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Isobaric Vapor−Liquid Equilibria in the Systems Methyl Acetate + 2,2′-Oxybis[propane], 2,2′-Oxybis[propane] + Toluene, and Methanol + 2-Methyl-2-butanol

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Vapor−liquid equilibrium at 94 kPa has been determined for the binary systems methyl acetate + 2,2′-oxybis[propane], 2,2′-oxybis[propane] + toluene, and methanol + 2-methyl-2-butanol. The system methyl acetate + 2,2′-oxybis[propane] deviates positively from ideal behavior and presents a minimum boiling azeotrope at 327.29 K with 78 mol % methyl acetate. The system 2,2′-oxybis[propane] + toluene exhibits slight positive deviations from ideal behavior. The system methanol + 2-methyl-2-butanol shows negative deviations from ideal behavior, and this experimental result is explained in terms of the competitive self- and cross-association of the constituent alcohols. The vapor−liquid equilibrium data of the measured systems were compared to predictions of the UNIFAC group contribution method and correlated by the Wohl, NRTL, Wilson, and UNIQUAC models. The boiling points of all the binary systems were correlated with mole fractions by the Wisniak−Tamir and Wisniak−Segura equations.

Introduction

Amendments of the U.S. Clean Air Act in 1990 have mandated that new gasoline formulations be sold in highly polluted areas of the country, with oxygenated gasolines being supplied particularly during the winter. MTBE, the primary oxygenated compound currently used to reformulate gasolines, is being phased out because of evidence that it accumulates in surface and underground water. There is a need to investigate additional oxygenated mixtures that may have potential to comply with environmental legislation. Possible candidates may contain methanol, methyl acetate, 2,2′-oxybis[propane] (diisopropyl ether or DIPE), and 2-methyl-2-butanol (*tert*-amyl alcohol). The only vapor−liquid equilibrium (VLE) data available in the literature for the systems investigated here are those of Barton et al.[1] for the binary system methanol (1) + 2-methyl-2-butanol (2) at 313.15 K. Barton et al. found that this system deviates negatively from Raoult's law and made no corrections for possible self- and cross-association of the alcohols. No data are available for the other two binaries.

Phase equilibrium data of oxygenated mixtures are important for predicting the vapor-phase composition that would be in equilibrium with hydrocarbon mixtures. The present work was undertaken to measure vapor−liquid equilibria data for the title systems for which isobaric data are not available.

Experimental Section

Materials. Methyl acetate (99.2 mass %), 2,2′-oxybis[propane] (99.9 mass %), toluene (99.8 mass %), methanol (99.9 mass %), and 2-methyl-2-butanol (99.5 mass %) were bought from Aldrich. The reagents were used without further purification after gas chromatography failed to show any significant impurities. The properties and purity (as determined by GLC) of the pure components appear in Table 1.

Table 1. Mole % GLC Purities (mass %), Refractive Index n_D at the Na D Line, and Normal Boiling Points *T* of Pure Components

component (purity/mass %)	n_D (298.15 K)	*T*/K
methyl acetate (99.2)	1.3588^a	330.08^a
	1.3589^b	330.09^b
2,2′-oxybis[propane] (99.9)	1.3654^a	341.55^a
	1.3655^b	341.45^b
toluene (99.8)	1.49383^a	381.83^a
	1.49396^b	383.78^b
methanol (99.9)	1.32656^a	337.88^a
	1.32562^b	337.85^b
2-methyl-2-butanol (99.5)	1.4020^a	375.19^a
	1.4024^b	373.15^b

[a] Measured. [b] TRC Tables a-5560. [c] TRC Tables a-6090. [d] TRC Tables a-3290. [e] TRC Tables a-5000. [f] TRC Tables a-5030.

Apparatus and Procedure. An all-glass vapor−liquid-equilibrium apparatus model 602, manufactured by Fischer Labor-und Verfahrenstechnik (Germany), was used in the equilibrium determinations. In this circulation method apparatus, the solution is heated to its boiling point by a 250 W immersion heater (Cottrell pump). The vapor−liquid mixture flows through an extended contact line that guarantees an intense phase exchange and then enters a separation chamber whose construction prevents an entrainment of liquid particles into the vapor phase. The separated gas and liquid phases are condensed and returned to a mixing chamber, where they are stirred by a magnetic stirrer, and returned again to the immersion heater. The equilibrium temperature is measured with a Hart Scientific thermometer, model 1502, provided with a 4 mm diameter Pt-100 temperature sensor, with an accuracy of ±0.005 K. The total pressure of the system is controlled by a vacuum pump capable to work under vacuum up to 0.25 kPa. The pressure is measured by a Vac

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Table 2. Experimental Vapor−Liquid Equilibrium Data for Methyl Acetate (1) + 2,2′-Oxybis[propane] (2) at 94 kPa

