Vapor−Liquid Equilibria at 101.32 kPa of the Ternary Systems 2-Methoxy-2-methylpropane + Methanol + Water and 2-Methoxy-2-methylpropane + Ethanol + Water

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Vapor−liquid equilibrium data were determined for the ternary systems 2-methoxy-2-methylpropane + methanol + water and 2-methoxy-2-methylpropane + ethanol + water at 101.32 kPa using a still recycling both liquid and vapor phases. The thermodynamic consistency of the experimental data was confirmed by the Wisniak−*LW* and McDermott−Ellis tests. The data were correlated using the Wilson, NRTL, and UNIQUAC equations and were compared to predictions obtained using ASOG-KT, UNIFAC, UNIFAC-Dortmund and UNIFAC-Lyngby group contribution methods.

Introduction

The growing importance of ethers and alcohols as gasoline additives has spurred research into the thermodynamic properties of mixtures containing these types of compound. The ether most commonly added to gasoline is 2-methoxy-2-methylpropane (methyl *tert*-butyl ether, MTBE), which can reduce engine knocking and boost the octane rating of gasoline. The vapor−liquid equilibria of mixtures containing MTBE have been the subject of several recent papers (see Aim and Ciprian, 1980; Velasco et al., 1990; Mato and Berro, 1991; Mato et al., 1991; Wu et al., 1991; Vetere et al., 1993; Bennet et al., 1993; Arce et al., 1996b). In the present work we report isobaric VLE data for the ternary systems MTBE + methanol + water and MTBE + ethanol + water. We have found only one reference to VLE data for the former system (Kubicek et al., 1992) and no VLE data for the latter. The thermodynamic consistency of the experimental VLE data was confirmed by the tests of Wisniak−*LW* (Wisniak, 1993) and McDermott−Ellis (McDermott and Ellis, 1965; Wisniak and Tamir, 1977). VLE data were correlated by the Wilson equation (Wilson, 1964), the NRTL equation (Renon and Prausnitz, 1968), and the UNIQUAC equation (Abrams and Prausnitz, 1975) and were compared to predictions obtained using the ASOG-KT (Kojima and Tochigi, 1979; Tochigi et al., 1990), UNIFAC (Fredenslund et al., 1977), UNIFAC-Dortmund (Weidlich and Gmehling, 1987; Gmehling et al., 1993), and UNIFAC-Lyngby (Larsen et al., 1987) group contribution methods.

Experimental Section

Materials. Water was purified using a Milli-Q Plus system. Methanol and ethanol were supplied by Merck with nominal purities >99.7 and >99.5 mass %, respectively. MTBE was from Aldrich and was redistilled before use, its final purity being >99.7 mass %. The purity of all products was verified by gas chromatography, for which an HP-FFAP capillary column was used. Water contents, as determined with a Metrohm 737 KF coulometer, were 0.03, 0.03 and 0.08 mass % for MTBE, methanol, and ethanol, respectively. For all these components, Table 1 lists experimental densities and refractive indices at 298.15 K and boiling temperatures at 101.32 kPa, together with published values for these parameters.

Apparatus and Procedure. All weighing was carried out on a Mettler AE 240 balance precise to within ±0.00001 g. Densities were measured to within ±0.000 01 g·cm^{-3} in an Anton Paar DMA 60 digital vibrating tube densimeter equipped with a DMA 602 measuring cell, and refractive indices were measured to within ±0.0001 with an ATAGO RX-1000 refractometer. In both cases a HetoTherm thermostat was used to maintain the temperature at (298.15 ± 0.02) K.

Vapor−liquid equilibrium data were determined in a Labodest 602 distillation apparatus that recycles both liquid and vapor phases (Fischer Labor und Verfahrenstechnik, Germany). This still was equipped with a Fischer digital manometer and a Heraeus Quat100 quartz thermometer that measured to within ± 0.01 kPa and ±0.02 K, respectively. Distillation was carried out at 101.32 kPa under an inert argon atmosphere. Liquid- and vapor-phase compositions were determined indirectly by densimetry and refractometry, making reference to published data for the composition dependence of the densities and refractive indices of the systems studied (Arce et al., 1995a,b). For certain compositions of the system MTBE + ethanol + water, this indirect method was not sufficiently precise owing to the lack of orthogonality of the density and refractive index isolines. Mixtures in these composition intervals were therefore analyzed directly by capillary gas chromatography, using a Hewlett-Packard Series II chromatograph (Model 5890) equipped with an HP-FFAP capillary column and a thermal conductivity detector linked to an HP Series II integrator (model 3396).

The precision of both the direct and indirect methods of composition determination was determined using test samples prepared by weighing; the maximum deviation between the measured and true compositions was ±0.002 mole fraction.

