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Experimental Determination of the Vapor−Liquid Equilibrium at 101.32 kPa of the Ternary System 1-Butanol + Methanol + TAME

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Experimental isobaric vapor−liquid equilibrium data are reported at 101.32 kPa for the ternary system 1-butanol + methanol + TAME (2-methoxy-2-methylbutane or *tert*-amyl methyl ether) and for one unmeasured constituent binary system (TAME + 1-butanol). These data were found to be thermodynamically consistent and were satisfactorily correlated with the Wilson, NRTL, and UNIQUAC equations. They have also been compared with predictions obtained from the application of ASOG and UNIFAC group contribution methods and from the correlation equations using interaction parameters of the constituent binary systems.

Introduction

In previous work[1,2] we have demonstrated that 1-butanol is a possible entrainer for the separation of MTBE (methyl *tert*-butyl ether) and methanol or ethanol by extractive distillation. To know if the same entrainer can be used in the separation of methanol + TAME (2-methoxy-2-methylbutane or *tert*-amyl methyl ether) mixtures, a rigorous determination of the involved ternary equilibrium is necessary. With this in mind, isobaric (P = 101.32 kPa) vapor−liquid equilibrium (VLE) data for the system 1-butanol + methanol + TAME will be determined and fitted with the equations of Wilson,[3] NRTL,[4] and UNIQUAC.[5] The prediction of equilibrium will also be tested, first using the Wilson, NRTL, and UNIQUAC equations with the interaction parameters of the corresponding binary systems, and then by the group contribution methods ASOG-KT,[6,7] UNIFAC,[8] UNIFAC−Dortmund,[9,10] and UNIFAC−Lyngby.[11]

Experimental Section

Materials. Methanol was supplied by Merck with nominal purity >99.8 mass %. 1-Butanol was supplied by Aldrich with nominal purity >99.9 mass %, and TAME was supplied by Fluka with nominal purity >98.9 mass %. The water contents of the methanol, 1-butanol, and TAME (determined with a Metrohm 737 KF coulometer) were 0.03, 0.1, and 0.02 mass %, respectively.

Table 1 lists the densities and refractive indices at 298.15 K and atmospheric pressure and boiling points at 101.32 kPa measured for the pure components, together with published values for these parameters.[12−14]

Apparatus and Procedure. The VLE experiments in this study were performed using a dynamic recirculating still equipped with a Cottrell pump. It is a commercial unit (Labodest model 602), built by Fischer, capable of handling pressures from 0.25 to 400 kPa and temperatures up to 513.15 K. The temperature was measured using a Heraeus QuaT100 quartz thermometer, with an accuracy of ±0.02 K, and pressure was measured with a Fischer digital manometer with an accuracy of ±0.01 kPa.

Table 1. Densities, ρ, Refractive Indices, n_D, and Boiling Points, T_b, of the Pure Components

component	ρ(298.15 K), g·cm^{-3} exptl	ρ(298.15 K), g·cm^{-3} lit.	n_D(298.15 K) exptl	n_D(298.15 K) lit.	T_b(101.32 kPa), K exptl	T_b(101.32 kPa), K lit.
1-butanol	0.8060	0.80575[a]	1.3975	1.39741[a]	390.88	390.875[a]
methanol	0.7866	0.78637[a]	1.3264	1.32652[a]	337.65	337.696[a]
TAME	0.7658	0.76577[b]	1.3858	1.38580[b]	359.33	359.39[c]

[a] Riddick et al.[12] [b] Linek.[13] [c] Krähenbühl and Gmehling.[14]

Table 2. Isobaric Vapor−Liquid Equilibrium Data for the TAME (1) + 1-Butanol (2) Binary System at 101.32 kPa