T/K	x_1	y_1	γ_1	γ_2	$-B_{11}$/cm^3·mol^{-1}	$-B_{22}$/cm^3·mol^{-1}	$-B_{12}$/cm^3·mol^{-1}
339.70	0.000	0.000		1.000			
338.65	0.010	0.028	2.016	1.002	1084	1376	912
337.91	0.023	0.060	1.920	1.005	1091	1384	917
337.60	0.035	0.087	1.846	0.998	1094	1388	919
334.38	0.121	0.232	1.570	1.022	1126	1424	941
334.54	0.131	0.245	1.523	1.011	1124	1423	940
333.69	0.142	0.266	1.567	1.023	1133	1432	946
333.75	0.159	0.283	1.485	1.018	1132	1432	946
332.55	0.186	0.326	1.519	1.028	1145	1446	954
332.68	0.196	0.333	1.466	1.026	1143	1444	953
331.85	0.222	0.375	1.496	1.021	1152	1454	959
330.66	0.287	0.430	1.378	1.058	1164	1469	968
329.68	0.338	0.475	1.334	1.085	1175	1481	975
329.29	0.367	0.506	1.325	1.083	1179	1486	978
328.25	0.468	0.574	1.219	1.152	1191	1499	986
328.01	0.500	0.596	1.194	1.173	1193	1502	988
327.70	0.539	0.618	1.160	1.216	1197	1506	990
327.68	0.562	0.641	1.155	1.205	1197	1506	990
327.55	0.589	0.647	1.117	1.268	1198	1508	991
327.42	0.597	0.644	1.102	1.310	1200	1509	992
327.31	0.667	0.687	1.055	1.401	1201	1511	993
327.25	0.719	0.737	1.051	1.401	1202	1511	994
327.24	0.814	0.802	1.010	1.597	1202	1512	994
327.29	0.836	0.824	1.009	1.609	1201	1511	993
327.52	0.907	0.889	0.995	1.781	1199	1508	992
327.61	0.924	0.906	0.992	1.841	1198	1507	991
327.80	0.951	0.936	0.989	1.934	1196	1504	990
327.93	0.964	0.952	0.988	1.967	1194	1503	989
328.07	0.982	0.975	0.989	2.042	1193	1501	988
327.97	1.000	1.000	1.000				

Probs with an accuracy of ±0.1 kPa. On the average, the system reaches equilibrium conditions after 1−2 h of operation. Samples, taken by syringing 0.7 μL after the system had achieved equilibrium, were analyzed by gas chromatography on a DANI model GC1000 apparatus provided with a thermal conductivity detector and a Spectra Physics Model Chromjet SP 4400 electronic integrator. The column was 3 m long and 0.2 cm in diameter, packed with SP-2100. Column, injector, and detector temperatures were (473.15, 493.15, and 448.15) K, respectively, for the three binaries. Very good separation was achieved under these conditions, and calibration analyses were carried out to convert the peak ratio to the mass composition of the sample. The pertinent polynomial fit had a correlation coefficient R^2 better than 0.99. Concentration measurements were accurate to better than ±0.009 mole fraction.

Results

The temperature T, the liquid-phase mole fraction x, and the vapor-phase mole fraction y measurements at $P = 94$ kPa are reported in Tables 2−4 and Figures 1−6, together with the activity coefficients γ_i that were calculated from the following equation:[2]

$$\ln \gamma_i = \ln \frac{y_i P}{x_i P_i^\circ} + \frac{(B_{ii} - V_i^{\mathrm{L}})(P - P_i^\circ)}{RT} + y_j^2 \frac{\delta_{ij} P}{RT} \qquad (1)$$

where T and P are the boiling point and the total pressure, V_i^{L} is the molar liquid volume of component i, B_{ii} and B_{jj} are the second virial coefficients of the pure gases, B_{ij} is the cross second virial coefficient, and

$$\delta_{ij} = 2B_{ij} - B_{jj} - B_{ii} \qquad (2)$$

Table 3. Experimental Vapor−Liquid Equilibrium Data for 2,2′-Oxybis[propane] (2) + Toluene (3) at 94 kPa