Experimental Results and Data Treatment

Results. Isobaric VLE data were determined only for homogeneous mixtures of the three components constituting each ternary system. The experimental liquid- and vapor-phase compositions (x_i and y_i, respectively) and

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Table 1. Densities (d), Refractive Indices (n_D), and Boiling Points (T_b) of the Pure Compounds

	d (298.15 K)/g·cm^{-3}		n_D (298.15 K)		T_b (101.325 kPa)/K	
compound	exptl	lit.	exptl	lit.	exptl	lit.
water	0.9970	0.997 05[a]	1.3324	1.332 50[a]	373.16	373.15[a]
methanol	0.7866	0.786 37[a]	1.3264	1.326 52[a]	337.65	337.696[a]
ethanol	0.7852	0.784 93[a]	1.3592	1.359 41[a]	351.44	351.443[a]
MTBE	0.7356	0.735 28[c]	1.3663	1.366 3[c]	328.11	328.32[b]

[a] Riddick et al., 1986. [b] Krähenbühl and Gmehling, 1994. [c] Daubert and Danner, 1989.

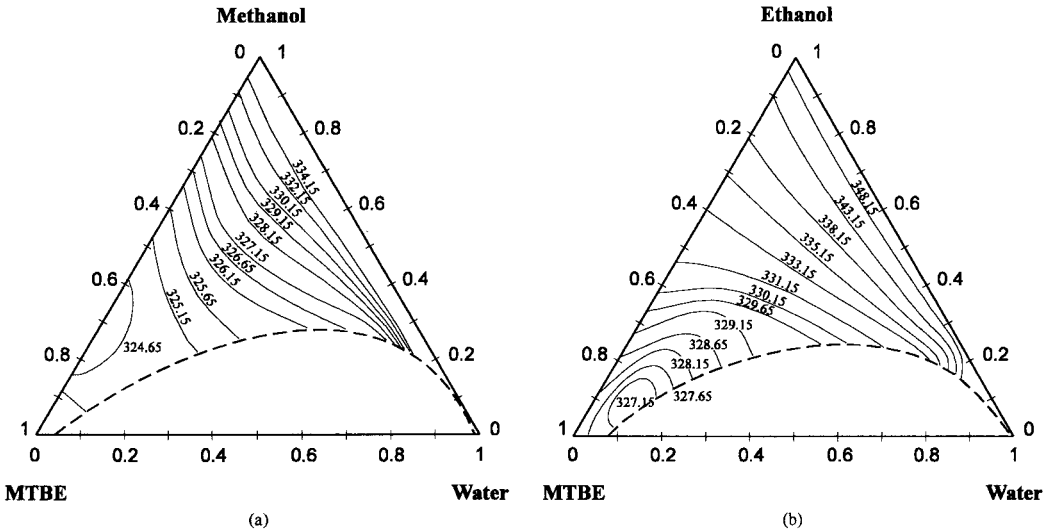

Figure 1. Calculated isotherms (T, K) for the vapor−liquid equilibria at 101.32 kPa of the ternary systems (a) MTBE + methanol + water and (b) MTBE + ethanol + water.

equilibrium temperatures (T) are listed in Table 2, together with the corresponding activity coefficients (γ_i). These activity coefficients were calculated using the equation

$$\gamma_i = \frac{y_i P \phi_i}{x_i P_i^s \phi_i^s \exp\left(\frac{V_i^L (P - P_i^s)}{RT}\right)} \quad (1)$$

where P is the total pressure of the system; P_i^s is the saturated vapor pressure of component i, as calculated from Antoine's equation

$$\log(P_i^s/\text{kPa}) = A - \frac{B}{T/\text{K} + C} \quad (2)$$

using the coefficients A, B, and C shown in Table 3; V_i^L is the molar volume of component i in the liquid phase, as calculated by Yen and Woods' (1966) equation using the critical properties listed in Table 3; and ϕ_i and ϕ_i^s are component i's coefficients of fugacity and fugacity at saturation, respectively, which were calculated from the second virial coefficient by the method of Hayden and O'Connell (1975).

For each system, Figure 1 shows the calculated isotherms for the homogeneous mixtures, together with the binodal curves marking the miscibility limit of the three components in the liquid phase (taken from Arce et al., 1994; 1996a).

The thermodynamic consistency of the VLE data was demonstrated using two tests: Wisniak's (1993) $L-W$ test and Wisniak and Tamir's (1977) modification of the McDermott−Ellis (1965) test. In Wisniak's (1993) test, deviations of 0.924 and 0.909 were obtained for the systems MTBE + methanol + water and MTBE + ethanol + water, respectively, thus confirming consistency. In the modified McDermott−Ellis test, local deviations (D) for the system MTBE + methanol + water did not exceed 0.159, while the maximum deviation was 0.239. Likewise, for the system MTBE + ethanol + water, D never exceeded 0.179, while D_{max} was 0.229. Thus, for both systems, the condition $D < D_{max}$ was satisfied, confirming consistency.

Data Treatment. The VLE data were correlated by least-squares regression (Simplex method), minimizing the objective function

$$F = \sum_i \{x_i(\text{calc}) - x_i\}^2 \quad (3)$$

where x_i is the mole fraction of component i in the liquid phase. Activity coefficients, γ_i, were calculated using the Wilson, NRTL, and UNIQUAC equations. For the NRTL equation, various values of the nonrandomness parameter, α, were used and the value affording the best correlation was selected. For the UNIQUAC equation, the structural parameters, r and q, were calculated by group contribution methods. The binary interaction parameters obtained for each activity coefficient model, and the mean deviations (δ) in equilibrium temperature (T) and vapor-phase composition (y_i) are listed in Table 4. Figure 2 compares the experimental temperature−composition data for each system with the corresponding NRTL correlation obtained with $\alpha = 0.3$ (for clarity's sake, a reduced number of data points are shown).