T/K	x_1/(mole fraction)	y_1/(mole fraction)	γ_1	γ_2
387.99	0.0279	0.0988	1.7434	1.0245
386.33	0.0508	0.1646	1.6551	1.0313
384.79	0.0763	0.2344	1.6241	1.0263
382.60	0.1118	0.3232	1.6066	1.0221
380.90	0.1395	0.3897	1.6151	1.0133
378.46	0.1897	0.4691	1.5152	1.0265
377.05	0.2170	0.5142	1.5024	1.0262
374.78	0.2715	0.5826	1.4387	1.0356
372.96	0.3183	0.6339	1.3975	1.0435
371.41	0.3577	0.6830	1.3939	1.0216
369.70	0.4169	0.7296	1.3347	1.0293
367.90	0.4816	0.7709	1.2797	1.0571
366.16	0.5648	0.8093	1.1997	1.1280
364.30	0.6571	0.8495	1.1381	1.2236
362.84	0.7503	0.8838	1.0791	1.3829
361.91	0.8143	0.9054	1.0450	1.5774
360.92	0.8911	0.9382	1.0171	1.8381
360.13	0.9382	0.9621	1.0157	2.0683

Distillation was performed under an inert argon atmosphere at constant pressure of 101.32 kPa, and the heating and stirring system of the liquid mixture was connected. The system was kept at boiling point for 20 min to ensure the stationary state, and then we extracted samples of liquid and vapor with syringes. The composition of liquid and vapor samples for the binary and ternary mixtures was determined by measuring their densities at 298.15 K with an Anton Paar DSA-48 vibrating tube densimeter and sound analyzer, and refractive indices were determined with an Atago RX-1000 refractometer at 298.15 K. The composition dependence of densities and refractive indices has previously been reported.[15] The greatest uncertainity found for these systems with this method of composition analysis was ±0.003 in mole fraction.

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Table 3. Isobaric Vapor−Liquid Equilibrium Data for the 1-Butanol (1) + Methanol (2) + TAME (3) Ternary System at 101.32 KPa

