.29	0.0976	0.6913	7.6572	1.0720	43.28	0.6997	0.7459	1.3022	2.9970
40.97	0.1503	0.7158	5.5066	1.1216	43.25	0.7499	0.7382	1.2016	3.7060
43.39	0.2010	0.7363	4.4858	1.1719	43.17	0.8001	0.7470	1.1375	4.4721
42.65	0.2474	0.7296	3.5494	1.2540	42.94	0.8498	0.7610	1.0852	5.5948
42.91	0.2988	0.7324	2.9689	1.3404	42.39	0.8996	0.7820	1.0400	7.5334
42.94	0.3493	0.7326	2.5413	1.4444	41.65	0.9251	0.8062	1.0245	8.8181
42.77	0.4013	0.7306	2.1977	1.5752	40.58	0.9497	0.8389	1.0118	10.6448
43.56	0.4501	0.7420	2.0271	1.6727	38.22	0.9799	0.9102	1.0020	13.9667
43.02	0.4992	0.7326	1.7818	1.8805					
				Methanol (1) + n-Heptane (2)					
26.64	0.0258	0.5465	15.9554	1.0029	42.77	0.5508	0.7275	1.5943	2.0983
36.05	0.0524	0.6714	13.0252	1.0112	43.27	0.6002	0.7423	1.5106	2.2560
38.21	0.0716	0.6917	10.4132	1.0263	43.43	0.6498	0.7478	1.4107	2.5300
39.92	0.0972	0.7067	8.1951	1.0490	43.51	0.7013	0.7515	1.3158	2.9275
40.14	0.1493	0.7085	5.3745	1.1126	43.47	0.7504	0.7436	1.2157	3.6114
41.44	0.2017	0.7207	4.1804	1.1726	43.42	0.8003	0.7486	1.1464	4.4212
43.03	0.2595	0.7355	3.4422	1.2432	43.30	0.8500	0.7556	1.0863	5.7076
42.66	0.2984	0.7318	2.9524	1.3193	42.88	0.9002	0.7712	1.0369	7.9523
43.05	0.3479	0.7362	2.5718	1.4085	42.32	0.9252	0.7878	1.0171	9.7050
43.38	0.3983	0.7401	2.2754	1.5153	40.56	0.9499	0.8396	1.0118	10.5107
43.18	0.4531	0.7373	1.9830	1.6775	38.27	0.9797	0.9087	1.0020	13.9026
43.36	0.5000	0.7403	1.8122	1.8215					

were prepared directly in a 10 cm^3 glass vial, equilibrium cell, using a digital microbalance (AND Co. HA-202M) with an accuracy of ±1 × 10^{-5} g. The procedure is described in detail elsewhere.[4−6]

Results and Discussion

The pure component properties, stored in the DDB,[7] were used to calculate the true liquid mole compositions with SRK equation.[8] Vapor pressures of the pure component at

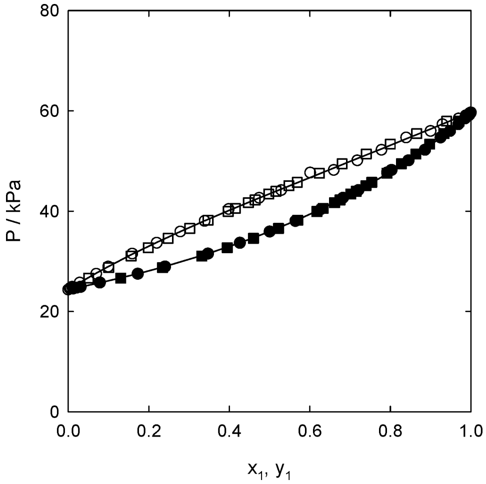

Figure 1. Comparison of isothermal VLE of the MTBE (1) + benzene (2) at 313.15 K with the literature value: ○, liquid phase; ●, vapor phase; □ and ■, ref 11 value.