Predictions of the VLE data for the two ternary systems were obtained using the ASOG-KT, UNIFAC, UNIFAC-Dortmund, and UNIFAC-Lyngby group contribution methods to calculate the liquid-phase activity coefficients. The parameters used were taken from the references given for each model in the Introduction, with the exception of the UNIFAC model, for which the structural and group interaction parameters recommended by Gmehling et al. (1982)

Table 2. VLE Data at 101.32 kPa of the Indicated Ternary Systems: Equilibrium Temperatures (T), Mole Fractions of Component i in the Liquid (x_i) and Vapor Phases (y_i), and the Activity Coefficient (γ_i) for Each Component

T/K	x_1	x_2	y_1	y_2	γ_1	γ_2	γ_3	T/K	x_1	x_2	y_1	y_2	γ_1	γ_2	γ_3
MTBE (1) + Methanol (2) + Water (3)															
324.59	0.7282	0.2219	0.7313	0.2232	1.1355	1.7408	6.9694	327.90	0.0730	0.2843	0.6668	0.2275	9.3118	1.2028	1.0659
324.60	0.7353	0.2211	0.7330	0.2255	1.1267	1.7646	7.2731	328.08	0.1082	0.3563	0.6503	0.2473	6.0962	1.0343	1.2277
324.60	0.7073	0.2445	0.7207	0.2384	1.1521	1.6851	6.4781	328.19	0.0782	0.3169	0.6545	0.2411	8.4586	1.1291	1.1025
324.63	0.7672	0.1921	0.7471	0.2118	1.0991	1.9077	7.7131	328.27	0.2266	0.6450	0.5191	0.4384	2.3246	0.9954	2.0939
324.64	0.7316	0.2150	0.7341	0.2161	1.1326	1.7365	7.1116	328.46	0.2107	0.5848	0.5369	0.4113	2.5677	1.0233	1.5890
324.64	0.7053	0.2277	0.7217	0.2253	1.1554	1.7076	6.0264	328.61	0.2051	0.6146	0.5207	0.4349	2.5485	1.0223	1.5330
324.66	0.7288	0.2100	0.7318	0.2149	1.1327	1.7662	6.6333	328.79	0.1692	0.5116	0.5715	0.3482	3.3621	0.9797	1.5555
324.66	0.7895	0.1736	0.7574	0.2033	1.0814	2.0256	8.1295	328.97	0.0820	0.3605	0.6218	0.2773	7.4881	1.1033	1.1122
324.66	0.6365	0.3076	0.6890	0.2751	1.2230	1.5373	4.8782	328.98	0.1861	0.6419	0.5010	0.4565	2.6740	1.0111	1.5104
324.66	0.7096	0.2217	0.7233	0.2220	1.1502	1.7270	6.0604	329.57	0.1768	0.6841	0.4604	0.4996	2.5452	1.0118	1.7071
324.67	0.6733	0.2590	0.7103	0.2398	1.1905	1.5941	5.6028	329.61	0.0619	0.3104	0.6203	0.2728	9.7004	1.2286	1.0153
324.68	0.6227	0.3274	0.6821	0.2863	1.2372	1.5009	4.8037	329.96	0.0775	0.3893	0.5907	0.3047	7.3073	1.0766	1.1487
324.68	0.7165	0.2123	0.7246	0.2161	1.1403	1.7544	6.3332	329.96	0.1030	0.4510	0.5748	0.3320	5.3543	1.0114	1.2229
324.69	0.7610	0.1764	0.7484	0.1932	1.1077	1.8910	7.1032	330.37	0.1416	0.7041	0.4358	0.5211	2.9381	0.9920	1.5959
324.72	0.7493	0.1705	0.7506	0.1783	1.1271	1.8041	6.7398	330.70	0.0803	0.4294	0.5562	0.3420	6.5002	1.0613	1.1726
324.72	0.7785	0.1430	0.7607	0.1685	1.0991	2.0347	6.8621	330.86	0.1269	0.7252	0.4081	0.5499	3.0288	0.9955	1.5845
324.74	0.7630	0.1391	0.7734	0.1350	1.1390	1.6772	7.1165	330.93	0.1256	0.8131	0.3539	0.6273	2.6581	1.0077	1.7041
324.74	0.7307	0.1827	0.7281	0.1985	1.1212	1.8689	6.4263	331.30	0.0919	0.4942	0.5241	0.3719	5.2618	0.9773	1.3780
324.75	0.6299	0.2946	0.6940	0.2573	1.2409	1.4966	4.8786	331.60	0.1101	0.7616	0.3708	0.5929	3.1076	0.9911	1.5241
324.75	0.7715	0.1311	0.7754	0.1318	1.1289	1.7370	7.2442	331.84	0.0984	0.8725	0.3011	0.6861	2.8170	0.9891	2.3410