T/K	x_2	y_2	γ_2	γ_3	$-B_{22}$/cm^3·mol^{-1}	$-B_{33}$/cm^3·mol^{-1}	$-B_{23}$/cm^3·mol^{-1}
381.19	0.000	0.000		1.000			
380.24	0.012	0.042	1.176	0.995	1014	1226	1119
378.40	0.035	0.112	1.122	0.994	1027	1242	1133
376.35	0.062	0.185	1.097	0.995	1041	1260	1149
375.57	0.072	0.217	1.129	0.989	1047	1267	1156
375.10	0.076	0.227	1.132	0.994	1050	1271	1159
373.16	0.107	0.294	1.090	0.994	1064	1289	1175
371.33	0.133	0.351	1.095	0.993	1078	1306	1191
368.74	0.165	0.436	1.169	0.968	1098	1331	1213
368.29	0.171	0.449	1.174	0.966	1101	1336	1217
366.46	0.200	0.496	1.161	0.968	1116	1354	1233
362.45	0.273	0.595	1.131	0.970	1148	1395	1270
360.86	0.303	0.629	1.123	0.974	1162	1412	1285
360.83	0.312	0.641	1.113	0.956	1162	1412	1285
358.75	0.351	0.687	1.120	0.944	1180	1435	1306
350.74	0.538	0.816	1.082	1.018	1252	1529	1388
344.27	0.784	0.924	1.014	1.127	1316	1612	1462
342.46	0.855	0.960	1.020	0.943	1335	1637	1483
342.02	0.874	0.963	1.015	1.020	1340	1643	1489
340.49	0.943	0.984	1.007	1.030	1356	1665	1507
339.70	1.000	1.000	1.000				

Table 4. Experimental Vapor−Liquid Equilibrium Data for Methanol (4) + 2-Methyl-2-butanol (5) at 94 kPa

T/K	x_4	y_4	γ_4	γ_5	$-B_{44}$/cm^3·mol^{-1}	$-B_{55}$/cm^3·mol^{-1}	$-B_{45}$/cm^3·mol^{-1}
373.06	0.000	0.000		1.000			
366.38	0.099	0.266	0.949	1.025	756	1753	926
364.47	0.139	0.352	0.948	1.017	777	1814	950
359.94	0.235	0.521	0.957	1.008	833	1972	1010
357.50	0.295	0.603	0.954	1.000	865	2066	1044
357.37	0.287	0.597	0.975	1.008	867	2071	1046
355.12	0.349	0.677	0.979	0.971	898	2164	1080
352.89	0.409	0.734	0.976	0.966	931	2262	1115
351.37	0.451	0.766	0.973	0.975	955	2334	1139
348.88	0.520	0.822	0.987	0.945	995	2457	1182
347.54	0.562	0.848	0.987	0.937	1018	2528	1206
346.45	0.593	0.868	0.995	0.919	1037	2588	1226
343.60	0.693	0.916	0.995	0.881	1089	2754	1280
342.27	0.738	0.933	0.999	0.875	1115	2837	1307
340.96	0.786	0.950	1.002	0.849	1141	2922	1334
340.18	0.818	0.958	0.999	0.870	1157	2974	1351
337.59	0.927	0.986	1.000	0.817	1212	3159	1408
336.00	1.000	1.000	1.000				

The standard state for calculation of activity coefficients is the pure component at the pressure and temperature of the solution. Equation 1 is valid at low and moderate pressures when the virial equation of state truncated after the second coefficient is adequate to describe the vapor phase of the pure components and their mixtures, and liquid volumes of the pure components are incompressible over the pressure range under consideration. The pure component vapor pressures P_i° were calculated according to the Antoine equation

$$\log(P_i^\circ/\mathrm{kPa}) = A_i - \frac{B_i}{(T/\mathrm{K}) - C_i} \qquad (3)$$

where the Antoine constants A_i, B_i, and C_i are reported in Table 5. The molar virial coefficients B_{ii} and B_{ij} were estimated by the method of Hayden and O'Connell[3] using the molecular and the association η parameters suggested by Prausnitz et al.[4] For the case of 2,2′-oxybis[propane] and 2-methyl-2-butanol, the parameters of the Hayden and O'Connell correlation were estimated from the second virial coefficient correlations available in DIPPR.[5] The last two

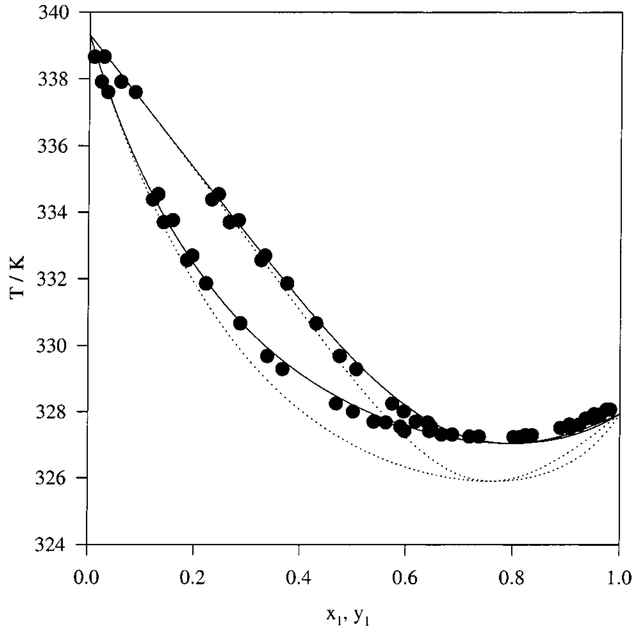

Figure 1. Boiling temperature diagram for the system methyl acetate (1) + 2,2′-oxybis[propane] (2) at 94.00 kPa: (●) experimental; (−) correlated by the Legendre polynomial, which gives consistency to the data; (· · ·) predicted by UNIFAC.[10]