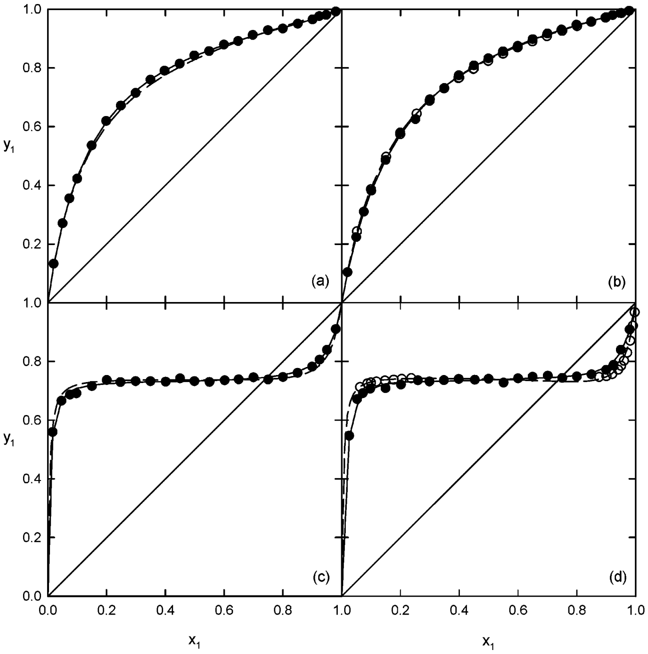

Figure 2. Isothermal VLE of the (a) MTBE (1) + MCH (2), (b) MTBE (1) + *n*-heptane (2), (c) methanol (1) + MCH (2), and (d) methanol (1) + *n*-heptane (2) at 313.15 K: ●, expimetnal values; ○, refs 16 and 17 values; —, calculated by best-fitted g^E model; - -, predicted with modified UNIFAC.

313.15 K were calculated from the Antoine equation. The Antoine constants that were used are listed also in Table 1.

According to the HSGC method used in this work, total pressure is not measured but calculated by using the chromatogram peak area and some thermodynamic relations. The detailed procedure of the calculation method is described in a previous work.[5] Although the total pressure is the calculated value, the calculated total pressures of the HSGC method have shown good agreement with direct measurements.[9,10] For example, calculated total pressure in a previous work[9] of isothermal VLE of MTBE (1) + benzene (2) at 313.15 K is shown in Figure 1 with the literature values.[11]

To check the consistency of the measured VLE, the Redlich−Kister thermodynamic consistency test[12] has been applied and showed good agreement within ±1 % deviations. Additional VLE data for the same binary and ternary systems were calculated through the activity coefficients with the aid of modified UNIFAC (Dortmund) group-contribution method.[13,14] Modified UNIFAC differs from the original UNIFAC[15] by the combinatorial part and the temperature dependence of the group interaction parameters. Only a small number of structural groups are necessary to predict the activity coefficients of binaries and multicomponent systems. The values of the modified UNIFAC (Dortmund) parameters are taken from the data of Gmehling et al.[14]

Table 3. g^E Model Parameters and Mean Deviation between Calculated and Experimental Vapor-Phase Mole Fraction (Δy_1) for the Binary Systems at 313.15 K

model equation	A_{12}	A_{21}	α	Δy_1[a]
		MTBE (1) + MCH (2)		
Margules	0.3363	0.6407		0.0036
van Laar	0.3640	0.7066		0.0028
Wilson	−530.3584	2500.1778		0.0028
NRTL	3361.2091	−1361.4987	0.3000	0.0031
UNIQUAC	1761.8511	−1087.3817	−1087.3817	0.0028
mod. UNIFAC				0.0077
		MTBE (1) + *n*-Heptane (2)		
Margules	0.1354	0.2344		0.0025
van Laar	0.1442	0.2496		0.0025
Wilson	−290.4733	1092.9235		0.0025
NRTL	2193.2116	−1336.8306	0.3000	0.0025
UNIQUAC	825.5885	−601.1777	−601.1777	0.0025
mod. UNIFAC				0.0052
		Methanol (1) + MCH (2)		
Margules	2.6347	2.3501		0.0303
van Laar	2.6578	2.3439		0.0300
Wilson	10215.2190	2299.8068		0.0054
NRTL	5307.9641	6423.0581	0.4450	0.0080
UNIQUAC	−211.5551	6135.2756	6135.2756	0.0200
mod. UNIFAC				0.0213
		Methanol (1) + *n*-Heptane (2)		
Margules	2.5115	2.4082		0.0283
van Laar	2.5183	2.4031		0.0282
Wilson	9600.4548	2228.9847		0.0080
NRTL	5402.0731	5806.9638	0.4460	0.0066
UNIQUAC	−226.8252	6037.6585	6037.6585	0.0192
mod. UNIFAC				0.0104

[a] $\Delta y_1 = |y_{1,\mathrm{exp}} - y_{1,\mathrm{calcd}}|/N$; N = number of data.