324.76	0.8107	0.1271	0.7773	0.1568	1.0766	2.1300	8.0565	332.15	0.0987	0.7773	0.3461	0.6173	3.1864	0.9885	1.5493
324.78	0.7054	0.1751	0.7233	0.2046	1.1525	2.0057	4.5642	332.28	0.0806	0.5221	0.4792	0.4208	5.3352	1.0046	1.3170
324.86	0.7549	0.1209	0.7753	0.1127	1.1495	1.6037	6.8176	332.53	0.0771	0.9179	0.2480	0.7502	2.9108	0.9991	1.8552
324.86	0.8350	0.1330	0.7902	0.1631	1.0589	2.1105	11.0584	332.83	0.0736	0.5821	0.4164	0.4938	5.0102	1.0316	1.3280
324.86	0.8403	0.0957	0.8040	0.1157	1.0702	2.0848	9.5127	333.08	0.0831	0.6470	0.3865	0.5325	4.0951	0.9898	1.5097
324.86	0.7981	0.0996	0.7876	0.1048	1.1042	1.8123	7.9604	333.13	0.0784	0.8098	0.2954	0.6707	3.3341	0.9906	1.5202
324.88	0.8457	0.1306	0.7935	0.1739	1.0491	2.2899	10.4182	333.54	0.0777	0.6697	0.3565	0.5646	3.9911	0.9948	1.5375
324.89	0.8443	0.1497	0.7934	0.1901	1.0505	2.1824	20.8240	333.64	0.0666	0.5496	0.4339	0.4573	5.6225	0.9814	1.3913
324.90	0.6893	0.1603	0.7620	0.1260	1.2362	1.3483	5.6131	333.95	0.0723	0.6991	0.3264	0.6005	3.8862	0.9965	1.5440
324.94	0.5122	0.4684	0.6155	0.3782	1.3500	1.3631	2.4236	334.10	0.0602	0.8392	0.2436	0.7242	3.4894	0.9927	1.5342
324.98	0.8586	0.0698	0.8107	0.0934	1.0519	2.2981	10.0988	334.21	0.0497	0.9427	0.1729	0.8251	3.0077	1.0009	1.2552
325.15	0.8766	0.1002	0.8159	0.1478	1.0312	2.5141	11.7164	334.62	0.0585	0.5721	0.3831	0.5142	5.5029	1.0184	1.3033
325.28	0.5264	0.2380	0.7425	0.1427	1.5590	1.0105	3.6000	334.99	0.0459	0.8621	0.1947	0.7774	3.5737	1.0013	1.3957
325.48	0.9066	0.0703	0.8515	0.0977	1.0289	2.3455	16.2502	335.25	0.0381	0.9217	0.1454	0.8427	3.2033	1.0043	1.3467
325.55	0.4509	0.2789	0.7277	0.1620	1.7692	0.9666	2.9737	335.39	0.0504	0.7598	0.2438	0.6939	4.0098	0.9999	1.4834
325.66	0.4460	0.4036	0.6470	0.2893	1.5896	1.1784	3.0548	335.42	0.0479	0.8087	0.2128	0.7387	3.6884	0.9982	1.5263
325.87	0.4151	0.3587	0.6670	0.2497	1.7473	1.1367	2.6317	335.59	0.0488	0.5979	0.3467	0.5439	5.8109	0.9917	1.3881
325.90	0.3996	0.3251	0.6783	0.2312	1.8432	1.1611	2.3472	335.75	0.0335	0.8834	0.1536	0.8197	3.7875	1.0001	1.4288
326.06	0.9502	0.0246	0.8890	0.0548	1.0055	3.6849	16.0737	336.29	0.0276	0.8995	0.1218	0.8545	3.5960	1.0027	1.4112
326.15	0.2257	0.2975	0.7243	0.1585	3.4514	0.8647	1.7388	337.29	0.0375	0.6303	0.2611	0.6328	5.4437	1.0233	1.3251
326.15	0.3770	0.4581	0.6209	0.3194	1.7785	1.1210	2.5464	337.29	0.0212	0.8522	0.1154	0.8409	4.3055	1.0028	1.4324
326.17	0.3519	0.6155	0.5485	0.4416	1.6887	1.1460	2.1279	338.19	0.0215	0.8035	0.1081	0.8317	3.8731	1.0169	1.3712
326.29	0.3522	0.4226	0.6392	0.2839	1.9494	1.0757	2.3875	338.88	0.0179	0.7483	0.1205	0.7983	5.0746	1.0215	1.3424
326.32	0.1889	0.2875	0.7198	0.1625	4.0765	0.9106	1.5767	339.55	0.0171	0.6713	0.1454	0.7473	6.2710	1.0401	1.2920
326.32	0.3113	0.3627	0.6728	0.2322	2.3160	1.0269	2.0382	340.24	0.0159	0.6018	0.1715	0.6936	7.7793	1.0502	1.2842
326.38	0.0865	0.2560	0.7277	0.1313	8.9806	0.8252	1.5001	341.61	0.0125	0.4929	0.1861	0.6478	10.3072	1.1391	1.1514