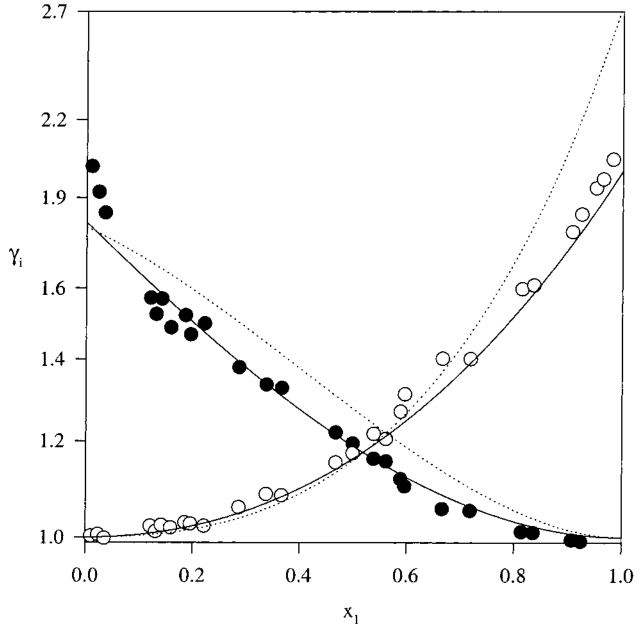

Figure 2. Activity coefficients for the system methyl acetate (1) + 2,2′-oxybis[propane] (2) at 94.00 kPa: (●) γ_1^{exptl}; (○) γ_2^{exptl}; (−) smoothed by the Legendre polynomial, which gives consistency to the data; (· · ·) predicted by UNIFAC.[10]

terms in eq 1, particularly the second one that expresses the correction due to the nonideal behavior of the vapor phase, contributed less than 3% to the activity coefficients. In general, their influence was important only at very dilute concentrations. The calculated activity coefficients are reported in Tables 2−4 and are estimated to be accurate to within ±3%. The results reported in these tables indicate that the system methyl acetate (1) + 2,2′-oxybis[propane] (2) deviates positively from ideal behavior and presents a minimum boiling azeotrope at 327.29 K with 78 mol % methyl acetate. The system 2,2′-oxybis[propane] (2) + toluene (3) exhibits a slight positive deviation from ideal behavior, while the methanol (4) +

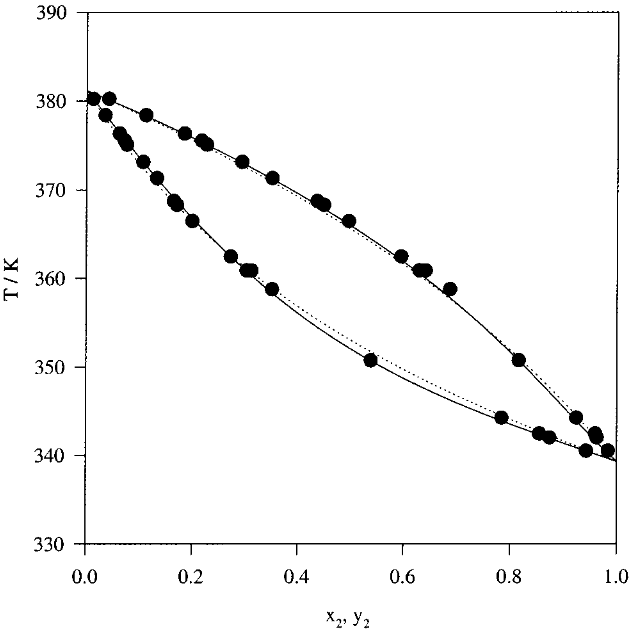

Figure 3. Boiling temperature diagram for the system 2,2′-oxybis[propane] (2) + toluene (3) at 94.00 kPa: (●) experimental; (−) correlated by the Legendre polynomial, which gives consistency to the data; (· · ·) predicted by UNIFAC.[10]

