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Isobaric Vapor−Liquid Equilibria at 101.32 kPa and Densities, Speeds of Sound, and Refractive Indices at 298.15 K for MTBE or DIPE or TAME + 1-Propanol Binary Systems

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The isobaric vapor−liquid equilibria (VLE) at 101.32 kPa and densities, speeds of sound, and refractive indices at 298.15 K have been measured for binary liquid mixtures of 2-methoxy-2-methylpropane (MTBE) or 2-isopropoxypropane (DIPE) or 2-methoxy-2-methylbutane (TAME) and 1-propanol. The molar volumes, molar refractions, and isentropic compressibilities have been calculated from these experimental data. The excess molar volumes and the deviations in molar refraction and isentropic compressibility upon mixing have been satisfactorily correlated by the Redlich−Kister polynomial. The vapor−liquid equilibrium data have been found thermodynamically consistent and have been adequately correlated by means of Wilson, NRTL, and UNIQUAC equations. The ASOG and the original and modified UNIFAC group contribution methods have not afforded very adequate predictions of data involved in this study.

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1. Introduction

Tertiary alkyl ethers, having similar properties (e.g., vapor pressures) to hydrocarbons and the potential to increase the octane number and to decrease the emission of carbon monoxide, have become important additives for gasoline. So, the use of ethers as 2-methoxy-2-methylpropane or 2-isopropoxypropane or 2-methoxy-2-methylbutane, pure or mixed with alkanols or alkanes, has been recommended as a high octane blending agent for motor gasoline. Moreover, these ethers are also increasingly used as solvents or chemical reactants in the manufacture of new other products. Knowledge of fluid phase equilibria and thermodynamic properties of the mixtures containing a tertiary alkyl ether are of interest to optimize the processes in which they are involved.

The present paper reports isobaric vapor−liquid equilibrium (VLE) data at 101.32 kPa and densities, refractive indices, and speeds of sound at 298.15 K for binary liquid mixtures of 2-methoxy-2-methylpropane (MTBE) or 2-isopropoxypropane (DIPE) or 2-methoxy-2-methylbutane (TAME) and 1-propanol. The molar volumes, molar refractions, and isentropic compressibilities were calculated from the experimental data. The excess molar volumes and the deviations in molar refraction and isentropic compressibility upon mixing were correlated by the Redlich−Kister polynomial. The VLE data were tested for thermodynamic consistency and correlated using the Wilson,[1] NRTL,[2] and UNIQUAC[3] equations. Furthermore, the data were compared with the predictions of various group contribution methods, ASOG,[4,5] original UNIFAC,[6,7] UNIFAC−Dormunt,[8−10] and UNIFAC−Lyngby,[11] with the aim of selecting the most suitable model for this kind of mixture.

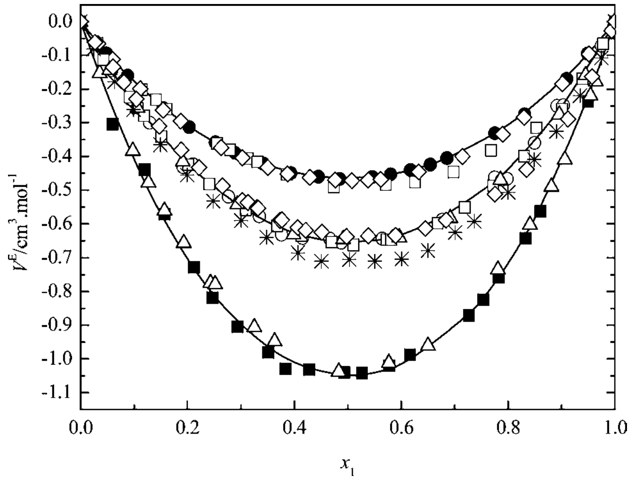

Figure 1. Excess molar volumes at 298.15 K and atmospheric pressure against mole fraction, x_1, for the binary systems: ○, MTBE (1) + 1-propanol (2); ●, TAME (1) + 1-propanol (2); ■, DIPE (1) + 1-propanol (2); □, ref 12; Δ, ref 13; ◇, ref 14; *, ref 15. The solid lines represent the theoretical fit of this data to eq 7.

There are some published data in the references for the excess molar volumes at 298.15 K and atmospheric pressure of MTBE + 1-propanol,[12−15] TAME + 1-propanol,[12,14] and DIPE + 1-propanol[13] systems. A survey of the literature showed that no isobaric VLE data at 101.32 kPa are available for these mixtures.