326.63	0.1622	0.3224	0.7147	0.1668	4.6684	0.8226	1.5882	342.39	0.0106	0.4254	0.2031	0.6129	12.9553	1.2140	1.0815
327.07	0.2083	0.3863	0.6556	0.2464	3.2954	0.9908	1.6291	343.05	0.0097	0.3457	0.2434	0.5550	16.6059	1.3219	1.0082
327.17	0.1415	0.3458	0.7013	0.1792	5.1640	0.8049	1.5674	344.20	0.0091	0.3119	0.2225	0.5520	15.6821	1.3973	1.0189
327.20	0.2810	0.5270	0.5820	0.3632	2.1670	1.0584	1.9051	345.11	0.0090	0.2781	0.2053	0.5601	14.2763	1.5385	0.9713
327.32	0.2312	0.4527	0.6273	0.2858	2.8217	0.9684	1.8280								
MTBE (1) + Ethanol (2) + Water (3)															
326.91	0.7907	0.1456	0.8042	0.1264	1.0651	2.4766	7.4877	338.48	0.1980	0.7583	0.5183	0.4526	1.9425	1.0106	2.6454
327.05	0.8990	0.0445	0.8721	0.0632	1.0104	4.0442	7.8593	338.70	0.0304	0.2144	0.5838	0.1876	14.1468	1.4705	1.1904
327.34	0.8564	0.1022	0.8679	0.0693	1.0460	1.9048	10.2636	339.00	0.1055	0.4134	0.5396	0.2375	3.7399	0.9520	1.7950
327.42	0.7285	0.1937	0.8100	0.1001	1.1457	1.4405	7.7494	339.70	0.0970	0.4650	0.5013	0.2828	3.7076	0.9776	1.8494
327.72	0.7038	0.1288	0.7839	0.1178	1.1375	2.5104	3.8739	340.07	0.0233	0.1973	0.5639	0.1834	17.1489	1.4743	1.1993
328.10	0.6655	0.1684	0.7712	0.1350	1.1696	2.1610	3.6556	340.40	0.0942	0.4900	0.4749	0.3135	3.5476	0.9982	1.8503
328.52	0.6083	0.2459	0.7966	0.0821	1.3040	0.8842	5.2855	340.58	0.0437	0.2969	0.5022	0.2572	8.0393	1.3426	1.3171
328.75	0.5868	0.2683	0.7603	0.1500	1.2817	1.4624	3.8828	340.60	0.1174	0.5700	0.4405	0.3948	2.6276	1.0708	1.8981
328.84	0.5781	0.2963	0.7658	0.1425	1.3065	1.2532	4.5614	340.94	0.1156	0.5871	0.4280	0.4095	2.5687	1.0630	1.9396
329.06	0.7277	0.2529	0.8370	0.1256	1.1252	1.2875	11.9942	341.06	0.1474	0.8484	0.4347	0.5623	2.0368	1.0056	2.5282
329.16	0.5562	0.3296	0.7479	0.1769	1.3135	1.3772	4.0487	341.13	0.0975	0.5019	0.4453	0.3460	3.1505	1.0429	1.8334
329.34	0.4816	0.3448	0.7398	0.1578	1.4925	1.1641	3.5921	341.46	0.1219	0.6349	0.4104	0.4442	2.3026	1.0433	2.0737
329.63	0.6427	0.3198	0.8021	0.1494	1.2001	1.1776	7.8108	341.56	0.0978	0.5460	0.4115	0.4080	2.8700	1.1097	1.7493
329.66	0.5263	0.3748	0.7483	0.1767	1.3674	1.1828	4.5541	341.70	0.1089	0.5882	0.4022	0.4301	2.5099	1.0794	1.8995
329.80	0.5192	0.3730	0.7377	0.1911	1.3608	1.2766	3.9379	341.87	0.1192	0.7508	0.4038	0.4981	2.2899	0.9727	2.5728
330.01	0.2764	0.2818	0.7367	0.1188	2.5370	1.0401	1.9280	342.11	0.1136	0.6727	0.4004	0.4537	2.3673	0.9791	2.3020
330.02	0.4549	0.3738	0.7273	0.1744	1.5214	1.1503	3.3821	342.12	0.1100	0.7151	0.3912	0.4863	2.3884	0.9866	2.3607
330.21	0.3160	0.3112	0.7338	0.1201	2.1968	0.9435	2.2880	342.77	0.0951	0.6168	0.3667	0.4613	2.5455	1.0561	1.9542
330.68	0.2042	0.2770	0.7263	0.1235	3.3170	1.0669	1.6526	345.15	0.0257	0.3051	0.3580	0.3639	8.6120	1.5300	1.2278
331.00	0.2491	0.3166	0.7212	0.1245	2.6739	0.9274	1.9972	345.23	0.0341	0.4945	0.3042	0.4471	5.5135	1.1550	1.5521
331.40	0.4446	0.4785	0.7190	0.2166	1.4749	1.0491	4.6282	345.35	0.0263	0.3184	0.3758	0.3197	8.7810	1.2782	1.3616
331.44	0.1719	0.2776	0.7182	0.1258	3.8072	1.0479	1.5604	345.50	0.0632	0.8271	0.2561	0.6558	2.4879	1.0013	2.3382