Table 2 gives total pressures, activity coefficients, and corresponding compositions of the liquid and vapor phases for the binary systems. The immisciblility was found in the methanol (1) + MCH (2) and the methanol (1) + *n*-heptane systems. The binary systems of MTBE (1) + MCH (2) and MTBE (1) + *n*-heptane (2) have no azeotropic points, while methanol (1) + MCH (2) and methanol (1) + *n*-heptane (2) binary mixtures have the minimum boiling azeotropes and show a strong positive deviation from the ideality at the measured temperature. The azeotropic points were determined by interpolation from the VLE data, which were x_1 = 0.7397 for the MTBE (1) + MCH (2) system and x_1 = 0.7445 for the MTBE (1) + *n*-heptane (2) system. The total pressures at these points are 43.26 kPa and 43.47 kPa, respectively.

The equilibrium vapor−liquid composition data for each binary system at 313.15 K are plotted in Figure 2 with some literature values.[16,17] Because of the immiscibility of the methanol (1) + *n*-heptane (2) binary system, small deviation was shown with literature values. For the MTBE (1) + *n*-heptane (2) systems, experimental values agree well with literature values. The activity coefficients of the experimental binary systems were correlated with the most common g^E models (Margules, van Laar, Wilson, NRTL, and UNIQUAC). The solid lines in Figure 2 are calculated values by the best-correlated equation. The mean deviations between calculated and experimental vapor compositions (Δy_1) are less than 1 mol % by almost all of the g^E model equations, and these small values of deviations indicate the quality of the measured data indirectly. The predicted isothermal VLE data for the same binaries using the modified UNIFAC (Dortmund) equation were also plotted as dashed lines in each of diagrams. The binary mixture containing methanol, such as methanol (1) + MCH (2) and methanol (1) + n-heptane (2), showed slightly larger deviations of 2 % between the measured values and the predicted values than MTBE containing binaries of <1 %. These comparisons are listed in Table 3 together with the correlated g^E model parameters. The non-randomness parameter (α) of the NRTL model was the adjusted value. According to the Renon and Prausnitz's result,[18] α was fixed at 0.3000 if the adjusted value was not converged between 0.1 and 0.8. The mean deviation of vapor-phase mole fraction (Δy_1) is given by

$$\Delta y_1 = |y_{1,\mathrm{exp}} - y_{1,\mathrm{calcd}}|/N \qquad (1)$$

where N is the number of experimental data. Wilson, NRTL, and UNIQUAC parameters (A_{ij}) for binary systems are as follow:

$$\text{Wilson:} \quad A_{ij} = (\lambda_{ij} - \lambda_{ii})\ \mathrm{J{\cdot}mol^{-1}}$$

$$\text{NRTL:} \quad A_{ij} = (g_{ij} - g_{jj})\ \mathrm{J{\cdot}mol^{-1}}$$

$$\text{UNIQUAC:} \quad A_{ij} = (u_{ij} - u_{jj})\ \mathrm{J{\cdot}mol^{-1}}$$

The experimental VLE data for the ternary systems of MTBE (1) + methanol (2) + MCH (3) and MTBE (1) + methanol (2) + n-heptane (3) at 313.15 K are listed and plotted in Tables 4 and 5 and Figures 3 and 4, respectively. The ternary systems have the azeotropic point in each system. The ternary VLE data were calculated by using following Wilson (eq 2) and NRTL (eq 3) with parameters obtained from the experimental constituent binary data and previous values.[9] Besides, the same ternary VLE data were predicted by using the modified UNIFAC (Dortmund). Predicted ternary VLE data are also plotted in Figures 3 and 4 as dotted lines:

$$\ln \gamma_i = -\ln\Big(\sum_{j=1}^{n} x_j \Lambda_{ij}\Big) + 1 - \sum_{k=1}^{n} \frac{x_j \Lambda_{ji}}{\sum_{j=1}^{n} x_j \Lambda_{kj}} \quad (i = 1, 2, 3) \qquad (2)$$

where

$$\Lambda_{ij} = \frac{v_j^{2}}{v_i^{2}} \exp\left(-\frac{\lambda_{ij} - \lambda_{ii}}{RT}\right) \ln \gamma_i = \frac{\sum_{j=1}^{n} \tau_{ji} G_{ji} x_j}{\sum_{k=1}^{n} G_{ki} x_k} + \sum_{j=1}^{n} \frac{x_j G_{ij}}{\sum_{k=1}^{n} G_{kj} x_k} \left(\tau_{ij} - \frac{\sum_{k=1}^{n} x_k \tau_{kj} G_{kj}}{\sum_{k=1}^{n} G_{kj} x_k}\right) \quad (i = 1, 2, 3) \qquad (3)$$