T/K	x_1	x_2	y_1	y_2	γ_1	γ_2	γ_3
338.63	0.1211	0.7060	0.0116	0.7870	0.8667	1.0792	2.3010
338.69	0.1241	0.6640	0.0140	0.7600	1.0173	1.1063	2.0976
338.82	0.1261	0.7449	0.0126	0.8213	0.8955	1.0590	2.5358
338.88	0.1262	0.6079	0.0140	0.7296	0.9908	1.1529	1.8793
338.94	0.1190	0.7893	0.0118	0.8583	0.8837	1.0391	2.7888
339.33	0.1195	0.8209	0.0121	0.8946	0.8851	1.0259	3.0532
339.66	0.1452	0.5440	0.0172	0.6990	1.0166	1.2000	1.7298
339.82	0.1217	0.8500	0.0132	0.9368	0.9255	1.0184	3.4053
340.27	0.1195	0.8698	0.0125	0.9699	0.8732	1.0132	3.1341
340.41	0.1512	0.4706	0.0213	0.6611	1.1640	1.2775	1.5474
340.60	0.1340	0.8548	0.0127	0.9666	0.7780	1.0150	3.4816
341.31	0.1657	0.8198	0.0183	0.9544	0.8744	1.0181	3.4605
341.36	0.1534	0.3928	0.0228	0.6190	1.1713	1.3858	1.4055
341.78	0.1829	0.8002	0.0191	0.9495	0.8075	1.0200	3.3605
343.18	0.1681	0.2956	0.0257	0.5718	1.1013	1.5944	1.2558
343.51	0.2531	0.7189	0.0288	0.9284	0.8069	1.0424	2.6079
344.14	0.1622	0.2584	0.0287	0.5382	1.2164	1.6603	1.2105
344.42	0.3033	0.5958	0.0343	0.8280	0.7655	1.0866	2.2395
344.81	0.2997	0.6671	0.0391	0.9093	0.8674	1.0500	2.5391
344.89	0.3205	0.5563	0.0400	0.7990	0.8252	1.1047	2.1077
345.50	0.1544	0.2075	0.0304	0.4968	1.2678	1.8207	1.1465
345.83	0.3437	0.5170	0.0458	0.7654	0.8415	1.1016	2.1159
346.17	0.3431	0.6170	0.0454	0.8922	0.8233	1.0611	2.4427
346.54	0.3612	0.4722	0.0502	0.7343	0.8479	1.1289	1.9700
346.90	0.3675	0.4390	0.0516	0.7055	0.8419	1.1527	1.8861
347.30	0.1450	0.1509	0.0328	0.4411	1.3376	2.0902	1.0898
347.30	0.3710	0.3993	0.0530	0.6715	0.8404	1.1903	1.7752
347.83	0.3966	0.5561	0.0522	0.8715	0.7560	1.0845	2.3867
348.19	0.1856	0.1254	0.0325	0.4408	0.9925	2.4355	1.0845
348.31	0.3839	0.3509	0.0565	0.6356	0.8253	1.2385	1.6612
349.10	0.3938	0.3034	0.0603	0.5980	0.8273	1.3123	1.5720
349.34	0.1438	0.0941	0.0350	0.3837	1.3087	2.7213	1.0421
349.50	0.4417	0.5078	0.0625	0.8495	0.7507	1.0921	2.4438
350.11	0.1365	0.1136	0.0384	0.3620	1.4596	2.0724	1.0662
350.31	0.3877	0.2655	0.0677	0.5510	0.8917	1.3267	1.4721
350.47	0.3788	0.2365	0.0659	0.5262	0.8823	1.4159	1.4106
351.66	0.1118	0.0840	0.0440	0.3019	1.9034	2.2220	1.0329
351.78	0.3615	0.2219	0.0732	0.4790	0.9669	1.3152	1.3713
352.60	0.0987	0.0685	0.0457	0.2585	2.1479	2.2645	1.0303
353.74	0.3519	0.1836	0.0795	0.4099	0.9876	1.2756	1.3186
354.06	0.5356	0.3875	0.1086	0.7631	0.8701	1.1003	2.0272
354.40	0.0934	0.0441	0.0366	0.2187	1.6787	2.8062	1.0083
354.60	0.2925	0.1025	0.0738	0.3230	1.0640	1.7568	1.1619
355.18	0.5638	0.3443	0.1199	0.7260	0.8672	1.1350	1.9664
356.01	0.5818	0.3100	0.1297	0.6915	0.8756	1.1684	1.8873
356.87	0.5057	0.1393	0.1053	0.4583	0.7894	1.6867	1.3493
357.05	0.5402	0.1526	0.1245	0.4631	0.8659	1.5455	1.4672
357.35	0.3774	0.0911	0.1028	0.2951	1.0151	1.6470	1.2184