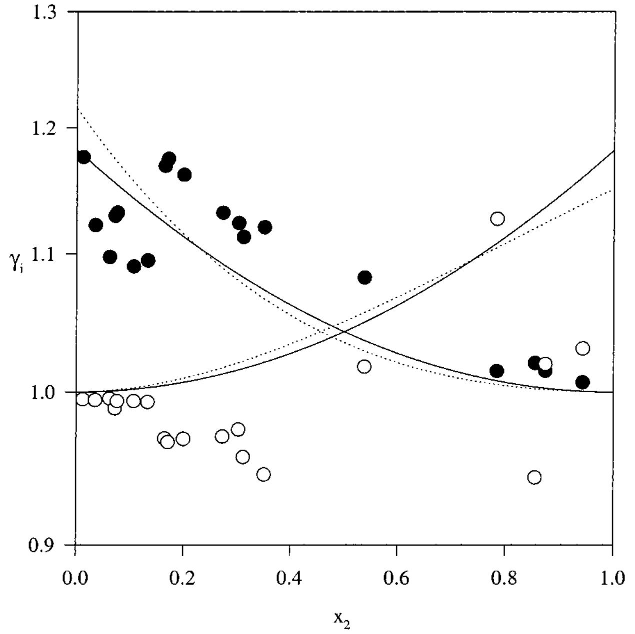

Figure 4. Activity coefficients for the system 2,2′-oxybis[propane] (2) + toluene (3) at 94.00 kPa: (●) γ_1^{exptl}; (○) γ_2^{exptl}; (−) smoothed by the Legendre polynomial, which gives consistency to the data; (· · ·) predicted by UNIFAC.[10]

2-methyl-2-butanol (5) system exhibits a negative deviation. The vapor−liquid equilibria data reported in Tables 2−4 were found to be thermodynamically consistent by the L−W method of Wisniak[6] and the point-to-point method of Van Ness et al.,[7] as modified by Fredenslund et al.[8] Pertinent consistency statistics for the point-to-point method are reported in Table 6.

The activity coefficients were correlated with the Wohl, NRTL, Wilson, and UNIQUAC equations[9] and predicted by the UNIFAC group contribution method.[8,10] The parameters of the Wohl, Wilson, NRTL, and UNIQUAC equations were obtained by minimizing the following objective function (OF):

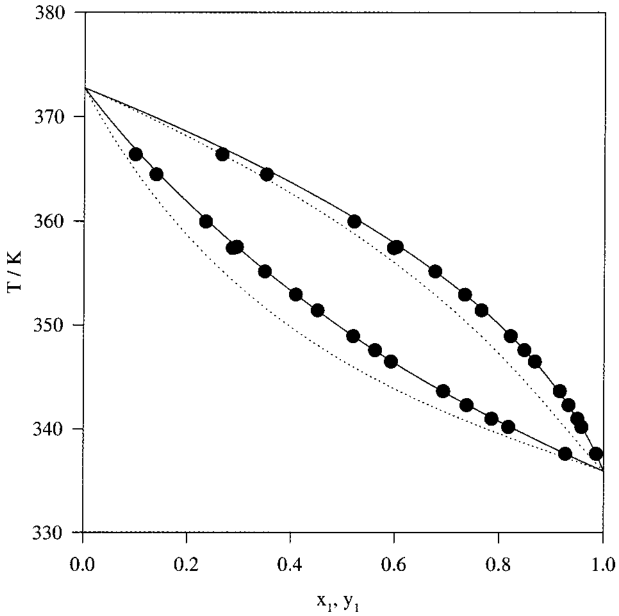

Figure 5. Boiling temperature diagram for the system methanol (4) + 2-methyl-2-butanol (5) at 94.00 kPa: (●) experimental; (—) correlated with the association model proposed in this work (eq 15) and the parameters given in Table 8; (· · ·) predicted by UNIFAC.[10]

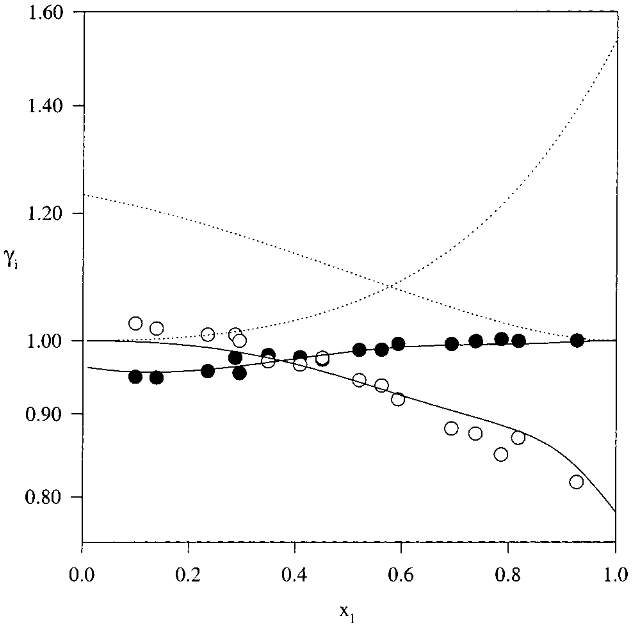

Figure 6. Activity coefficients for the system methanol (4) + 2-methyl-2-butanol (5) at 94.00 kPa: (●) $\gamma_1^{\rm exptl}$; (○) $\gamma_2^{\rm exptl}$; (—) smoothed by the association model proposed in this work (eq 15) and the parameters given in Table 8; (· · ·) predicted by UNIFAC.[10]