Table 2 (Continued)

T/K	x_1	x_2	y_1	y_2	γ_1	γ_2	γ_3	T/K	x_1	x_2	y_1	y_2	γ_1	γ_2	γ_3
MTBE (1) + Ethanol (2) + Water (3)															
331.48	0.3208	0.3213	0.7106	0.1370	2.0163	0.9839	2.3394	345.56	0.0320	0.3921	0.3383	0.3651	6.4679	1.1747	1.4947
331.54	0.3456	0.3904	0.7012	0.1657	1.8437	0.9764	2.7616	345.67	0.0285	0.3624	0.3367	0.3652	7.2064	1.2657	1.4137
331.65	0.1347	0.2424	0.7246	0.1220	4.8698	1.1535	1.3435	346.30	0.0536	0.8439	0.2202	0.6985	2.4707	1.0121	2.2319
331.87	0.3394	0.4333	0.6740	0.2221	1.7874	1.1606	2.4632	346.39	0.0512	0.8139	0.2199	0.6720	2.5771	1.0060	2.2457
332.57	0.2704	0.3796	0.7005	0.1322	2.2818	0.7654	2.4948	346.42	0.0504	0.7883	0.2189	0.6556	2.6044	1.0121	2.1772
332.86	0.1566	0.3060	0.6914	0.1427	3.8555	1.0115	1.5891	346.51	0.0269	0.4118	0.2635	0.4443	5.8554	1.3093	1.4497
332.96	0.2315	0.3546	0.6846	0.1486	2.5750	0.9047	2.0641	346.53	0.0502	0.7321	0.2230	0.6120	2.6559	1.0130	2.1103
332.99	0.3621	0.5440	0.6763	0.2559	1.6245	1.0142	3.6982	346.73	0.0250	0.3742	0.2952	0.4011	7.0071	1.2901	1.3956
333.08	0.2953	0.5035	0.6524	0.2461	1.9177	1.0484	2.5681	346.80	0.0220	0.3413	0.3034	0.3843	8.1660	1.3516	1.3504
333.15	0.0981	0.2582	0.6821	0.1513	6.0201	1.2544	1.3139	346.81	0.0514	0.8970	0.2082	0.7448	2.4028	0.9950	2.5098
333.38	0.3178	0.5070	0.6431	0.2718	1.7410	1.1345	2.4384	346.82	0.0509	0.8676	0.2020	0.7297	2.3545	1.0073	2.3073
333.60	0.2077	0.3346	0.6812	0.1381	2.8016	0.8663	1.9628	346.85	0.0557	0.6676	0.2162	0.5876	2.3015	1.0531	1.9472
334.11	0.1468	0.3333	0.6719	0.1492	3.8510	0.9185	1.6706	347.19	0.0252	0.4855	0.2335	0.4926	5.4424	1.1982	1.5149
334.16	0.0519	0.2257	0.6779	0.1401	10.9720	1.2713	1.2207	347.26	0.0471	0.6365	0.2050	0.5760	2.5536	1.0653	1.8679
334.25	0.2957	0.5740	0.6364	0.2806	1.8040	0.9958	3.0724	347.68	0.0431	0.9290	0.1669	0.8100	2.2467	1.0092	2.1997
334.35	0.0818	0.2611	0.6616	0.1570	6.7581	1.2205	1.3249	347.92	0.0349	0.6136	0.1782	0.5849	2.9461	1.0933	1.7688
334.57	0.0410	0.2089	0.6705	0.1433	13.5723	1.3796	1.1800	348.23	0.0242	0.5249	0.1916	0.5263	4.5287	1.1363	1.6207
334.59	0.2955	0.6260	0.6287	0.3152	1.7655	1.0104	3.3944	348.59	0.0244	0.5940	0.1556	0.5906	3.6171	1.1107	1.6972
334.65	0.3156	0.6581	0.6438	0.3304	1.6889	1.0057	4.6531	348.84	0.0198	0.5674	0.1521	0.5785	4.3290	1.1280	1.6480
335.95	0.1824	0.4671	0.5899	0.2468	2.5812	0.9981	2.0733	349.22	0.0152	0.3325	0.2011	0.4745	7.3665	1.5565	1.2367
336.09	0.0629	0.2612	0.6302	0.1675	7.9562	1.2059	1.3253	349.52	0.0142	0.3234	0.1964	0.4688	7.6411	1.5627	1.2413
336.37	0.2600	0.7083	0.5941	0.3800	1.7998	0.9960	3.5772	349.69	0.0140	0.3156	0.1949	0.4669	7.6566	1.5844	1.2304
336.43	0.1910	0.5043	0.5669	0.2892	2.3368	1.0604	2.0554	349.72	0.0146	0.3511	0.1879	0.4746	7.0747	1.4459	1.2960
336.74	0.2028	0.5840	0.5570	0.3289	2.1430	1.0274	2.2972								
336.84	0.0414	0.2297	0.6225	0.1696	11.6817	1.3443	1.2207								
336.94	0.2353	0.7044	0.5631	0.4034	1.8552	1.0364	2.3674								
337.29	0.2288	0.7346	0.5582	0.4161	1.8722	1.0099	2.9458								
337.66	0.0289	0.2045	0.6100	0.1739	16.0145	1.4946	1.1624								
338.21	0.1127	0.3931	0.5584	0.2256	3.7049	0.9837	1.7548								

Table 3. Antoine Coefficients *A*, *B*, and *C* for Eq 2 and Critical Temperatures and Volumes Used in Yen and Woods' Equation

compound	A	B	C	T_C/K	V_C/m^3·kmol^{-1}
water	7.074 06	1657.459	−46.130[a]	647.13[d]	0.055 95[d]
methanol	7.205 19	1581.993	−33.439[b]	512.58[d]	0.117 80[d]
ethanol	7.168 79	1552.601	−50.731[b]	516.25[d]	0.166 92[d]
MTBE	6.0703 43	1158.912	−43.200[c]	497.10[d]	0.329 00[d]