2. Experimental Section

Materials. 1-Propanol was supplied by Riedel-de Haën with a nominal mass fraction purity > 0.999; 2-methoxy-2-methylpropane (MTBE) was supplied by Sigma-Aldrich with a nominal mass fraction purity > 0.998; and 2-isopropoxypropane (DIPE) and 2-methoxy-2-methylbutane (TAME) were supplied by Fluka and had nominal mass fraction purities > 0.99 and > 0.97, respectively. Those purities were verified chromatographically, even in the case of TAME, and despite its nominal purity, no appreciable peaks of impurities have been found. No further purification of these products was carried out. The water contents of 1-propanol, DIPE, TAME, and MTBE were determined as

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Table 1. Density, ρ, and Refractive Index, n_D, at 298.15 K, and Normal Boiling Temperatures, T_b, of the Pure Components

	$\rho/g\cdot cm^{-3}$		n_D		T_b/K	
component	exptl	lit.	exptl	lit.	exptl	lit.
1-propanol	0.79964	0.79960[a]	1.38308	1.38370[a]	370.29	370.30[a]
MTBE	0.73556	0.73528[b]	1.36628	1.36630[b]	328.12	328.32[d]
DIPE	0.71832	0.71854[a]	1.36523	1.3655[a]	341.50	341.66[a]
TAME	0.76592	0.76577[c]	1.38587	1.38580[c]	359.45	359.39[d]

[a] From ref 16. [b] From ref 17. [c] From ref 18. [d] From ref 19.

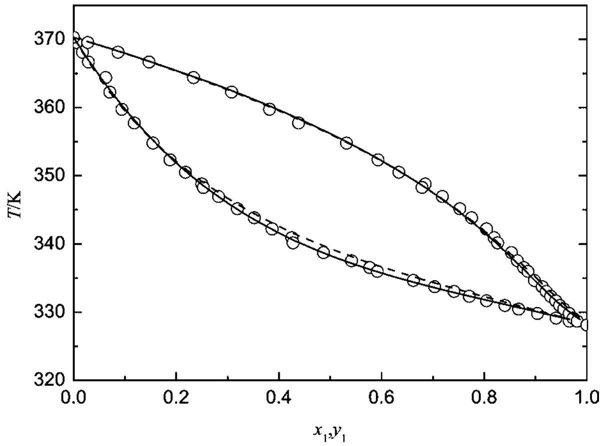

Figure 2. VLE data for MTBE (1) + 1-propanol (2) binary system. ○, Experimental results; continuous lines, calculated values using the NRTL ($\alpha = 0.1$) equation; dashed lines, predicted values using the UNIFAC−Dortmund equation with binary parameters.

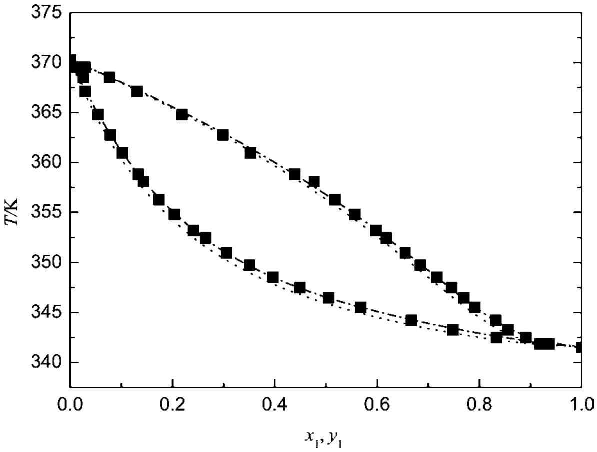

Figure 3. VLE data for the DIPE (1) + 1-propanol (2) binary system. ■, Experimental results; dashed-dotted lines, calculated values using the UNIQUAC equation; dashed lines, predicted values using the UNIFAC−Dortmund equation with binary parameters.