Table 5. Antoine Coefficients, Eq 3

compound	A_i	B_i	C_i
methyl acetate[a]	6.18621	1156.430	53.460
2,2′-oxybis[propane][b]	5.97678	1143.073	53.810
toluene[c]	6.07954	1344.800	53.668
methanol[d]	7.02240	1474.080	44.020
2-methyl-2-butanol[e]	5.64420	863.4000	137.85

[a] TRC k-5560. [b] Ambrose et al. [c] TRC k-3200. [d] TRC k-5030. [e] TRC k-5031.

Table 6. Consistency Test Statistics for the Binary Systems Methyl Acetate (1) + 2,2′-Oxybis[propane] (2), 2,2′-Oxybis[propane] (2) + Toluene (3) and Methanol (4) + 2-Methyl-2-butanol (5)

system	N_p[a]	$100\Delta y$[b]	ΔP[c]/kPa
1 + 2	2	0.55	0.64
2 + 3	1	1.00	0.89
4 + 5	3	0.75	0.27

[a] Number of parameters for the Legendre polynomial used in consistency. [b] Average absolute deviation in vapor-phase mole fractions $\Delta y = 1/N\sum_{i=1}^{N}|y_1^{\rm exptl} - y_1^{\rm calc}|$ (N: number of data points). [c] Average absolute deviation in pressure $\Delta P = 1/N\sum_{i=1}^{N}|P^{\rm exptl} - P^{\rm calc}|$.

$$\mathrm{OF} = \sum_{i=1}^{N}(|P_i^{\rm exptl} - P_i^{\rm calc}|/P_i^{\rm exptl} + |y_i^{\rm exptl} - y_i^{\rm calc}|)^2 \qquad (4)$$

and are reported in Table 7, together with the relative deviation of the vapor mole fraction. Inspection of the results given in Table 7 shows that all four models gave a reasonable fit of the binary systems, with the best fit corresponding to the Wohl model. The capability of predicting the vapor-phase mole fraction has been used as the ranking factor. Table 7 and Figures 1−6 show that UNIFAC[10] yields fair predictions for the systems methyl acetate (1) + 2,2′-oxybis[propane] (2) and 2,2′-oxybis[propane] (2) + toluene (3). However, according to deviation statistics in Table 7 and Figures 5 and 6, neither the VLE data nor the deviation of the system methanol (4) + 2-methyl-2-butanol (5) is predicted by UNIFAC.

Notwithstanding the fact that the VLE data of the system methanol (4) + 2-methyl-2-butanol (5) are fairly well correlated (exception being UNIFAC), none of the fitted models is able to represent consistently the experimental trend of activity coefficients on liquid-phase mole fraction (shown in Figure 6). In fact, different deviation statistics in bubble and dew-point pressure calculations are achieved for the system in question, as shown by Table 7, suggesting some anomalies in the smoothing of activity coefficients. The probable reason for this is that association effects were not considered when correlating the VLE data, and such a simplification is not adequate for modeling the data.

According to the chemical theory,[11] positive deviations from ideal behavior may be explained in terms of self-association, while negative deviations may be attributed to cross-association between the components of a mixture. The negative deviation observed in the system methanol + 2-methyl-2-butanol suggests that a reasonable scenario for the association regime is a simultaneous self- and cross-association of the alcohols. Following the approach of Nath and Bender,[12] the enthalpy of association and the equilibrium constant for pure liquids may be calculated from saturation data. From this approach it is possible to predict that, at 323.15 K, the equilibrium association constants for methanol and 2-methyl-2-butanol are in the ratio 25:1. Consequently, the self-association of 2-methyl-2-butanol may be neglected when compared to the case of methanol, and this may be reasonable explained in terms of the steric constraints for the first molecule. In addition, the cross-association between methanol and 2-methyl-2-butanol is to be expected on the basis of the negative deviations observed in the system. According to the association theory of Nath and Bender,[13] when a self-associating molecule A (methanol) forms linear polymers by successive chemical reactions expressed by

$$\mathrm{A}_1 + \mathrm{A}_{i-1} \underset{K_\mathrm{A}}{\leftrightarrow} \mathrm{A}_i$$