Table 4. Isothermal VLE for the Ternary System of MTBE (1) + Methanol (2) + MCH (3) at 313.15 K

P (calcd) kPa	x_1	x_2	y_1	y_2	γ_1	γ_2	γ_3
48.07	0.0905	0.8091	0.1769	0.6679	1.5747	1.1199	6.0827
47.28	0.0802	0.7191	0.1278	0.6662	1.2619	1.2364	3.9723
46.29	0.0699	0.6295	0.0999	0.6692	1.1076	1.3887	2.9112
45.41	0.0604	0.5402	0.0806	0.6781	1.0152	1.6090	2.2451
44.57	0.0496	0.4510	0.0617	0.6933	0.9276	1.9334	1.7905
43.96	0.0432	0.3583	0.0530	0.6956	0.9033	2.4090	1.5115
43.10	0.0304	0.2694	0.0368	0.7019	0.8751	3.1694	1.3165
52.36	0.1789	0.7213	0.2930	0.5911	1.4368	1.2110	4.9758
50.73	0.1592	0.6411	0.2258	0.5991	1.2052	1.3382	3.6406
49.21	0.1409	0.5602	0.1857	0.6093	1.0865	1.5109	2.7624
47.91	0.1240	0.4783	0.1561	0.6213	1.0105	1.7565	2.1947
46.47	0.1001	0.4003	0.1242	0.6501	0.9656	2.1305	1.7183
45.35	0.0827	0.3197	0.1004	0.6607	0.9221	2.6456	1.4843
44.03	0.0602	0.2404	0.0725	0.6724	0.8884	3.4764	1.3144
55.51	0.2696	0.6300	0.3873	0.5203	1.3364	1.2937	4.1800
53.44	0.2408	0.5598	0.3177	0.5339	1.1817	1.4389	3.2530
51.48	0.2103	0.4893	0.2616	0.5545	1.0731	1.6464	2.5805
49.68	0.1789	0.4207	0.2163	0.5871	1.0066	1.9570	1.9961
48.09	0.1508	0.3497	0.1810	0.5939	0.9677	2.3054	1.7732
46.49	0.1207	0.2806	0.1457	0.6177	0.9400	2.8885	1.5036
44.88	0.0929	0.2104	0.1134	0.6386	0.9181	3.8454	1.3072
42.79	0.0618	0.1389	0.0821	0.6491	0.9523	5.6443	1.1778
57.82	0.3606	0.5399	0.4724	0.4536	1.2692	1.3711	3.5197
55.48	0.3202	0.4806	0.3940	0.4822	1.1439	1.5712	2.8211
53.38	0.2819	0.4191	0.3351	0.5031	1.0633	1.8085	2.3637
51.38	0.2416	0.3603	0.2834	0.5271	1.0098	2.1216	2.0020
49.37	0.1991	0.3010	0.2343	0.5561	0.9732	2.5745	1.6947
47.46	0.1604	0.2413	0.1921	0.5732	0.9525	3.1823	1.5232
45.32	0.1192	0.1816	0.1487	0.5941	0.9469	4.1844	1.3647
59.46	0.4477	0.4540	0.5265	0.4096	1.1716	1.5141	3.1651
57.02	0.3985	0.4030	0.4552	0.4305	1.0912	1.7191	2.6887
54.78	0.3516	0.3484	0.3963	0.4540	1.0346	2.0145	2.2376
52.57	0.2999	0.2998	0.3423	0.4821	1.0053	2.3859	1.8877
50.39	0.2496	0.2508	0.2918	0.5113	0.9869	2.8991	1.6257
48.14	0.1981	0.2059	0.2389	0.5480	0.9728	3.6155	1.4089
45.65	0.1492	0.1547	0.1877	0.5691	0.9621	4.7406	1.3054
43.04	0.1002	0.1142	0.1314	0.5875	0.9459	6.2505	1.2602
36.83	0.0498	0.0477	0.0835	0.5774	1.0331	12.5874	1.1327
60.61	0.5393	0.3604	0.5827	0.3576	1.0971	1.6971	2.9573
58.09	0.4767	0.3238	0.5124	0.3765	1.0462	1.9066	2.6469
55.81	0.4233	0.2778	0.4600	0.4009	1.0160	2.2726	2.1269
53.37	0.3595	0.2387	0.4004	0.4241	0.9962	2.6765	1.9079
50.98	0.2992	0.2010	0.3433	0.4539	0.9803	3.2498	1.6927
48.59	0.2414	0.1676	0.2910	0.4866	0.9815	3.9823	1.4966
45.48	0.1786	0.1244	0.2319	0.5205	0.9895	5.3730	1.3225
61.28	0.6286	0.2727	0.6437	0.3090	1.0513	1.9597	2.4050
58.71	0.5596	0.2413	0.5873	0.3221	1.0323	2.2121	2.1869
56.31	0.4817	0.2239	0.5170	0.3655	1.0128	2.5950	1.8392
53.66	0.4208	0.1782	0.4767	0.3771	1.0184	3.2041	1.6021
51.09	0.3484	0.1544	0.4102	0.4200	1.0078	3.9219	1.4289
48.15	0.2791	0.1243	0.3505	0.4293	1.0132	4.6953	1.4542
44.58	0.2087	0.0920	0.2806	0.4759	1.0044	6.5089	1.2706
40.47	0.1397	0.0636	0.2081	0.5052	1.0103	9.0770	1.1919
61.22	0.7174	0.1836	0.7092	0.2437	1.0140	2.2937	2.3833
58.50	0.6366	0.1625	0.6511	0.2589	1.0024	2.6310	2.1456
55.87	0.5602	0.1401	0.6005	0.2762	1.0035	3.1094	1.8808
53.08	0.4791	0.1200	0.5425	0.3089	1.0070	3.8570	1.6107
50.37	0.3965	0.1070	0.4773	0.3359	1.0162	4.4613	1.5512
46.76	0.3193	0.0817	0.4194	0.3701	1.0291	5.9776	1.3449
42.88	0.2386	0.0628	0.3425	0.4009	1.0313	7.7207	1.2890
60.00	0.8067	0.0937	0.7992	0.1555	0.9961	2.8092	2.2329
57.11	0.7186	0.0819	0.7515	0.1641	1.0006	3.2302	1.9776
54.39	0.6271	0.0751	0.6972	0.1776	1.0132	3.6299	1.8716
51.09	0.5397	0.0605	0.6529	0.1978	1.0356	4.7135	1.5618
47.82	0.4496	0.0520	0.5952	0.2350	1.0606	6.1006	1.3333
43.50	0.3597	0.0386	0.5310	0.2240	1.0759	7.1266	1.4500
38.89	0.2713	0.0287	0.4640	0.2537	1.1144	9.6900	1.2838

