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Isobaric Vapor−Liquid Equilibria for Binary and Ternary Mixtures of Diisopropyl Ether, 2-Propyl Alcohol, and 3-Methyl-1-Butanol

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Consistent vapor−liquid equilibrium data for the binary and ternary systems diisopropyl ether (1) + 2-propyl alcohol (2) + 3-methyl-1-butanol (3) are reported at 101.3 kPa. The diisopropyl ether (1) + 3-methyl-1-butanol (3) system shows positive deviations from ideal behavior, and the 2-propyl alcohol (2) + 3-methyl-1-butanol (3) system exhibits slight deviations from ideal behavior. The activity coefficients and the boiling points were correlated with their compositions by the Wilson, NRTL, UNIQUAC, and Wisniak−Tamir equations. It is shown that these models allow a very good prediction of the phase equilibria of the ternary system using the pertinent parameters of the binary systems. 3-Methyl-1-butanol eliminates the diisopropyl ether (1) + 2-propyl alcohol (2) binary azeotrope. The change of phase equilibria behavior is significant; therefore, this solvent seems to be an effective agent for the separation of the azeotropic mixture by extractive distillation.

Introduction

Some ethers like methyl 1,1-dimethylethyl ether (MTBE), ethyl 1,1-dimethylethyl ether (ETBE), methyl 1,1-dimethylpropyl ether (TAME), and diisopropyl ether (DIPE), used in the last years like oxygenated compounds to reformulate gasoline to improve their octane rating, have been the object of numerous studies.

Aliphatic ethers are obtained normally by dehydration of the corresponding alcohol in the presence of an adequate catalyst. In many cases, the system formed by the ether and the homologous alcohol forms an azeotropic mixture; therefore, final purification of aliphatic ether in traditional technologies is a relative complex procedure. The separation can be improved by adding an agent that alters the relative volatility of the components (extractive distillation[1,2]) or by making a simple change in pressure, provided that the azeotropic composition is sensitive to pressure (pressure swing distillation[3]).

It is evident that the selection of a suitable solvent is very important to ensure an effective and economical design of extractive distillation. The thermodynamic analysis prediction and computer simulation of phase equilibria help to understand the separation process. However, when dealing with complex mixtures, experimental data are still needed for reliable design.

The study of the separation of the azeotropic system diisopropyl ether (1) and 2-propyl alcohol (2) by extractive distillation requires a previous selection of possible solvents. In general, qualitative indicators[4] show that the homologous series of ethers or alcohols looks promising. In a previous work,[5] we chose 2-ethoxyethanol as an entrainer for the extractive distillation to separate the azeotropic mixture. In the present paper, the behavior of 3-methyl-1-butanol (3) as a possible entrainer is investigated.

We measured isobaric vapor−liquid equilibria (VLE) data for the ternary system diisopropyl ether (1) + 2-propyl alcohol (2) + 3-methyl-1-butanol (3) and two constituent binary systems diisopropyl ether (1) + 3-methyl-1-butanol (3) and 2-propyl alcohol (2) + 3-methyl-1-butanol (3) at 101.3 kPa. In a previous work,[5] we reported VLE data for the binary system diisopropyl ether (1) + 2-propyl alcohol (2) at (30 and 101.3) kPa.

VLE data of binary and ternary systems were found to be thermodynamically consistent. Data reduction was carried out using the Wilson,[6] NRTL,[7] and UNIQUAC[8] equations to relate activity coefficients with compositions.

Table 1. Density *d*, Refractive Index n_D, and Normal Boiling Point T_b of Pure Components

component	d (298.15 K) kg·m^{-3} exptl	lit.[a]	n_D (298.15 K) exptl	lit.[a]	T^b (101.3 kPa) K exptl	lit.[b]
diisopropyl ether (1)	718.32	718.20	1.3652	1.3655	341.49	341.45
2-propyl alcohol (2)	782.69	781.26	1.3754	1.3752	355.35	355.41
3-methyl-1-butanol (3)	804.46	807.10	1.4047	1.4052	404.63	404.35

[a] Ref 9. [b] Ref 10.