[a] Reid et al., 1977. [b] Riddick et al., 1986. [c] Krähenbühl and Gmehling, 1994. [d] Daubert and Danner, 1989.

were used. Table 5 lists the root-mean-squared (*rms*) deviations between the experimental VLE data and the data predicted by each model. Figure 3a compares the experimental VLE data for the system MTBE + methanol + water with the prediction of the UNIFAC-Lyngby model, and Figure 3b compares the experimental VLE data for the system MTBE + ethanol + water with the prediction of the UNIFAC-Dortmund model (again, for clarity's sake, a reduced number of data points are shown).

Discussion

Vapor−liquid equilibrium (VLE) data were determined for the range of homogeneous mixtures of MTBE + methanol + water, and of MTBE + ethanol + water. From the ternary diagrams (Figures 1−3), it can be seen that the isotherms for methanol close in on a single point, which corresponds to the binary azeotrope formed by the system MTBE + methanol and is the focus of the arrows in Figures

Table 4. Correlation of the VLE Data of the Indicated Ternary Systems: Model Parameters and Mean Deviations (δ) in Equilibrium Temperature and Vapor-Phase Compositions (Mole Fractions)

model	parameters/J·mol^{-1}		$\delta(T/\mathrm{K})^a$	$\delta(y)_1{}^b$	$\delta(y)_2{}^b$
	MTBE (1) + Methanol (2) + Water (3)				
UNIQUAC	$\Delta u_{12} = 3774.51$	$\Delta u_{21} = -1336.70$			
	$\Delta u_{13} = 3319.79$	$\Delta u_{31} = 1239.47$	0.46	0.0134	0.0187
	$\Delta u_{23} = -134.46$	$\Delta u_{32} = 1304.99$			
WILSON	$\Delta\lambda_{12} = -754.96$	$\Delta\lambda_{21} = 4104.37$			
	$\Delta\lambda_{13} = 10432.79$	$\Delta\lambda_{31} = 10455.39$	0.87	0.0212	0.0246
	$\Delta\lambda_{23} = -1447.45$	$\Delta\lambda_{32} = 4389.85$			
NRTL ($\alpha = 0.3$)	$\Delta g_{12} = 3474.92$	$\Delta g_{21} = -62.47$			
	$\Delta g_{13} = 4562.89$	$\Delta g_{31} = 15141.46$	0.41	0.0133	0.0183
	$\Delta g_{23} = -494.97$	$\Delta g_{32} = 5346.07$			
	MTBE (1) + Ethanol (2) + Water (3)				
UNIQUAC	$\Delta u_{12} = 3525.14$	$\Delta u_{21} = -573.42$			
	$\Delta u_{13} = 5298.19$	$\Delta u_{31} = 121.97$	0.34	0.0120	0.0114
	$\Delta u_{23} = 865.21$	$\Delta u_{32} = -675.34$			
WILSON	$\Delta\lambda_{12} = -124.98$	$\Delta\lambda_{21} = 4126.05$			
	$\Delta\lambda_{13} = 8148.33$	$\Delta\lambda_{31} = 10456.64$	0.93	0.0128	0.0157
	$\Delta\lambda_{23} = -4174.92$	$\Delta\lambda_{32} = 6123.28$			
NRTL ($\alpha = 0.3$)	$\Delta g_{12} = 1756.83$	$\Delta g_{21} = 1775.95$			
	$\Delta g_{13} = 4720.77$	$\Delta g_{31} = 11046.81$	0.32	0.0103	0.0106
	$\Delta g_{23} = -346.26$	$\Delta g_{32} = 2328.83$			

[a] $\delta(T/\mathrm{K}) = \Sigma|T_{\mathrm{exp}} - T_{\mathrm{calc}}|/N$. [b] $\delta(y) = \Sigma|y_{\mathrm{exp}} - y_{\mathrm{calc}}|/N$. ($N$ = number of experimental points.)