357.81	0.3215	0.0614	0.1120	0.2141	1.2750	1.7534	1.1566
357.89	0.2787	0.0513	0.1003	0.2003	1.3143	1.9606	1.1024
358.09	0.3855	0.0770	0.1099	0.2746	1.0287	1.7706	1.2051
358.32	0.4308	0.1056	0.1198	0.3105	0.9917	1.4455	1.2865
358.33	0.0221	0.0064	0.0099	0.0534	1.6268	4.1902	1.0023
358.42	0.0725	0.0082	0.0374	0.0770	1.8594	4.6858	0.9992
358.42	0.4646	0.1148	0.1274	0.3295	0.9727	1.4047	1.3492
358.46	0.4980	0.1234	0.1346	0.3641	0.9559	1.4395	1.3840
358.46	0.5723	0.1524	0.1474	0.4560	0.9088	1.4539	1.5125
358.95	0.6078	0.1699	0.1551	0.5020	0.8806	1.4103	1.6010
359.55	0.0847	0.0144	0.0492	0.0380	1.9949	1.2711	1.0175
359.56	0.4375	0.0724	0.1302	0.2610	1.0064	1.7050	1.2537
359.70	0.6383	0.1872	0.1669	0.5537	0.8728	1.3751	1.6319
359.78	0.1443	0.0193	0.0698	0.0555	1.6406	1.3714	1.0437
359.90	0.2234	0.0247	0.0793	0.1051	1.1939	2.0131	1.0796
360.88	0.6655	0.1978	0.1648	0.5819	0.7858	1.3153	1.8288
361.18	0.2779	0.0254	0.1016	0.0927	1.1624	1.6552	1.1104
362.11	0.4535	0.0442	0.1606	0.1795	1.0745	1.7732	1.2324
362.19	0.6802	0.1903	0.2014	0.5680	0.8876	1.2791	1.6953
362.27	0.3337	0.0126	0.1155	0.0778	1.0501	2.7035	1.1494
362.41	0.3752	0.0171	0.1178	0.1155	0.9452	2.9365	1.1712
362.60	0.4143	0.0271	0.1224	0.1501	0.8808	2.3877	1.2035
363.23	0.4883	0.0427	0.1746	0.1830	1.0338	1.8036	1.2461
363.98	0.5280	0.0445	0.1861	0.2242	0.9857	2.0648	1.2309
364.90	0.7269	0.1797	0.2418	0.5806	0.8894	1.2694	1.6831
365.71	0.5569	0.0568	0.2350	0.1115	1.0994	0.7647	1.4375
367.59	0.5985	0.0551	0.2576	0.1164	1.0369	0.7749	1.4606
368.10	0.7440	0.1038	0.2839	0.3980	0.8947	1.3683	1.6831
368.53	0.7794	0.1503	0.3112	0.5359	0.9191	1.2514	1.7452
368.86	0.6213	0.0573	0.2719	0.1182	1.0008	0.7270	1.4831
369.02	0.7714	0.1202	0.3058	0.4547	0.8949	1.3099	1.7420
369.74	0.6424	0.0544	0.2755	0.1374	0.9461	0.8654	1.4793
369.95	0.7888	0.1407	0.3346	0.5177	0.9221	1.2365	1.6185
371.15	0.6937	0.0102	0.3047	0.1272	0.9153	4.0909	1.4130
373.39	0.7394	0.0103	0.3656	0.0981	0.9423	2.9189	1.4901
373.53	0.7791	0.0269	0.3344	0.2461	0.8120	2.7779	1.5033
373.70	0.7616	0.0157	0.3585	0.1545	0.8855	2.9816	1.5106
375.71	0.8125	0.0216	0.4073	0.1953	0.8710	2.5744	1.5759
376.44	0.8524	0.1042	0.5000	0.3744	0.9885	0.9961	1.8887
376.79	0.8600	0.0800	0.4970	0.3530	0.9611	1.2112	1.6153
376.86	0.8361	0.0277	0.5021	0.1330	0.9976	1.3226	1.7139
377.71	0.8753	0.0557	0.5173	0.2934	0.9492	1.4091	1.7288
377.81	0.8785	0.0916	0.5299	0.3959	0.9651	1.1507	1.5679
378.93	0.8641	0.0236	0.5548	0.1232	0.9859	1.3533	1.7440
379.06	0.8935	0.0671	0.5725	0.3081	0.9779	1.1806	1.8514
380.15	0.8837	0.0280	0.5952	0.1379	0.9877	1.2316	1.7870
380.98	0.9017	0.0394	0.6358	0.1804	1.0022	1.1167	1.8130
382.62	0.9110	0.0235	0.6746	0.1159	0.9914	1.1495	1.7835
382.91	0.9344	0.0571	0.6983	0.2906	0.9897	1.1728	0.7288