Table 2. Experimental Vapor Pressure (P_i^o) of 3-Methyl-1-butanol

T/K	P/kPa	T/K	P/kPa
404.63	101.30	377.78	37.95
402.56	94.77	375.80	34.92
400.93	89.72	374.29	32.83
399.26	84.72	371.30	28.98
397.48	79.75	368.75	25.99
395.68	74.86	365.94	22.96
393.73	69.87	362.80	19.94
391.63	64.77	360.46	17.99
389.53	59.91	357.91	15.99
387.17	54.88	355.04	13.96
384.70	49.95	351.82	11.99
382.56	45.93	348.11	9.98
380.22	41.89		

Experimental Section

Chemicals. Diisopropyl ether (w = 99.0 %, analytical grade) was purchased from Fluka, and 2-propyl alcohol (w > 99.8 %,

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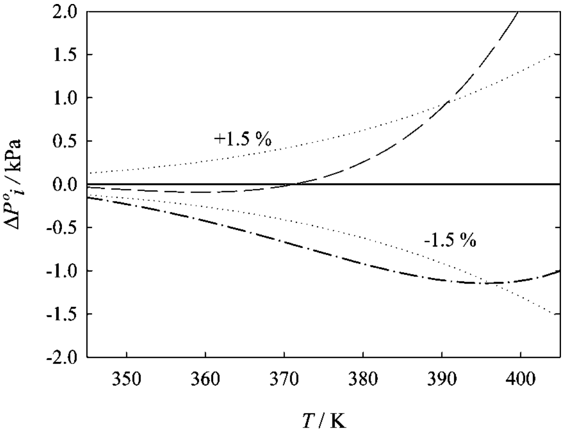

Figure 1. Differences, $\Delta P^o_i = P^o_{i,\mathrm{lit.}} - P^o_{i,\mathrm{exptl}}$, obtained for vapor pressures of 3-methyl-1-butanol (3) using the parameters given in Table 3. -•-•-, ref 11; - - - -, ref 10.

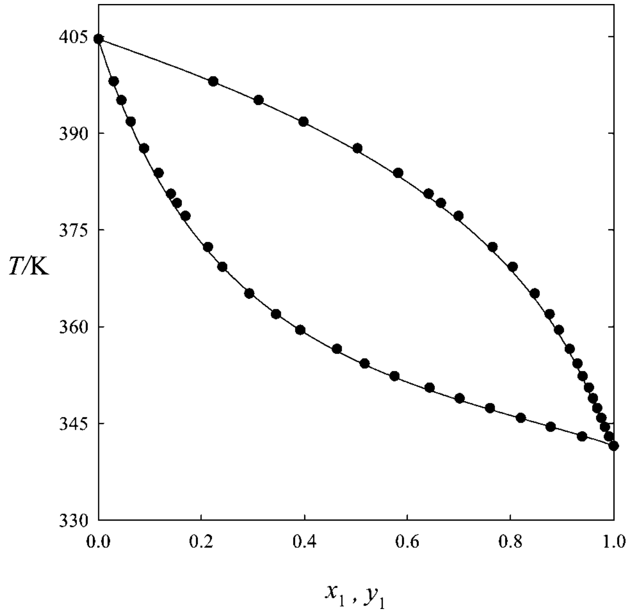

Figure 2. Experimental VLE data for the system diisopropyl ether (1) + 3-methyl-1-butanol (3) at 101.3 kPa: ●, experimental data. Smoothed data using the Wilson model with the parameters given in Table 7.

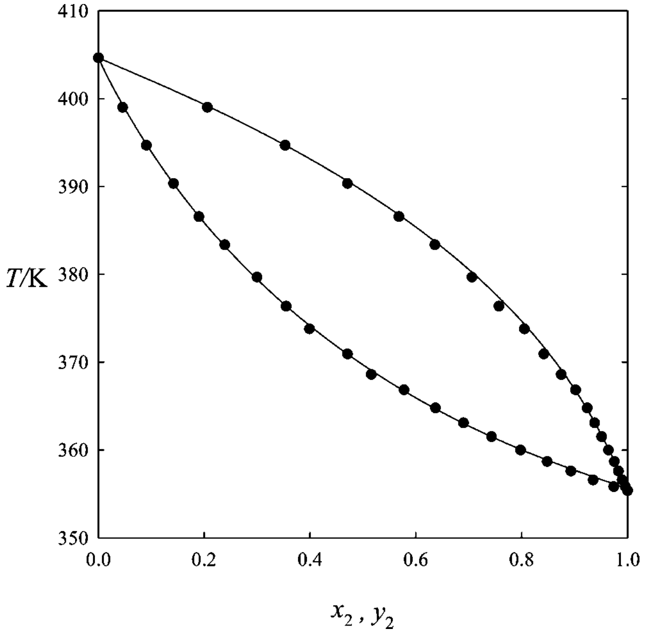

Figure 3. Experimental VLE data for the system 2-propyl alcohol (2) + 3-methyl-1-butanol (3) at 101.3 kPa: ●, experimental data. Smoothed data using the Wilson model with the parameters given in Table 7.