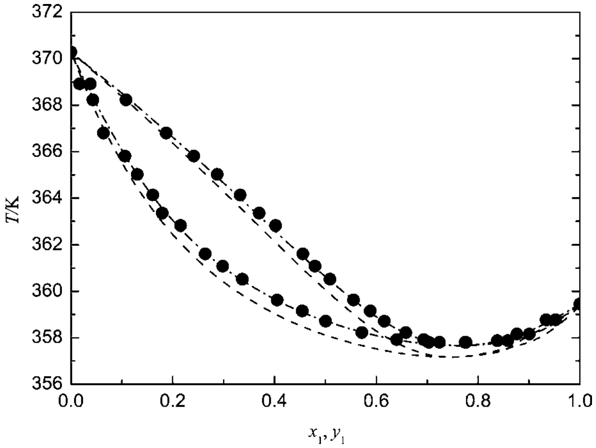

Figure 4. VLE data for the TAME (1) + 1-propanol (2) binary system. ●, Experimental results; dashed-dotted lines, calculated values using the UNIQUAC equation; dashed lines, predicted values using the UNIFAC equation with binary parameters.

(0.04, 0.02, 0.02, and 0.03) % in mass, respectively, using a Metrohm 737 KF coulometer. The relevant physical properties of these components are listed in Table 1 together with previously published values.[16−19]

Apparatus and Procedure. Mixtures of the required composition were prepared by mass using a Mettler Toledo AT 261 balance with an uncertainty of $\pm\ 10^{-4}$ g. Densities were measured in an Anton Paar DMA 5000 densimeter. The uncertainty in the measurement is $\pm\ 10^{-5}\ g\cdot cm^{-3}$. Speeds of sound were measured in an Anton Paar DSA 48 digital vibrating tube apparatus with uncertainty of $\pm\ 1\ m\cdot s^{-1}$. Refractive indices were measured in an ATAGO RX-5000 refractometer with a Hero Therm thermostat to maintain the temperature. The uncertainty in the refractive index measurement is $\pm\ 4\cdot 10^{-5}$. Temperatures of densimeter, sound analyzer, and refractometer were measured with uncertainties of (± 0.01, ± 0.01, and ± 0.02) K, respectively.

VLE data were determined in a Labodest 602 Distillation apparatus that recycles both liquid and vapor phases (Fische Labor and Verfahrenstechnik, Germany). This is a recirculating still of the type described by Walas.[20] It is equipped with a Fischer digital manometer that measured to within ± 0.01 kPa and an ASL F250 Mk II Precision Thermometer, operating with a wired PT100 PRT, that provides the temperature of the system with an uncertainty of ± 0.02 K. Distillation is carried out at 101.32 kPa under an inert argon atmosphere. The compositions of the phases in equilibrium were determined using the densities and refractive index measurements as an analysis method. The uncertainty in the composition determination is ± 0.002 mol fraction.

3. Results and Discussion

The measured densities, ρ, refractive indices, n_D, and speeds of sound, u, at 298.15 K and atmospheric pressure are listed in Table 2 for MTBE + 1-propanol, DIPE + 1-propanol, and TAME + 1-propanol binary systems. This table also includes the calculated values of excess molar volumes, V^E, isentropic compressibility, κ_S, isentropic compressibility changes of mixing, $\Delta\kappa_S$, and molar refraction changes of mixing, ΔR, calculated by means of the following expressions.

Excess molar volumes, V^E

$$V^E = \frac{1}{\rho}\sum_{i=1}^{n} x_i M_i - \sum_{i=1}^{n} \frac{x_i M_i}{\rho_i} \qquad (1)$$

where x_i and M_i are the mole fraction and molar mass of component i in the mixture. The molar refractions, R, were calculated using the Lorentz−Lorenz equation

Table 2. Densities ρ, Speeds of Sound u, Isentropic Compressibilities κ_s, Refractive Indices n_D, Excess Molar Volumes V^E, and Changes of Mixing $\Delta\kappa_s$ and ΔR for Mixtures at 298.15 K and Atmospheric Pressure