Table 7. Parameters and Prediction Statistics for Different G^E Models

					bubble-point pressures		dew-point pressures	
model	ij	A_{ij}	A_{ji}	α_{ij}	ΔP^f (%)	$100\Delta y_i$	ΔP (%)	$100\Delta x_i$
Wohl	1 + 2	0.57	0.50	0.43[e]	0.46	0.6	0.46	0.6
	2 + 3	0.12	0.19	0.15[e]	0.60	0.8	1.50	0.9
	4 + 5	−0.09	−0.08	0.81[e]	0.60	0.4	1.45	0.8
NRTL[a]	1 + 2	1372.34	520.53	0.30	0.62	0.5	0.62	0.6
	2 + 3	2206.08	−1336.46	0.30	0.67	0.9	1.50	1.0
	4 + 5	−1883.38	2013.77	0.30	0.54	0.4	1.37	0.8
Wilson[a,b]	1 + 2	1914.15	51.72		0.63	0.5	0.62	0.6
	2 + 3	−613.00	1149.01		0.87	1.0	1.50	1.0
	4 + 5	1504.77	−1012.76		0.69	0.4	1.53	0.8
UNIQUAC[a,c]	1 + 2	−497.14	1300.62		0.62	0.5	0.61	0.6
	2 + 3	−35.21	64.36		1.10	1.1	1.60	1.1
	4 + 5	−103.33	875.28		1.00	0.4	1.78	0.8
UNIFAC[d]	1 + 2				2.71	1.5	2.00	1.7
	2 + 3				1.19	1.2	1.66	1.2
	4 + 5				9.39	2.5	8.14	3.2

[a] Parameters in J·mol $^{-1}$. [b] Liquid volumes have been estimated from the Rackett equation.[15] [c] Molecular parameters are those calculated from UNIFAC.[10] [d] Calculations based on original UNIFAC.[10] [e] "q" parameter for the Wohl's model. [f] $\Delta P = 100/N\sum_i^N|P_i^{\text{exptl}} - P_i^{\text{calc}}|P_i^{\text{exptl}}$.

and by

$$B_1 + A_i \underset{K_{AB}}{\Leftrightarrow} A_iB$$

for the cross-association with a molecule B (2-methyl-2-butanol), whose self-association is negligible, the chemical contribution to activity coefficients is given by

$$\ln \gamma_A^{\text{chem}} = \ln\left(\frac{\phi_{A_1}}{x_A\phi_{A_1}^\circ}\right) - \frac{v_A}{v_{AB}} + \frac{v_A}{v_A^\circ} \tag{5}$$

$$\ln \gamma_B^{\text{chem}} = \ln\left(\frac{\phi_{0B}}{x_B}\right) + 1 - \frac{v_B}{v_{AB}} \tag{6}$$

where v_i is the apparent molar volume of component i and ϕ_{A1} and ϕ_{0B} are the volume fractions of the monomer A_1 and of the unreacted component B, respectively. v_{AB} corresponds to the molar volume of the solution, which, in turn, may be calculated from

$$\frac{1}{v_{AB}} = \frac{\phi_{A_1}}{v_A(1 - K_A\phi_{A_1})} + \frac{\phi_{0B}}{v_B}\left[\frac{1 - (K_A - K_{AB})\phi_{A_1}}{1 - K_A\phi_{A_1}}\right] \tag{7}$$

In eqs 5−7, ϕ_{A1}° and v_A° are the volume fraction and the molar volume of pure component A, present as the monomer, and these properties depend on the self-association equilibrium constant K_A as follows

$$\phi_{A_1}^\circ = [(2K_A + 1) - (1 + 4K_A)^{1/2}]/2K_A^2 \tag{8}$$

$$\frac{1}{v_A^\circ} = \frac{\phi_{A_1}^\circ}{v_A(1 - K_A\phi_{A_1}^\circ)} \tag{9}$$

ϕ_{A1} and ϕ_{0B} are related to apparent properties by the following relations

$$\phi_A = [\phi_{A_1}/(1 - K_A\phi_{A_1})^2][1 + K_{AB}\phi_{0B}v_A/v_B] \tag{10}$$

$$\phi_B = \phi_{0B}[1 - (K_A - K_{AB})\phi_{A_1}][1 - K_A\phi_{A_1}]^{-1} \tag{11}$$

where ϕ_A and ϕ_B are apparent volume fractions defined as

$$\phi_i = \frac{x_iv_i}{x_Av_A + x_Bv_B} \qquad (i = A, B) \tag{12}$$

K_A and K_{AB} are equilibrium constants for self- and cross-association, and in the approach of Nath and Bender they depend only on temperature as follows

$$K_i = K_i^{323K}\exp\left[-\frac{h_i}{R}\left(\frac{1}{T/K} - \frac{1}{323.15}\right)\right] \qquad (i = A, AB) \tag{13}$$