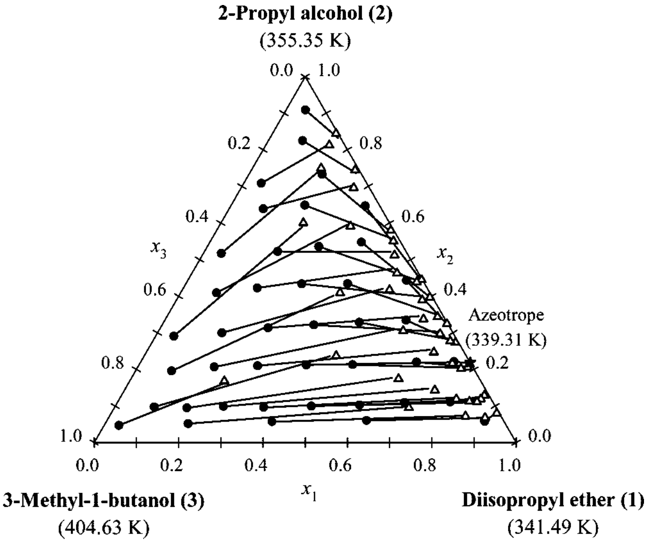

Figure 4. Diagram of VLE for the ternary system diisopropyl ether (1) + 2-propyl alcohol (2) + 3-methyl-1-butanol (3) at 101.3 kPa: ●, liquid-phase mole fraction; Δ, vapor-phase mole fraction; ★, azeotrope.[5] Smoothed lines calculated with the Wilson equation with the parameters given in Table 7.

analytical grade) and 3-methyl-1-butanol (w > 99.0 %, anhydrous grade) were supplied from Aldrich Ltd. The reagents were used without further purification after chromatography failed to show any significant impurities. The water content, determined using a Karl Fischer volumetric automatic titrator (Metrohm, 701 KF Titrino), was small in all chemicals (w < 0.05 %). Before measurements, the liquids were degassed and subsequently dried over molecular sieves (Union Carbide, type 4 Å, 1/16 in. pellets). The refractive indexes of the pure components were measured at 298.15 K using an Abbe refractometer Atago 3T, and the densities were measured at 298.15 K using an Anton Paar DMA 58 densimeter. Temperature was controlled to ± 0.01 K with a thermostatted bath. The uncertainties in refractive index and density measurements are ± 0.0002 and ± 0.01 kg·m^{-3}, respectively. The experimental values of these properties and the boiling points are given in Table 1 together with those given in the literature. Appropriate precautions were taken when handling the reagents to avoid hydration.

Apparatus and Procedure. The equilibrium vessel used in the measurements (Labodest VLE 602/D) was an all-glass dynamic recirculating still equipped with a Cottrell circulation pump, manufactured by Fischer Labor and Verfahrenstechnik (Germany). The apparatus is capable of handling pressures from (0.25 to 130) kPa and temperatures up to 523.15 K. The Cottrell pump ensures that both liquid and vapor phases are in intimate contact during boiling and also in contact with the temperature-sensing element. The equilibrium temperature was measured with a digital Hart Scientific thermometer model 1502A and a Pt 100 probe Hart Scientific model 5622 calibrated at the ENAC-Spanish Instituto Nacional de Técnica Aeroespacial. The uncertainty is estimated to be ± 0.01 K. The temperature probe was checked against the ice and steam points of distilled water. A Fisher M101 pressure control system was used to measure and control the pressure and the heating power. The measured pressure in the still was (101.3 ± 0.1) kPa. The manometer was calibrated using the vapor pressure of ultrapure water.