x_1	ρ / $g\cdot cm^{-3}$	u / $m\cdot s^{-1}$	κ_s / TPa^{-1}	n_D	V^E / $cm^3\cdot mol^{-1}$	$\Delta\kappa_s$ / TPa^{-1}	ΔR / $cm^3\cdot mol^{-1}$
			MTBE (1) + 1-Propanol (2)				
0.0000	0.79964	1207	858	1.38308	0.000	0	0.000
0.0584	0.79535	1196	878	1.38233	−0.144	−16	−0.001
0.0942	0.79282	1190	891	1.38191	−0.230	−25	−0.001
0.1293	0.79029	1184	902	1.38154	−0.300	−33	0.005
0.1923	0.78606	1173	925	1.38064	−0.432	−44	0.000
0.2104	0.78445	1168	935	1.38021	−0.423	−44	0.001
0.2769	0.77997	1156	959	1.37933	−0.519	−53	0.006
0.3348	0.77607	1146	981	1.37842	−0.577	−57	0.006
0.3760	0.77356	1139	997	1.37743	−0.632	−60	−0.015
0.4154	0.77088	1132	1013	1.37690	−0.642	−60	−0.006
0.4663	0.76749	1123	1033	1.37600	−0.644	−61	−0.005
0.4881	0.76616	1119	1042	1.37558	−0.655	−61	−0.010
0.5644	0.76134	1107	1073	1.37419	−0.644	−59	−0.013
0.5901	0.75975	1102	1083	1.37380	−0.634	−57	−0.009
0.6768	0.75454	1089	1117	1.37239	−0.588	−52	−0.004
0.7881	0.74798	1072	1164	1.37033	−0.469	−41	−0.007
0.8496	0.74433	1062	1191	1.36915	−0.360	−32	−0.007
0.8918	0.74170	1056	1209	1.36836	−0.250	−26	0.000
0.9035	0.74117	1054	1215	1.36811	−0.248	−22	−0.006
0.9746	0.73703	1042	1250	1.36673	−0.071	−6	−0.004
1.0000	0.73556	1037	1263	1.36628	0.000	0	0.000
			DIPE (1) + 1-Propanol (2)				
0.0000	0.79964	1207	858	1.38308	0.000	0	0.000
0.0602	0.79389	1189	891	1.38242	−0.304	−26	−0.016
0.1201	0.78709	1168	931	1.38153	−0.439	−39	−0.006
0.1569	0.78368	1162	945	1.38101	−0.571	−54	−0.011
0.2127	0.77846	1147	976	1.38022	−0.728	−66	−0.013
0.2472	0.77539	1137	997	1.37959	−0.818	−69	−0.021
0.2939	0.77116	1128	1020	1.37874	−0.905	−77	−0.026
0.3513	0.76609	1113	1054	1.37774	−0.981	−79	−0.026
0.3835	0.76345	1107	1069	1.37719	−1.029	−82	−0.028
0.4282	0.75951	1097	1093	1.37637	−1.032	−83	−0.023
0.4934	0.75416	1083	1130	1.37518	−1.040	−79	−0.020
0.5267	0.75159	1077	1148	1.37447	−1.042	−78	−0.026
0.5772	0.74770	1067	1175	1.37356	−1.020	−74	−0.023
0.6167	0.74473	1060	1195	1.37281	−0.987	−71	−0.022
0.7267	0.73698	1042	1251	1.37073	−0.871	−60	−0.024
0.7533	0.73513	1037	1264	1.37025	−0.824	−56	−0.021
0.7824	0.73309	1033	1278	1.36964	−0.758	−52	−0.022
0.8325	0.72972	1025	1304	1.36871	−0.643	−44	−0.018
0.8608	0.72780	1021	1318	1.36811	−0.563	−39	−0.019
0.9496	0.72177	1006	1368	1.36638	−0.237	−17	−0.002
1.0000	0.71832	997	1400	1.36523	0.000	0	0.000
			TAME (1) + 1-Propanol (2)				
0.0000	0.79964	1207	858	1.38308	0.000	0	0.000
0.0485	0.79780	1203	866	1.38373	−0.094	−8	−0.004
0.0884	0.79627	1199	873	1.38420	−0.160	−13	−0.006
0.1546	0.79380	1193	885	1.38487	−0.257	−20	−0.010
0.2036	0.79196	1188	894	1.38525	−0.313	−23	−0.012
0.2523	0.79015	1184	903	1.38557	−0.358	−26	−0.014
0.2890	0.78884	1180	911	1.38579	−0.389	−27	−0.015
0.3413	0.78697	1175	921	1.38602	−0.421	−29	−0.016
0.3936	0.78518	1170	931	1.38623	−0.449	−29	−0.018
0.4451	0.78340	1165	941	1.38636	−0.460	−29	−0.018
0.4847	0.78208	1161	948	1.38646	−0.467	−29	−0.018
0.5461	0.78004	1156	960	1.38654	−0.461	−28	−0.018
0.5802	0.77892	1153	966	1.38657	−0.453	−27	−0.018
0.6175	0.77772	1149	973	1.38660	−0.440	−26	−0.016
0.6546	0.77655	1147	980	1.38660	−0.424	−25	−0.016
0.6858	0.77556	1144	986	1.38659	−0.405	−23	−0.015
0.7750	0.77278	1136	1003	1.38650	−0.331	−19	−0.011
0.8308	0.77110	1132	1012	1.38640	−0.275	−16	−0.010
0.9096	0.76873	1125	1028	1.38619	−0.170	−11	−0.008
0.9486	0.76747	1121	1036	1.38605	−0.095	−7	−0.004
1.0000	0.76592	1116	1048	1.38587	0.000	0	0.000