where

$$G_{ij} = \exp(-\alpha_{ij}\tau_{ij})$$

$$\tau_{ij} = (g_{ij} - g_{jj})/RT$$

The experimental VLE data were compared with calculated ones and showed relatively good agreements. The

Table 5. Isothermal VLE for the Ternary System of MTBE (1) + Methanol (2) + *n*-Heptane (3) at 313.15 K

P (calcd) kPa	x_1	x_2	y_1	y_2	γ_1	γ_2	γ_3
47.58	0.0900	0.8098	0.1684	0.6761	1.4910	1.1211	5.9755
46.77	0.0804	0.7211	0.1244	0.6789	1.2131	1.2428	3.7479
45.89	0.0700	0.6298	0.0990	0.6821	1.0867	1.4029	2.7071
45.17	0.0603	0.5403	0.0777	0.6921	0.9747	1.6333	2.1061
44.53	0.0502	0.4506	0.0604	0.7035	0.8971	1.9621	1.7032
43.90	0.0407	0.3587	0.0480	0.7106	0.8689	2.4548	1.4267
43.13	0.0299	0.2696	0.0342	0.7224	0.8269	3.2613	1.2123
51.35	0.1793	0.7209	0.2926	0.5974	1.4041	1.2011	4.5774
49.59	0.1602	0.6396	0.2288	0.6089	1.1865	1.3324	3.2523
48.13	0.1407	0.5600	0.1873	0.6291	1.0738	1.5260	2.3871
46.85	0.1198	0.4787	0.1483	0.6460	0.9719	1.7846	1.9414
45.77	0.0999	0.3992	0.1197	0.6655	0.9186	2.1539	1.5875
44.75	0.0803	0.3224	0.0941	0.6787	0.8787	2.6587	1.3773
43.53	0.0599	0.2391	0.0690	0.6911	0.8407	3.5512	1.2052
54.32	0.2702	0.6300	0.3868	0.5285	1.3028	1.2860	3.7291
51.94	0.2408	0.5593	0.3139	0.5544	1.1343	1.4532	2.7671
49.97	0.2097	0.4903	0.2562	0.5826	1.0230	1.6760	2.1719
48.33	0.1795	0.4210	0.2149	0.6022	0.9697	1.9514	1.7896
46.87	0.1493	0.3537	0.1752	0.6242	0.9217	2.3348	1.5299
45.43	0.1200	0.2823	0.1396	0.6417	0.8855	2.9151	1.3446
43.89	0.0907	0.2155	0.1072	0.6595	0.8686	3.7908	1.1941
41.62	0.0596	0.1433	0.0737	0.6629	0.8622	5.4350	1.1125
56.57	0.3596	0.5412	0.4643	0.4693	1.2239	1.3844	3.0654
53.84	0.3207	0.4800	0.3900	0.4982	1.0969	1.5774	2.4442
51.56	0.2805	0.4194	0.3304	0.5294	1.0175	1.8369	1.9488
49.57	0.2384	0.3637	0.2740	0.5492	0.9544	2.1126	1.7814
47.72	0.1996	0.3007	0.2302	0.5856	0.9224	2.6227	1.4230
45.94	0.1543	0.2541	0.1846	0.6028	0.9209	3.0761	1.3354
43.86	0.1193	0.1833	0.1459	0.6294	0.8985	4.2506	1.1434
58.29	0.4506	0.4492	0.5209	0.4243	1.1290	1.5540	2.5799