Table 3. Vapor Pressure Parameters

compound	eq[a]	A_i	B_i	C_i	D_i	E_i	ref
diisopropyl ether (1)	2	41.631	−4668.70	−2.8551	$6.3693 \cdot 10^{-4}$	1	[b]
2-propyl alcohol (2)	2	92.935	−8177.10	−10.031	$3.9988 \cdot 10^{-6}$	2	[b]
3-methyl-1-butanol (3)	1	14.069	2694.36	−119.489			this work[c]
	2	109.75	−10394.00	−12.083	$6.2013 \cdot 10^{-18}$	6	[b]
	3	7.3339	1353.30	172.190			[d]

[a] Vapor pressure equations: (1) $\ln P°/\text{kPa} = A - B/[(T/\text{K} + C]$; (2) $\ln P°/\text{Pa} = A + B/(T/\text{K}) + C \ln T/\text{K} + D\,(T/\text{K})^E$; (3) $\log P°/\text{mmHg} = A - B/[(T/°\text{C}) + C]$. [b] Parameters taken from Daubert and Danner.[10] [c] Antoine's parameters were calculated from the experimental data in Table 2. [d] Parameters taken from the Dortmund Data Bank.[11]

Table 4. Experimental Vapor−Liquid Equilibrium Data for the Binary System Diisopropyl Ether (1) + 3-Methyl-1-butanol (3) at 101.3 kPa

T/K	x_1	y_1	γ_1	γ_3
404.63	0.000	0.000		1.000
398.06	0.030	0.223	1.599	0.999
395.14	0.045	0.311	1.591	0.996
391.80	0.063	0.398	1.577	1.001
387.66	0.089	0.503	1.546	0.990
383.84	0.117	0.582	1.504	0.993
380.61	0.141	0.641	1.487	0.994
379.19	0.153	0.665	1.478	0.996
377.18	0.169	0.699	1.478	0.989
372.36	0.213	0.765	1.454	0.996
369.30	0.241	0.804	1.468	0.981
365.15	0.293	0.847	1.429	0.985
361.96	0.345	0.876	1.370	0.998
359.49	0.392	0.894	1.322	1.027
356.56	0.463	0.915	1.248	1.070
354.30	0.517	0.930	1.215	1.095
352.33	0.575	0.940	1.169	1.180
350.56	0.643	0.952	1.117	1.238
348.90	0.701	0.960	1.088	1.329
347.37	0.760	0.968	1.061	1.415
345.86	0.820	0.976	1.039	1.549
344.44	0.878	0.983	1.022	1.747
342.96	0.939	0.991	1.011	1.986
341.49	1.000	1.000	1.000	

Table 5. Experimental Vapor−Liquid Equilibrium Data for the Binary System 2-Propyl Alcohol (2) + 3-Methyl-1-butanol (3) at 101.3 kPa

T/K	x_2	y_2	γ_2	γ_3
404.63	0.000	0.000		1.000
399.01	0.046	0.206	1.023	1.004
394.68	0.091	0.353	1.008	0.999
390.33	0.142	0.471	0.985	1.013
386.55	0.190	0.568	1.000	1.009
383.34	0.239	0.636	0.987	1.023
379.68	0.300	0.706	0.985	1.037
376.37	0.355	0.757	0.998	1.063
373.78	0.399	0.805	1.032	1.019
370.92	0.471	0.842	1.011	1.058
368.58	0.516	0.875	1.042	1.012
366.84	0.578	0.902	1.021	0.981
364.78	0.637	0.924	1.024	0.970
363.08	0.690	0.938	1.022	1.000
361.52	0.743	0.951	1.020	1.024
359.99	0.798	0.964	1.020	1.027
358.68	0.848	0.975	1.021	1.008
357.58	0.893	0.983	1.020	1.026
356.58	0.935	0.990	1.020	1.042
355.82	0.974	0.996	1.015	1.081
355.35	1.000	1.000	1.000	

In each experiment, the pressure was fixed, and the heating and stirring system of the liquid mixture was turned on. The still was operated at constant pressure until equilibrium was reached. Equilibrium conditions were assumed when constant temperature and pressure were obtained for 45 min or longer. Then, samples of liquid and condensate were taken for analysis. The sampling was carried out with special syringes that allowed withdrawal of small volume samples.