$$R = V_{\mathrm{M}}\frac{(n_{\mathrm{D}}^2 - 1)}{(n_{\mathrm{D}}^2 + 2)} \tag{2}$$

where V_{M} is molar volume and molar refraction changes of mixing, ΔR

$$\Delta R = R_{\mathrm{M}} - \sum_{i=1}^{n} x_i R_i \tag{3}$$

R_i being the molar refraction of pure component i, and R_{M} represents the molar refraction of the mixture. The isentropic compressibilities were calculated as

$$\kappa_{\mathrm{s}} = u^{-2}\rho^{-1} \tag{4}$$

and $\Delta\kappa_{\mathrm{s}}$ from

$$\Delta\kappa_{\mathrm{s}} = \kappa_{\mathrm{s}} - \sum_{i=1}^{n} \phi_i \kappa_{\mathrm{s}i} \tag{5}$$

where ϕ_i, the volume fraction of component i, is defined by

$$\phi_i = x_i V_i / \sum_j x_j V_j \tag{6}$$

Figure 1 shows the calculated excess molar volumes plotted against the mole fraction of ether for the three binary systems, MTBE + 1-propanol, DIPE + 1-propanol, and TAME + 1-propanol, and also shows several comparative values previously published by other authors.[12−15] As shown, the excess molar volumes for the three binary systems studied are negative over the entire composition range, with a minimum around $x_1 = 0.5$ and with the following negative trend DIPE > MTBE > TAME. This could indicate that interactions between different molecules are stronger than interactions between molecules in the pure liquids and that associative forces dominate the behavior of these solutions. The excess molar volumes determined in this work are in good agreement with those of Letcher et al.,[12] Mato et al.,[13] Amalendu et al.,[14] and So-Jin Park et al.,[15] reported previously.

The boiling temperature, T, the mole fractions of ether in the liquid, x_i, and vapor, y_i, phases, and activity coefficients, γ_i, for the VLE at 101.32 kPa of the three binary systems are reported in Table 4. Figures 2 to 4 show the VLE experimental data for the three binary systems. As we can see, only the binary system TAME + 1-propanol is azeotropic, with a minimum point at $T = 357.8$ K and $x_1 = 0.775$.

4. Data Treatment

Physical Properties. The V^{E}, ΔR, and $\Delta\kappa_{\mathrm{s}}$ data were correlated with the composition data by means of the Redlich−Kister polynomial,[21] which for binary mixtures is

$$\Delta M = x_i x_j \sum_n A_n (x_i - x_j)^n \tag{7}$$

where ΔM is V^{E} or ΔR and x_i is the mole fraction of component i in the mixture or ΔM is $\Delta\kappa_{\mathrm{s}}$ and x_i is the volume fraction of component i in the mixture; A_n is the polynomial coefficient; and n is the number of the polynomial coefficient.

Table 3. Polynomial Coefficients (A_n) and Standard Deviations (σ) Obtained for the Fits of Equation 7 to the V^{E}, $\Delta\kappa_{\mathrm{s}}$, and ΔR Composition Data for the Binary Systems (for $\Delta\kappa_{\mathrm{s}}$, System Compositions Were in Volume Fraction, ϕ_i)