Results

The VLE data and the activity coefficients for TAME + 1-butanol and for ternary mixtures at 101.32 kPa are shown in Tables 2 and 3, respectively. Results for the binary mixtures methanol + TAME and methanol + 1-butanol have been given in previous works.[2,16] Thermodynamic consistency of data has been demonstrated. Binary data passed both Fredenslund's test[8] (median deviation between calculated and experimental $y_i < 0.01$) and Wisniak's L−W test[17] ($D < 3$), and the ternary data passed both Wisniak's L−W test[17] of thermodynamic consistency ($0.92 < L_i/W_i < 1.08$ at all data points) and Wisniak and Tamir's modification[18] of the test of McDermott−Ellis[19] ($D < D_{\max}$ at all data points). Figure 1 shows the isotherms of the liquid phase for the ternary system.

Data Treatment

Correlation. All data processing was performed using the program ChemCAD IV. For the ternary system and each binary system, the binary interaction parameters of the Wilson, NRTL, and UNIQUAC equations for activity coefficients were optimized by means of a simplex method for the minimum mean squared deviation between calculated and experimental liquid-phase mole fractions,

$$F = \sum_{i=1}^{N}(x_{i,\text{calc}} - x_{i,\text{exp}})^2 \qquad (1)$$

the calculated values being obtained from the equilibrium equations

$$y_i\phi_iP = x_i\gamma_iP^{\text{S}}_i\phi^{\text{S}}_i \exp[\nu^{\text{L}}_i(P - P^{\text{S}}_i)/RT] \qquad (2)$$

where $P = 101.32$ kPa, x_i and y_i are the mole fractions of component i in the liquid and vapor phases respectively, γ_i is its activity coefficient, ν^{L}_i is its molar volume in the liquid phase, ϕ_i and ϕ^{S}_i are its fugacity coefficients under unsaturated and saturated conditions, respectively, and P^{S}_i is its vapor pressure at saturation; vapor pressures and liquid-phase molar volumes were calculated using data contained in the ChemCAD IV database, and the fugacity coefficients using the Soave−Redlich−Kwong equation. The

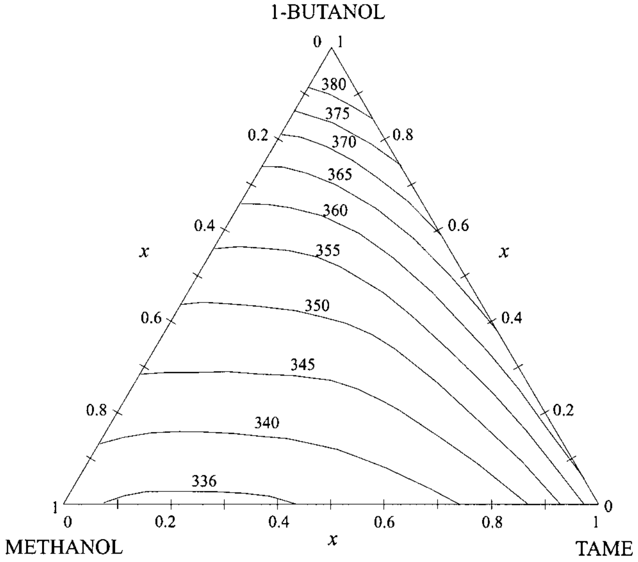

Figure 1. Isothermal liquid-phase compositions of 1-butanol + methanol + TAME at equilibrium with its vapor at 101.32 kPa (temperatures in K).

Table 4. Binary Interaction Parameters (J·mol^{-1}) of the Wilson, NRTL, and UNIQUAC Equations As Obtained by Correlating the VLE Data for the Binary Systems, Together with rms Deviations in Equilibrium Temperature and Vapor-Phase Composition

model	parameters	rms T/K	rms y_1
	Methanol (1) + TAME (2)		
Wilson	$\Delta\lambda_{12} = 5206.2$, $\Delta\lambda_{21} = -612.91$	0.25	0.0084
UNIQUAC	$\Delta u_{12} = -611.36$, $\Delta u_{21} = 4002.4$	0.26	0.0088
NRTL ($\alpha = 0.3$)	$\Delta g_{12} = 2640.5$, $\Delta g_{21} = 1499.1$	0.26	0.0113
	Methanol (1) + 1-Butanol (2)		
Wilson	$\Delta\lambda_{12} = 560.61$, $\Delta\lambda_{21} = 673.66$	0.54	0.0127
UNIQUAC	$\Delta u_{12} = 783.33$, $\Delta u_{21} = -176.06$	0.66	0.0113
NRTL ($\alpha = 0.3$)	$\Delta g_{12} = 258.31$, $\Delta g_{21} = -88.960$	0.56	0.0132
	TAME (1) + 1-Butanol (2)		
Wilson	$\Delta\lambda_{12} = -1797.2$, $\Delta\lambda_{21} = 4850.5$	0.44	0.0052
UNIQUAC	$\Delta u_{12} = 2581.5$, $\Delta u_{21} = -1337.3$	0.38	0.0063
NRTL ($\alpha = 0.3$)	$\Delta g_{12} = 3955.4$, $\Delta g_{21} = -1121.6$	0.42	0.0057

optimal value of the NRTL nonrandomness parameter α was found by trial and error to be 0.3 in all cases.