and are assumed independent of the length of the polymer chain. In eq 13, h_i is the association enthalpy and K_i^{323K} corresponds to the equilibrium association constant, normalized to 323.15 K. The approach of Nath and Bender[12] provides a predictive scheme for calculating h_i and K_i^{323K} for pure fluids that self-associate. In the case of cross-association, both the enthalpy and the normalized equilibrium constant can be calculated from experimental VLE data. Once activity coefficients have been calculated from eqs 5−13 (numerical details are discussed in ref 13), the chemical contribution to the excess energy may be calculated with

$$\left(\frac{G^E}{RT}\right)^{\text{chem}} = x_A \ln \gamma_A^{\text{chem}} + x_B \ln \gamma_B^{\text{chem}} \tag{14}$$

while the excess Gibbs energy, including physical contributions, is given by

$$\frac{G^E}{RT} = \left(\frac{G^E}{RT}\right)^{\text{phys}} + \left(\frac{G^E}{RT}\right)^{\text{chem}} \tag{15}$$

According to DIPPR,[5] the critical volumes of methanol and 2-methyl-2-butanol are in the ratio 1:3, indicating that physical effects may yield an important contribution to the excess energy. The intrinsic excess model associated with the van der Waals equation of state, which is able to reproduce the molecular size effect in phase equilibria,[14] is the van Laar equation

$$\left(\frac{G^E}{RT}\right)^{\text{phys}} = \frac{A_{AB}A_{BA}x_Ax_B}{A_{AB}x_A + A_{BA}x_B} \tag{16}$$

Equation 16 will be used for modeling the physical contribution in eq 15. The association model proposed here depends on four parameters and on pure (apparent) fluid volumes v_A and v_B. Two parameters A_{AB} and A_{BA} are needed in eq 16 for modeling the physical contribution to the excess energy. Additional parameters are the cross-association enthalpy h_{AB} and the equilibrium constant K_{AB}^{323K}. All

Table 8. Data Treatment for the System Methanol (4) + 2-Methy-2-butanol (5) Using the Association Approach in Eq 15: Model Parameters and Correlation Statistics

I. Parameters

K_4^{323K}	h_4/J·mol^{-1}	K_{45}^{323K}	h_{45}/J·mol^{-1}	A_{45}	A_{54}
250.90[a]	−19917[a]	487.80[b]	−25698[b]	0.4836[b]	1.0318[b]

II. Correlation Statistics

bubble-point pressures		dew-point pressures	
ΔP (%)	$100\Delta y_4$	ΔP (%)	$100\Delta x_i$
0.5	0.3	0.7	0.3

[a] Calculated according to the approach of Nath and Bender from saturation data. [b] Calculated from the experimental data presented in Table 4.

Table 9. Coefficients and Statistics in Correlation of Boiling Points, Eqs 17 and 18

A. Wisniak−Tamir Model (Eq 17)

system	C_0	C_1	C_2	avg dev/K	max dev/K	std dev/K
1 + 2	−23.2448	10.2500	−5.6198	0.14	0.66	0.22
2 + 3	−32.5542	9.3646	−0.5796	0.15	0.35	0.17
4 + 5	−19.5467	7.1902	−6.9467	0.10	0.35	0.12

B. Wisniak−Segura Model (Eq 18)

system	A	B	n	avg dev/K	max dev/K	std dev/K
1 + 2	−523.2720	−3.5967	−0.9092	0.17	0.70	0.24
2 + 3	−328.5781	−4.2628	−0.5693	0.15	0.32	0.17
4 + 5	−299.2028	−3.8340	−0.7394	0.16	0.58	0.18

these parameters have been calculated by fitting the experimental VLE data reported in Table 4, using the objective function indicated in eq 4, and are reported in Table 8. Pure fluid volumes have been estimated from the Rackett[15] equation. The pure component saturation data, needed for evaluating the association enthalpy and equilibrium constant of methanol, have been taken from DIPPR[5] and the vapor pressure data reported in Table 5. From Table 8 it is possible to conclude an excellent representation of the data. In addition, from Figure 6, it is possible to conclude a good representation of activity coefficients.

The boiling points of the solutions were correlated with its composition by the equation proposed by Wisniak and Tamir,[16]

$$T/\mathrm{K} = x_i T_i^\circ + x_j T_j^\circ + x_i x_j \sum_{k=1}^{m} C_k (x_i - x_j)^k \tag{17}$$

and also by a new three-parameter equation proposed by Wisniak and Segura,[17]

$$T/\mathrm{K} = x_i T_i^\circ + x_j T_j^\circ + A x_i x_j \cosh^n (B - x_i) \tag{18}$$

In eqs 17 and 18, T_i°/K is the boiling point of the pure component i and m is the number of terms in the series expansion of $(x_i - x_j)$. The various constants of eqs 17 and 18 are reported in Table 9, which also contains information indicating the degree of goodness of the correlation.

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