property	A_0	A_1	A_2	A_3	σ
		MTBE (1) + 1-Propanol (2)			
V^{E}/cm^3·mol^{-1}	−2.6252	−0.0771	−0.1862	−	0.009
$\Delta\kappa_{\mathrm{s}}$/TPa^{-1}	−237.21	−58.201	−65.153	−63.030	0.6
ΔR/cm^3·mol^{-1}	−0.0316	−0.0448	0.0433	−	0.004
		DIPE (1) + 1-Propanol (2)			
V^{E}/cm^3·mol^{-1}	−4.2026	0.0691	−0.7007	−	0.02
$\Delta\kappa_{\mathrm{s}}$/TPa^{-1}	−316.58	−81.487	−61.241	−128.66	1.6
ΔR/cm^3·mol^{-1}	−0.0991	0.0124	−0.0425	−	0.004
		TAME (1) + 1-Propanol (2)			
V^{E}/cm^3·mol^{-1}	−1.8587	0.0044	−0.1974	−	0.002
$\Delta\kappa_{\mathrm{s}}$/TPa^{-1}	−114.93	−17.195	−36.096	−52.931	0.4
ΔR/cm^3·mol^{-1}	−0.0715	0.0038	−0.0042	−	0.001

Table 4. Isobaric Vapor−Liquid Equilibrium Data at 101.32 kPa for the Binary Systems

T_{b}/K	x_1	y_1	γ_1	γ_2
		MTBE (1) + 1-Propanol (2)		
369.54	0.006	0.028	1.688	1.005
368.12	0.017	0.087	1.725	1.007
366.67	0.029	0.147	1.806	1.005
362.26	0.071	0.308	1.727	1.010
359.74	0.094	0.382	1.705	1.023
354.78	0.155	0.532	1.631	1.017
352.31	0.188	0.593	1.595	1.021
350.49	0.218	0.634	1.540	1.032
348.77	0.250	0.685	1.519	0.997
348.26	0.253	0.679	1.508	1.043
346.93	0.282	0.718	1.481	1.010
345.14	0.319	0.752	1.440	1.015
343.81	0.352	0.775	1.396	1.027
342.19	0.387	0.805	1.380	1.017
340.94	0.425	0.819	1.323	1.063
340.18	0.428	0.826	1.356	1.065
338.76	0.487	0.853	1.281	1.072
337.55	0.542	0.865	1.208	1.172
336.56	0.577	0.877	1.185	1.208
335.99	0.592	0.885	1.185	1.204
334.67	0.662	0.898	1.118	1.379
333.75	0.704	0.913	1.099	1.398
333.05	0.741	0.921	1.074	1.512
332.34	0.771	0.930	1.066	1.571
331.67	0.805	0.939	1.053	1.641
331.00	0.840	0.947	1.037	1.820
330.46	0.867	0.955	1.031	1.906
329.81	0.904	0.966	1.020	2.084
329.13	0.940	0.973	1.010	2.675
328.68	0.966	0.981	1.005	3.397
		DIPE (1) + 1-Propanol (2)		
341.86	0.918	0.936	1.014	2.542
342.48	0.833	0.890	1.043	2.085
343.27	0.748	0.856	1.091	1.749
344.20	0.667	0.832	1.157	1.480
345.52	0.568	0.791	1.245	1.330
346.50	0.505	0.769	1.322	1.229
347.46	0.449	0.746	1.403	1.164
348.53	0.397	0.717	1.481	1.129
349.72	0.350	0.685	1.548	1.109
350.98	0.306	0.655	1.641	1.074
352.44	0.264	0.618	1.719	1.054
353.19	0.241	0.598	1.786	1.042
354.80	0.204	0.557	1.884	1.024
356.27	0.174	0.517	1.974	1.010
358.09	0.143	0.477	2.109	0.980
358.82	0.133	0.439	2.048	1.008
360.96	0.102	0.352	2.032	1.030
362.78	0.079	0.299	2.136	1.012
364.78	0.055	0.219	2.150	1.016
367.12	0.030	0.131	2.243	1.008
		TAME (1) + 1-Propanol (2)		
358.77	0.952	0.934	0.998	2.205
358.16	0.901	0.876	1.008	2.025
357.87	0.859	0.838	1.019	1.882
357.80	0.776	0.775	1.045	1.653
357.80	0.703	0.724	1.079	1.522
357.92	0.640	0.693	1.131	1.388
358.22	0.572	0.658	1.193	1.282
358.71	0.500	0.616	1.259	1.209
359.15	0.455	0.588	1.308	1.165
359.62	0.405	0.555	1.367	1.132
360.52	0.337	0.509	1.471	1.080
361.08	0.298	0.480	1.542	1.057
361.61	0.264	0.456	1.631	1.032
362.82	0.215	0.402	1.707	1.014
363.35	0.180	0.370	1.858	1.000
364.13	0.161	0.333	1.824	1.005
365.02	0.130	0.288	1.903	1.000
365.81	0.106	0.242	1.923	1.004
368.23	0.043	0.108	1.989	1.006

Table 5. Antoine Coefficients *A*, *B*, and *C* for Equation 10

compound	*A*	*B*	*C*
1-propanol[a]	6.87613	1441.705	−74.291
MTBE[b]	6.07034	1158.912	−43.200
DIPE[c]	5.97300	1143.070	−53.810
TAME[b]	6.06782	1256.258	−50.100

[a] From ref 16. [b] From ref 19. [c] From ref 23.