55.36	0.3989	0.4040	0.4515	0.4535	1.0499	1.7541	2.1574
52.81	0.3518	0.3470	0.3925	0.4859	0.9872	2.0871	1.7235
50.51	0.3005	0.2990	0.3366	0.5066	0.9477	2.4154	1.6001
48.37	0.2500	0.2538	0.2838	0.5437	0.9201	2.9243	1.3607
46.01	0.2000	0.1992	0.2400	0.5495	0.9253	3.5831	1.3044
43.53	0.1532	0.1497	0.1858	0.5905	0.8846	4.8467	1.1300
40.21	0.1007	0.1018	0.1287	0.6223	0.8606	6.9399	1.0155
34.60	0.0519	0.0539	0.0775	0.6251	0.8662	11.3328	0.9308
59.48	0.5355	0.3645	0.5759	0.3761	1.0717	1.7318	2.3114
56.41	0.4801	0.3197	0.5153	0.4002	1.0144	1.9933	1.9260
53.68	0.4197	0.2818	0.4549	0.4335	0.9750	2.3312	1.6223
51.07	0.3600	0.2405	0.3925	0.4511	0.9331	2.7033	1.6169
48.55	0.2987	0.2036	0.3384	0.4918	0.9214	3.3095	1.3398
45.74	0.2402	0.1589	0.2838	0.5252	0.9054	4.2669	1.1762
42.80	0.1783	0.1224	0.2214	0.5531	0.8905	5.4598	1.1161
60.22	0.6299	0.2696	0.6396	0.3220	1.0245	2.0298	1.8643
56.97	0.5600	0.2396	0.5789	0.3480	0.9868	2.3352	1.6809
53.98	0.4902	0.2100	0.5175	0.3741	0.9548	2.7137	1.5783
51.16	0.4176	0.1856	0.4572	0.4058	0.9387	3.1577	1.4274
48.03	0.3509	0.1488	0.4058	0.4376	0.9305	3.9863	1.2162
45.00	0.2794	0.1225	0.3405	0.4728	0.9188	4.9004	1.1363
41.22	0.2118	0.0892	0.2789	0.4932	0.9096	6.4328	1.0868
36.53	0.1439	0.0585	0.2174	0.5126	0.9250	9.0389	1.0000
60.34	0.7103	0.1917	0.6996	0.2644	0.9958	2.3487	1.7915
56.75	0.6391	0.1603	0.6518	0.2835	0.9697	2.8323	1.4790
53.59	0.5551	0.1464	0.5912	0.3175	0.9561	3.2794	1.3261
50.17	0.4770	0.1226	0.5379	0.3403	0.9480	3.9323	1.2339
46.99	0.3959	0.1065	0.4747	0.3555	0.9440	4.4268	1.2974
43.23	0.3204	0.0829	0.4154	0.3964	0.9392	5.8377	1.1028
39.86	0.2395	0.0690	0.3320	0.4286	0.9259	6.9904	1.1164
59.03	0.8076	0.0928	0.8002	0.1660	0.9800	2.9807	1.6224
55.45	0.7152	0.0865	0.7496	0.1855	0.9738	3.3586	1.4684
51.99	0.6242	0.0795	0.6949	0.2132	0.9697	3.9371	1.3037
47.70	0.5393	0.0604	0.6529	0.2199	0.9676	4.8984	1.2260
43.81	0.4519	0.0503	0.5971	0.2433	0.9700	5.9772	1.1362
39.15	0.3625	0.0373	0.5386	0.2525	0.9746	7.4744	1.1020
34.43	0.2722	0.0278	0.4629	0.2753	0.9810	9.6238	1.0420