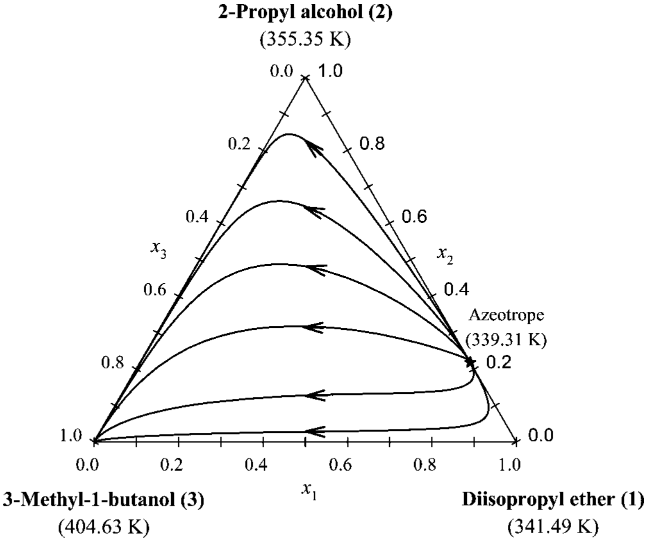

Figure 5. Residual curve map for the ternary diisopropyl ether (1) + 2-propyl alcohol (2) + 3-methyl-1-butanol (3). Continuous lines simulated by AspenSplit using the Wilson model with the parameters given in Table 7: ★, azeotrope.[5]

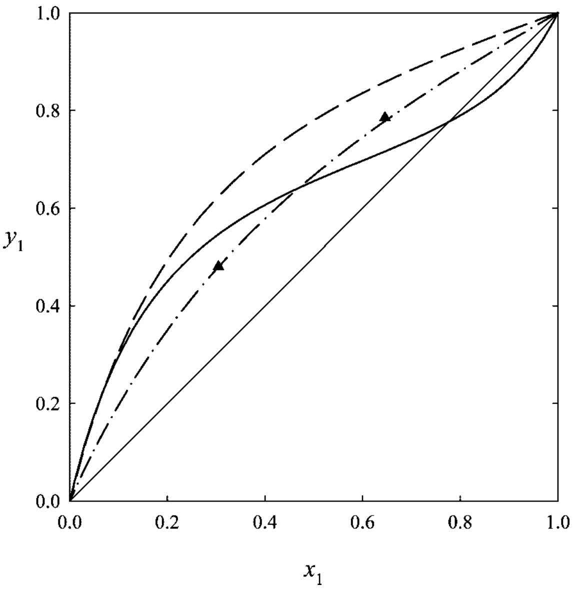

Figure 6. VLE data plotted on a solvent-free basis for the system diisopropyl ether (1) + 2-propyl alcohol (2) + solvent (3) at 101.3 kPa. Continuous line[5] for $x_3 = 0.00$. Dashed line calculated using the Wilson equation with the parameters given in Table 7 for $x_3 = 0.70$; - - - -, with 2-ethoxyethanol;[5] and -•-•-, with 3-methyl-1-butanol (in this work). Experimental points for $x_3 \approx 0.70$: ▲, with 3-methyl-1-butanol.

Analysis. The compositions of the sampled liquid and condensed vapor phase were determined using a CE Instruments GC 8000 Top gas chromatograph (GC), after calibration with gravimetrically prepared standard solutions. A flame ionization detector was used together with a 30 m, 0.454 mm i.d., capillary

Table 6. Consistency Test for the Binary Systems Considered in VLE Measurements

system $i + j$	A_1[a]	A_2[a]	A_3[a]	AADy_i[b]	AADP[c]/kPa
diisopropyl ether (1) + 3-methyl-1-butanol (3)	0.6288	0.1856	−0.0067	0.0027	0.57
2-propyl alcohol (2) + 3-methyl-1-butanol (3)	0.0604	0.0870	0.0582	0.0035	0.59

[a] Legendre polynomial parameters. [b] Average absolute deviation in vapor-phase composition. [c] Average absolute deviation in pressure.

Table 7. Parameters and Deviations between Experimental and Calculated Values for Different G^E Models for the System Diisopropyl Ether (1) + 2-Propyl Alcohol (2) + 3-Methyl-1-butanol (3)