Equation 7 was fitted to the appropriate parameter−composition data for the binary systems by least-squares regression, applying Fisher's *F*-test to establish the number of coefficients. These coefficients and their mean standard deviations are listed in Table 3 for the three binary systems. The mean standard deviation was calculated by the usual equation

$$\sigma = \left[\frac{1}{n-1}(\Delta M_{\text{expt}} - \Delta M_{\text{calc}})^2\right]^{1/2} \qquad (8)$$

where *n* is the number of points.

VLE Data. At the equilibrium between the vapor and the liquid phases at pressure *P* and temperature *T*

$$y_i\phi_i P = x_i\gamma_i P_i^{\text{s}}\phi_i^{\text{s}} \exp\left[\frac{V_i^{\text{L}}(P - P_i^{\text{s}})}{RT}\right] \qquad (9)$$

where x_i and y_i are the mole fraction of component *i* in the liquid and vapor phases, respectively, γ_i is its activity coefficient; V_i^{L} is its molar volume in the liquid phase; ϕ_i and ϕ_i^{s} are its fugacity coefficient and fugacity coefficient at saturation, respectively; and P_i^{s} is its saturated vapor pressure. In this work, V_i^{L} is calculated from the Rackett equation, ϕ_i and ϕ_i^{s} from the second virial coefficient using the method of Hayden and O'Connell,[22] and P_i^{s} from the Antoine equation

$$\log(P_i^{\text{s}}/\text{kPa}) = A - \frac{B}{(T/\text{K}) + C} \qquad (10)$$

using coefficients *A*, *B*, and *C* reported in Table 5 as taken from the literature.[16,19,23]

The thermodynamic consistency of the binary systems was checked out by means of two tests: (1) the point-to-point Fredenslund's test,[6] for which the condition $y_i < 0.01$ is met for all data using a second-order polynomial of Legendre to fit the excess Gibbs energy (G^{E}/RT), and (2) the Wisniak's *L*−*W* test,[24,25] for which ($D < 3$) is found for all the data points.

The correlation of the experimental (*P*, *T*, *x*, *y*) results is performed with a computer program that runs a nonlinear regression method based on the maximum likelihood principle. The models used to calculate the liquid-phase activity coefficients are Wilson, NRTL, setting the nonrandomness parameter, α, to different values and selecting the value giving the best correlation, and UNIQUAC equations. The binary interaction parameters and root mean standard deviation in temperature, pressure, and liquid and vapor compositions are listed for each activity coefficient model in Table 6 for all the binary systems. Figures 2 to 4 compare the experimental with the correlated, using the model with the best results, VLE data in each binary system.

Table 7. Root Mean Square Deviations (*σ*) between the Experimental Equilibrium Temperatures (*T*) and Vapor-Phase Compositions (*y*) and Those Calculated by the ASOG, UNIFAC, and Modified UNIFAC Methods for the Indicated Binary Systems

models	$\sigma(T/\text{K})$	$\sigma(y_1)$	$\sigma(y_2)$
MTBE (1) + 1-Propanol (2)			
ASOG-KT	1.16	0.021	0.021
UNIFAC	0.92	0.019	0.019
UNIFAC−Dortmund	0.61	0.014	0.014
UNIFAC−Lyngby	0.89	0.021	0.021
DIPE (1) + 1-Propanol (2)			
ASOG-KT	0.34	0.013	0.013
UNIFAC	2.79	0.046	0.046
UNIFAC−Dortmund	0.66	0.016	0.016
UNIFAC−Lyngby	1.73	0.033	0.033
TAME (1) + 1-Propanol (2)			
ASOG-KT	0.92	0.023	0.023
UNIFAC	0.56	0.020	0.020
UNIFAC−Dortmund	0.61	0.024	0.024
UNIFAC−Lyngby	0.48	0.021	0.021

The VLE data were predicted using the following group-contribution methods for the calculation of the liquid-phase activity coefficients: the ASOG method,[4,5] the original UNIFAC method,[6,7] with the structural and group interaction parameters recommended by Gmehling et al.,[7] the UNIFAC−Dormund method,[8−10] and the UNIFAC−Lyngby method.[11] Table 7 lists the rms deviations between the experimental VLE data and the predicted values by each model. Figures 2 to 4 compare the experimental VLE data with the VLE data predicted using the model with the best results in each binary system.