The results for the binary systems are listed in Table 4, and those for the ternary system in Table 5. For the binary systems TAME + methanol[16] and TAME + 1-butanol, a well-defined unique optimal pair of binary interaction parameters was found for each of the fitted equations. However, the parameter pairs listed in Table 4 for methanol + 1-butanol[2] only provided a slightly better fit than virtually any other parameter pairs in the region explored.

Figure 2 compares, for the ternary system, the calculated values using the NRTL equation ($\alpha = 0.3$) with the experimental VLE data (for the sake of clarity, the number of data points shown has been reduced).

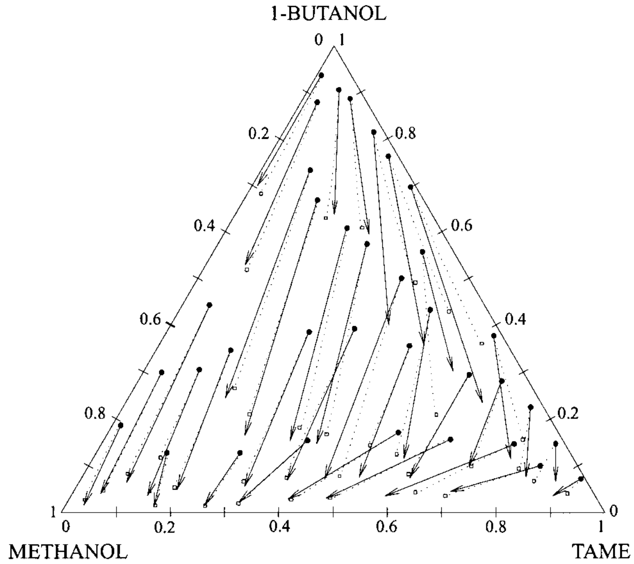

Figure 2. Comparison of the experimental VLE data (→) for 1-butanol + methanol + TAME with calculated values using the NRTL ($\alpha = 0.3$) equations (- - - □).

Table 6. Root Mean Square Deviations in Equilibrium Temperature and Vapor-Phase Composition of VLE Predictions for TAME + 1-Butanol Obtained by Group Contribution Methods

model	rms T/K	rms y_1
ASOG	0.23	0.0109
UNIFAC	0.41	0.0146
UNIFAC−Dortmund	0.91	0.0230
UNIFAC−Lyngby	0.33	0.0147

Prediction. VLE data for the binary system TAME + 1-butanol were predicted using the following group contribution methods to calculate the liquid-phase activity coefficients: the ASOG-KT method; the original UNIFAC method, with the structural and group-interaction parameters recommended by Gmehling et al.;[20] the UNIFAC−Dortmund method; and the UNIFAC−Lyngby method. Table 6 lists the rms deviations between the experimental VLE data and those predicted. Figure 3 shows the vapor−liquid equilibrium composition of the binary system TAME + 1-butanol, comparing the correlation result with the NRTL ($\alpha = 0.3$) equation and prediction with the ASOG-KT method.

For the ternary system, 1-butanol + methanol + TAME, calculations were carried out by means of two methods. Using the group contribution methods cited above along with ternary equations of Wilson, NRTL, and UNIQUAC, models were constructed with the binary interaction parameters of the constituent binary systems (Table 4). Table 7 lists the rms deviations between the experimental VLE data and those predicted by both methods.