		A_{ij}	A_{ji}		bubble point		
model	system $i + j$	J·mol^{-1}	J·mol^{-1}	α_{ij}	AADT[a]	AADy_1[b]	AADy_2[b]
Wilson[c]	1 + 2[d]	−476.15	4397.34		0.07	0.0064	
	1 + 3	−1246.33	3879.71		0.22	0.0032	
	2 + 3	−1310.44	3210.19		0.15		0.0040
	1 + 2 + 3[e]				0.26	0.0078	0.0045
NRTL	1 + 2[d]	2733.36	898.07	0.30	0.11	0.0066	
	1 + 3	3718.44	−1093.74	0.30	0.20	0.0031	
	2 + 3	4875.06	−3199.83	0.30	0.17		0.0046
	1 + 2 + 3[e]				0.25	0.0060	0.0034
UNIQUAC[f]	1 + 2[d]	2561.80	−877.48		0.11	0.0071	
	1 + 3	2243.70	−1233.68		0.22	0.0033	
	2 + 3	3278.04	−2060.85		0.10		0.0037
	1 + 2 + 3[e]				0.49	0.0121	0.0072

[a] Average absolute deviation in temperature. [b] Average absolute deviation in vapor-phase composition. [c] Molar liquid volumes of pure components from ref 13. [d] Ref 5. [e] Ternary prediction from binary parameters. [f] Volume and surface parameters from ref 13.

Table 8. Coefficients in Correlation of Boiling Points, Equations 4 and 5, Average Deviation, and Root Mean Square Deviation in Temperature

system $i + j$	C_0	C_1	C_2	C_3	AADT[a]/K	rmsd[b]/K
1 + 2[c]	−31.45	10.04	−18.11	1.53	0.07	0.06
1 + 3	−72.72	54.05	−24.238	3.169	0.15	0.09
2 + 3	−40.96	18.56	−9.88	1.642	0.11	0.08

system $i + j + k$	A	B	C	D	AADT[a]/K	rmsd[b]/K
1 + 2 + 3	−11.22	−12.37	2.722	−33.55	0.19	0.04

[a] Average absolute deviation in temperature. [b] Root mean square deviation: $1/N\{\Sigma(T_{\text{exptl}} - T_{\text{calcd}})^2\}^{0.5}$. [c] Ref 5.

column (DB-MTBE, J & Scientific). The GC response peaks were treated with Chrom-Card for Windows. Column, injector, and detector temperatures were (423, 473, and 498) K respectively, for all systems. Very good peak separation was achieved under these conditions, and calibration analyses were carried out to convert the peak area ratio to the mass composition of the sample. At least two analyses were made of each liquid and vapor composition. The standard deviation in the mole fraction was usually less than 0.001.

Results and Discussion

Pure Component Vapor Pressures. The pure component vapor pressure for 3-methyl-1-butanol (3), P_i°, was determined experimentally as a function of the temperature using the same equipment as that used to obtain the VLE data. The pertinent results appear in Table 2. The measured vapor pressures were correlated using the Antoine equation

$$\ln P_i^{\circ}/\text{kPa} = A_i - \frac{B_i}{T/\text{K} + C_i} \qquad (1)$$

whose parameters A_i, B_i, and C_i are reported in Table 3 together with some literature values. The deviations, $\Delta P_i^{\circ} = P_{i,\text{lit.}}^{\circ} - P_{i,\text{exptl}}^{\circ}$, calculated by means of the Antoine equation using the constant values of Table 3, have been graphically represented in Figure 1.

The pure component vapor pressures for diisopropyl ether (1) and 2-propyl alcohol (2) were taken from Daubert and Danner.[10]

Table 9. Experimental Vapor−Liquid Equilibrium Data for Diisopropyl Ether (1) + 2-Propyl Alcohol (2) + 3-Methyl-1-butanol (3) at 101.3 kPa