5. Conclusions

Molar volumes, molar refractions, and isentropic compressibilities were evaluated at 298.15 K and atmospheric pressure for binary mixtures of MTBE + 1-propanol, DIPE + 1-propanol, and TAME + 1-propanol from measurements of their densities and refractive indices and the speeds of sound through them. The effects of mixing on these properties were determined.

For the three binary systems, the excess molar volumes are negative over the whole composition range. The system with MTBE leads to a minimum around −0.656 cm^3·mol^{-1}; the

Table 6. Correlation of VLE Data of the Indicated Binary Systems: Model Parameters (Wilson, NRTL, and UNIQUAC) and Root Mean Deviations (*σ*) in Equilibrium Temperature (*T*), Liquid- and Vapor-Phase Compositions (*x*, *y*), and Pressure (*P*)

model	parameters/J·mol^{-1}		$\sigma(T/\text{K})$	$\sigma(x)$	$\sigma(y)$	$\sigma(P/\text{kPa})$
MTBE (1) + 1-Propanol (2)						
Wilson	$\Delta\lambda_{12} = -1159.9$	$\Delta\lambda_{21} = 3954.5$	0.19	0.003	0.004	0.014
NRTL (α = 0.1)	$\Delta g_{12} = 7224.1$	$\Delta g_{21} = -3943.2$	0.20	0.003	0.004	0.016
UNIQUAC	$\Delta u_{12} = 6360.9$	$\Delta u_{21} = -2156.1$	0.21	0.003	0.004	0.016
DIPE (1) + 1-Propanol (2)						
Wilson	$\Delta\lambda_{12} = -672.74$	$\Delta\lambda_{21} = 4281.6$	0.13	0.003	0.003	0.009
NRTL (α = 0.1)	$\Delta g_{12} = 5228.7$	$\Delta g_{21} = -1776.5$	0.14	0.003	0.003	0.010
UNIQUAC	$\Delta u_{12} = 7008.7$	$\Delta u_{21} = -2002.9$	0.13	0.003	0.003	0.009
TAME (1) +1-Propanol (2)						
Wilson	$\Delta\lambda_{12} = -605.41$	$\Delta\lambda_{21} = 3545.1$	0.21	0.007	0.005	0.016
NRTL (α = 0.1)	$\Delta g_{12} = 3377.5$	$\Delta g_{21} = -630.01$	0.22	0.007	0.005	0.016
UNIQUAC	$\Delta u_{12} = 6309.3$	$\Delta u_{21} = -2024.3$	0.20	0.007	0.004	0.015

system with DIPE leads to a minimum around -1.04 $\text{cm}^3 \cdot \text{mol}^{-1}$; and the system with TAME leads to a minimum around -0.465 $\text{cm}^3 \cdot \text{mol}^{-1}$, all around 0.5 mol fraction of ether. The isentropic compressibility changes of mixing are negative over the whole composition range and for all the ethers, with a minimum around $x_1 = 0.52$ volume fraction and with the following negative trend DIPE > MTBE > TAME. The minimum varies from -29 TPa^{-1} for TAME to -83 TPa^{-1} for DIPE. Values of molar refraction changes of mixing are so small that it is difficult to establish any conclusion. In all the cases, the property changes of mixing are satisfactorily correlated with the composition by the Redlich−Kister polynomial.

Vapor−liquid equilibrium data at 101.32 kPa for the three binary systems were determined and found to be thermodynamically consistent. Correlation of experimental data using NRTL ($\alpha = 0.1$), Wilson, and UNIQUAC equations yielded similar results for the three equations, with a satisfactory deviation. The group contributions methods used for the prediction of the VLE of these systems do not show good agreement with the experimental results. Any of the used methods proportionate better results, the deviations in all cases being relatively high.

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