Table 5. Binary Interaction Parameters (J·mol^{-1}) of the Wilson, NRTL, and UNIQUAC Equations As Obtained by Correlating the VLE Data for the 1-Butanol (1) + Methanol (2) + TAME (3) Ternary System, Together with rms Deviations in Equilibrium Temperature and Vapor-Phase Composition

model	parameters (J·mol^{-1})	rms T	rms y_1	rms y_2	rms y_3
Wilson	$\Delta\lambda_{12} = -579.78$, $\Delta\lambda_{13} = 4306.6$ $\Delta\lambda_{21} = 1590.63$, $\Delta\lambda_{23} = 5816.6$ $\Delta\lambda_{31} = -1528.87$, $\Delta\lambda_{32} = -1258.1$	0.94	0.0228	0.0341	0.0199
UNIQUAC	$\Delta u_{12} = 1593.5$, $\Delta u_{13} = -1334.8$ $\Delta u_{21} = -583.58$, $\Delta u_{23} = -520.49$ $\Delta u_{31} = 2603.2$, $\Delta u_{32} = 3932.9$	0.94	0.0225	0.0339	0.0197
NRTL ($\alpha = 0.3$)	$\Delta g_{12} = -1499.5$, $\Delta g_{13} = -1040.7$ $\Delta g_{21} = 2593.9$, $\Delta g_{23} = 2686.8$ $\Delta g_{31} = 3831.7$, $\Delta g_{32} = 1489.3$	0.93	0.0229	0.0342	0.0196

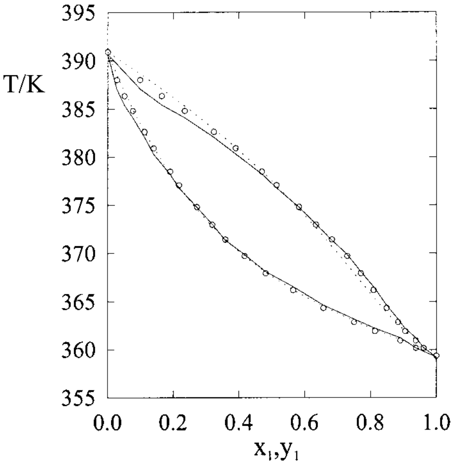

Figure 3. Vapor−liquid equilibrium compositions of TAME + 1-butanol at 101.32 kPa: ○, experimental; —, NRTL ($\alpha = 0.3$) equation; · · ·, ASOG method.

Table 7. Root Mean Square Deviations in Equilibrium Temperature and Vapor-Phase Composition of VLE Predictions for 1-Butanol (1) + Methanol (2) + TAME (3) Obtained by Group Contribution Methods or from the Equations of Wilson, NRTL, and UNIQUAC Parametrized Using Data for the Binary Systems

model	rms T/K	rms y_1	rms y_2	rms y_3
ASOG	1.22	0.0233	0.0372	0.0218
UNIFAC	0.88	0.0247	0.0372	0.0206
UNIFAC−Dortmund	0.81	0.0245	0.0438	0.0241
UNIFAC−Lyngby	1.30	0.0237	0.0355	0.0240
Wilson	0.96	0.0268	0.0394	0.0204
NRTL	1.13	0.0289	0.0417	0.0213
UNIQUAC	0.97	0.0271	0.0397	0.0205

Conclusions

Thermodynamically consistent VLE data were determined for the ternary system 1-butanol + methanol + TAME and the unmeasured constituent binary system TAME + 1-butanol. As can be seen from the ternary diagrams, Figures 1 and 2, the isotherm liquid-phase compositions close in on a single point, which corresponds to the binary azeotrope formed by the system TAME + methanol and is the focus of arrows in diagram compositions.

The Wilson, NRTL ($\alpha = 0.3$), and UNIQUAC equations correlate the ternary VLE data adequately; the deviations found in temperature and vapor composition were very similar with all three equations. When these equations were used to predict the VLE of the ternary system with binary interaction parameters obtained from the constituent binary systems, the deviations are only slightly greater than those afforded by direct optimization of the parameters of the ternary equations. This fact is attributable to the optimized parameters of the ternary and binary systems, generally being of the same order of magnitude, and to the correlation of the only system that is exceptional in this respect, methanol + 1-butanol, which is very insensitive to changes in the parameter values. This is the same behavior as has been found in previous works.[1−2]

For this ternary system, predictions using group contribution methods present deviations in composition and temperature similar to those found when the prediction is carried out with correlation equations; nonetheless, UNIFAC (without modifications) can be selected as the best method of prediction for VLE data of the 1-butanol + methanol + TAME system.

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