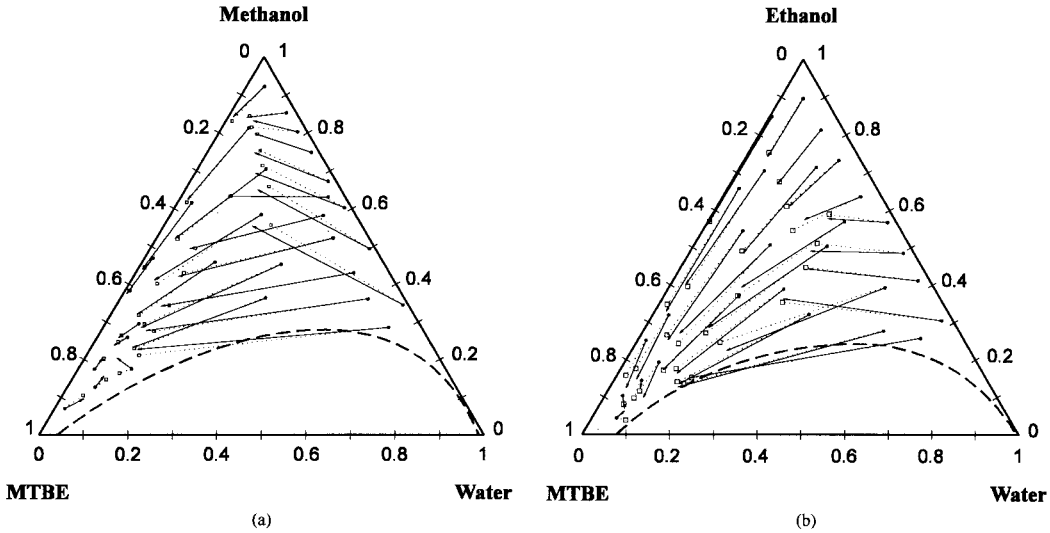

Figure 2. Experimental VLE data at 101.32 kPa (→), and the corresponding NRTL (α = 0.3) correlation (- - □), for the ternary systems (a) MTBE + methanol + water and (b) MTBE + ethanol + water. Lines start from the liquid compositions, and the arrowheads and squares indicate the experimental and correlated vapor compositions, respectively.

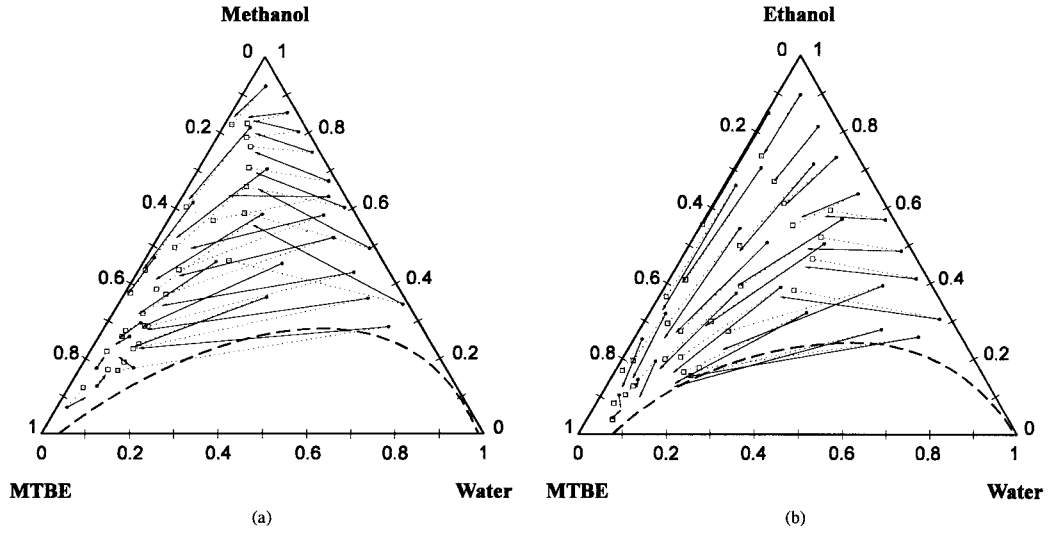

Figure 3. (a) Experimental VLE data at 101.32 kPa of the system MTBE + methanol + water (→), and the data predicted using the UNIFAC-Lyngby method (- - □). b) Experimental VLE data at 101.32 kPa (→) of the system MTBE + ethanol + water, and the data predicted using the UNIFAC-Dortmund method (- - □). Lines start from the liquid compositions, and the arrowheads and squares indicate the experimental and predicted vapor compositions, respectively.

Table 5. Prediction of the VLE Data for the Ternary Systems: Root-Mean-Squared Deviations (rmsd) in Vapor-Phase Compositions (Mole Fraction) and in Equilibrium Temperature

method	rmsd y_1	rmsd y_2	rmsd y_3	rmsd T/K
MTBE (1) + Methanol (2) + Water (3)				
ASOG-KT	0.0520	0.0618	0.0320	2.86
UNIFAC	0.0584	0.0487	0.0275	2.67
UNIFAC-Dortmund	0.0681	0.0575	0.0185	3.58
UNIFAC-Lyngby	0.0427	0.0393	0.0109	2.24
MTBE (1) + Ethanol (2) + Water (3)				
ASOG-KT	0.0698	0.0564	0.0410	4.67
UNIFAC	0.1159	0.0754	0.0544	5.15
UNIFAC-Dortmund	0.0366	0.0350	0.0129	1.14
UNIFAC-Lyngby	0.0277	0.0294	0.0147	1.31

2 and 3. It is also clear from these figures that the system containing ethanol forms a ternary azeotrope, whereas the system containing methanol does not.

The Wisniak *L*−*W* and McDermott−Ellis tests confirmed the VLE data for both systems to be thermodynamically consistent.

The VLE data for both systems were satisfactorily correlated using the UNIQUAC model or the NRTL model with α set to 0.3 to calculate the liquid-phase activity coefficients. By contrast, correlation using the Wilson equation afforded somewhat larger deviations in composition and equilibrium temperature, especially the latter.

In predicting the VLE data for the system MTBE + methanol + water, the UNIFAC-Lyngby method gave the smallest deviations in equilibrium temperature and composition. For the system MTBE + ethanol + water, both the Dortmund and Lyngby modifications of the UNIFAC method afforded good predictions of the experimental VLE data.

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