mean deviations of vapor-phase mole fraction (Δy_{mean}) between experimental and calculated data for the ternary systems calculated according to eq 4 are listed in Table 6. The mean deviations of calculated data by the NRTL equation were 2.37 mol % for the MTBE (1) + methanol (2) + MCH (3) system and 1.50 mol % for the MTBE (1) + methanol (2) + *n*-heptane (3) system and that of predicted

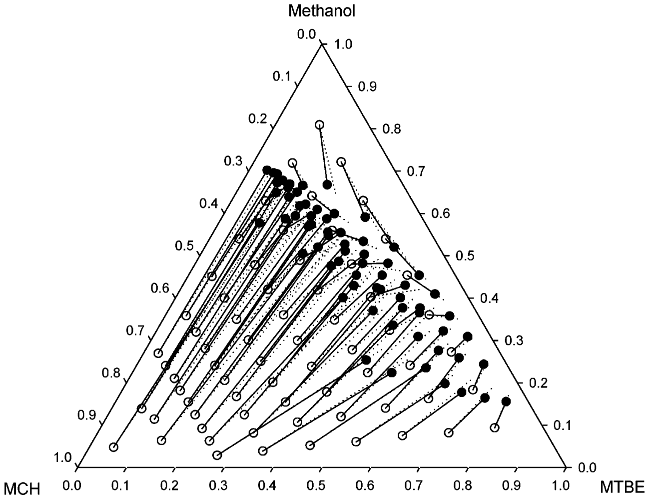

Figure 3. Isothermal VLE of the ternary systems of MTBE (1) + methanol (2) + MCH (3) at 313.15 K: ○, liquid phase; ●, vapor phase; · · ·, modified UNIFAC.

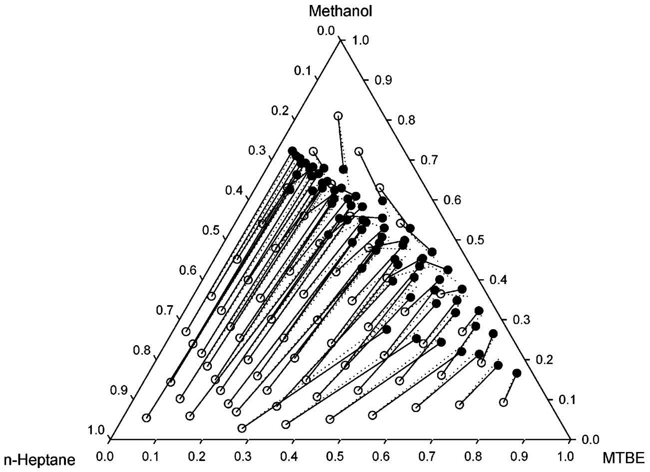

Figure 4. Isothermal VLE of the ternary systems of MTBE (1) + methanol (2) + *n*-heptane (3) at 313.15 K: ○, liquid phase; ●, vapor phase; · · ·, modified UNIFAC.

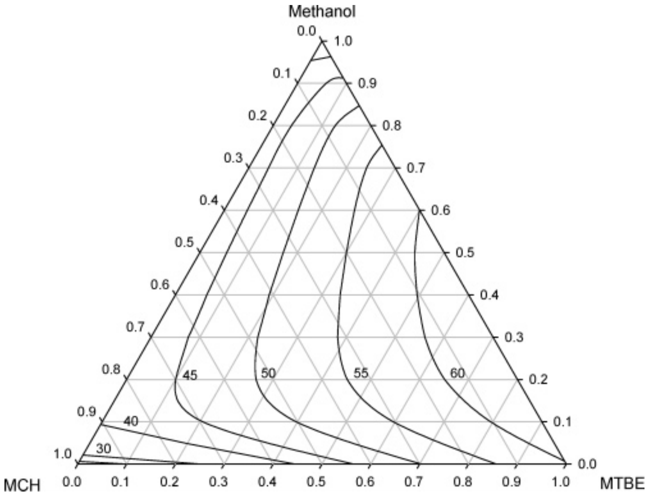

Figure 5. Isobar lines in kPa as a function of the ternary liquid composition for the VLE at 313.15 K of the ternary system MTBE (1) + methanol (2) + MCH (3).

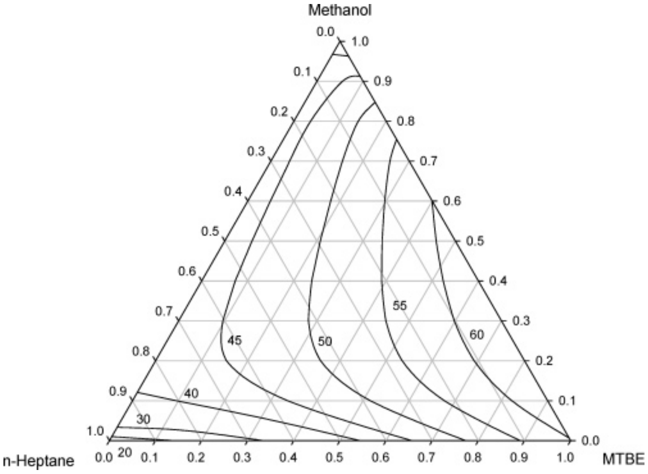

Figure 6. Isobar lines in kPa as a function of the ternary liquid composition for the VLE at 313.15 K of the ternary system MTBE (1) + methanol (2) + *n*-heptane (3).

Table 6. Deviations between Calculated and Experimental Vapor-Phase Mole Fraction (Δy) for the Ternary Systems at 313.15 K

		Δy_1	Δy_2	Δy_3	Δy_{mean}
MTBE (1) + Methanol (2) + MCH(3)					
Wilson	mean	0.0423	0.0214	0.0212	0.0283
	max	0.0715	0.0416	0.0591	
	min	0.0135	0.0020	0.0000	
NRTL	mean	0.0343	0.0122	0.0247	0.0237
	max	0.0678	0.0439	0.0622	
	min	0.0092	0.0009	0.0002	
mod. UNIFAC	mean	0.0232	0.0124	0.0241	0.0199
	max	0.0442	0.0347	0.0559	
	min	0.0026	0.0000	0.0054	
MTBE (1) + Methanol (2) + *n*-Heptane (3)					
Wilson	mean	0.0219	0.0179	0.0071	0.0156
	max	0.0359	0.0430	0.0306	
	min	0.0050	0.0016	0.0002	
NRTL	mean	0.0212	0.0162	0.0077	0.0150
	max	0.0426	0.0441	0.0306	
	min	0.0042	0.0017	0.0002	
mod. UNIFAC	mean	0.0131	0.0141	0.0085	0.0119
	max	0.0356	0.0396	0.0315	
	min	0.0006	0.0000	0.0000	

data by the modified UNIFAC (Dortmund) were 1.99 mol % and 1.19 mol %, respectively:

$$\Delta y_{\text{mean}} = \frac{|\Delta y_1| + |\Delta y_2| + |\Delta y_3|}{3} \tag{4}$$

Figures 5 and 6 show isobar lines, calculated with constituent binary NRTL parameters as a function of the ternary liquid composition.

Conclusions

Vapor−liquid equilibrium data have been reported for the binary systems of MTBE (1) + MCH (2), MTBE (1) +*n*-heptane (2), methanol (1) + MCH (2), and methanol (1) + *n*-heptane (2) and also for the ternary systems of MTBE (1) + methanol (2) + MCH (3) and MTBE (1) + methanol (2) + *n*-heptane (3) using the HSGC static measuring method. They show positive deviations from Raoult's law. Besides, methanol (1) + MCH (2) and methanol (1) + *n*-heptane (2) binary systems and two measured ternary systems have a minimum boiling azeotrope. All the binary systems can be correlated well with common g^E model equations within the deviation of vapor mole fraction of 1 %. The ternary VLE data were also predicted relatively well with the binary Wilson and NRTL parameters. For all the considered binary and ternary systems, the VLE data were predicted by the modified UNIFAC (Dortmund) model. Almost all deviations of vapor-phase mole fractions between predicted and measured ones for binary and ternary systems were less than 2 %.

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Received for review January 20, 2005. Accepted May 30, 2005. The authors are grateful to the KOSEF-DEG Cooperative Program (the Joint Research Project) for the financial support.

JE050029O