T/K	x_1	x_2	y_1	y_2	γ_1	γ_2	γ_3
340.30	0.742	0.221	0.783	0.214	1.101	1.827	1.418
341.43	0.518	0.443	0.674	0.324	1.307	1.314	0.984
341.45	0.896	0.057	0.914	0.080	1.024	2.505	2.027
342.14	0.572	0.334	0.720	0.273	1.237	1.421	1.136
342.36	0.788	0.111	0.860	0.129	1.065	2.004	1.579
342.67	0.654	0.220	0.782	0.205	1.155	1.592	1.404
343.72	0.319	0.646	0.553	0.444	1.622	1.120	0.812
344.25	0.359	0.548	0.597	0.396	1.527	1.152	0.867
345.30	0.680	0.109	0.857	0.119	1.119	1.656	1.385
345.54	0.464	0.328	0.705	0.277	1.341	1.271	1.022
345.83	0.384	0.434	0.642	0.343	1.464	1.177	0.938
347.21	0.506	0.212	0.768	0.202	1.271	1.335	1.157
348.46	0.264	0.536	0.545	0.438	1.661	1.091	0.838
348.47	0.577	0.103	0.852	0.111	1.188	1.436	1.190
348.54	0.173	0.733	0.413	0.579	1.911	1.052	0.830
348.92	0.615	0.060	0.892	0.068	1.151	1.476	1.228
349.66	0.360	0.321	0.671	0.297	1.449	1.172	0.955
350.46	0.275	0.434	0.583	0.389	1.604	1.103	0.882
350.46	0.175	0.649	0.434	0.550	1.883	1.043	0.821
351.25	0.396	0.212	0.741	0.215	1.382	1.209	0.987
352.41	0.465	0.099	0.833	0.112	1.279	1.282	1.048
352.53	0.081	0.825	0.246	0.744	2.152	1.019	0.861
353.40	0.046	0.909	0.151	0.844	2.283	1.014	0.875
353.90	0.173	0.522	0.456	0.512	1.794	1.049	0.823
355.04	0.255	0.313	0.612	0.337	1.581	1.102	0.864
356.73	0.175	0.422	0.486	0.462	1.743	1.048	0.856
356.94	0.282	0.209	0.681	0.247	1.505	1.119	0.943
357.30	0.393	0.057	0.844	0.072	1.327	1.176	1.007
357.45	0.081	0.638	0.267	0.696	2.022	1.015	0.860
357.58	0.354	0.096	0.799	0.119	1.383	1.148	0.966
359.03	0.041	0.708	0.151	0.813	2.136	1.005	0.884
362.80	0.153	0.300	0.492	0.417	1.697	1.056	0.846
363.47	0.257	0.098	0.736	0.143	1.482	1.075	0.926
364.16	0.181	0.206	0.580	0.305	1.623	1.067	0.896
364.79	0.085	0.409	0.312	0.591	1.823	1.020	0.887
365.32	0.043	0.517	0.163	0.749	1.865	1.003	0.898
370.92	0.173	0.095	0.634	0.174	1.550	1.039	0.927
371.27	0.197	0.052	0.698	0.095	1.482	1.027	0.961
374.69	0.086	0.195	0.378	0.409	1.685	1.038	0.895
374.96	0.044	0.290	0.196	0.600	1.696	1.015	0.916
380.08	0.094	0.097	0.455	0.237	1.612	1.008	0.926
393.35	0.036	0.046	0.225	0.168	1.511	0.980	0.974

Binary Systems. The temperature T and the liquid-phase x_i and vapor-phase y_i mole fractions at 101.3 kPa for the systems diisopropyl ether (1) + 3-methyl-1-butanol (3) and 2-propyl alcohol (2) + 3-methyl-1-butanol (3) are reported in Tables 4 and 5 and plotted in Figures 2 and 3. The activity coefficients γ_i for these systems were calculated from the following equation

$$\gamma_i = \frac{y_i P}{x_i P_i^{\mathrm{o}}} \tag{2}$$

where y_i is the mole fraction of component i in the vapor phase; x_i is the mole fraction of component i in the liquid phase; γ_i is the activity coefficient of the component i in the liquid phase; P is the total pressure; and P_i^{o} is the saturation vapor pressure for the pure liquid i. In eq 2, the vapor phase is assumed to be an ideal gas, and the pressure dependence of the liquid phase fugacity is neglected. To calculate activity coefficients, eq 2 was selected because the low pressure used in the present experimental data makes these simplifications reasonable.

The activity coefficients presented in Tables 4 and 5 indicate that the diisopropyl ether (1) + 3-methyl-1-butanol (3) system shows positive deviations from ideal behavior and the 2-propyl alcohol (2) + 3-methyl-1-butanol (3) system exhibits slight deviation from ideal behavior and no additional azeotropes are present.

The test of Fredenslund[12] was applied to the binary experimental data to test thermodynamic consistency. In Table 6, the parameters of the Legendre polynomial together with the pertinent statistics required by the Fredenslund test are given. The residuals for both systems at 101.3 kPa show a reasonable random distribution.

The activity coefficients were correlated with the Wilson, NRTL, and UNIQUAC equations. The parameters of these equations were obtained by minimizing the following objective function (OF)

$$\mathrm{OF} = \sum_{i=1}^{N} \left(\left| \frac{T_i^{\mathrm{exptl}} - T_i^{\mathrm{calcd}}}{T_i^{\mathrm{exptl}}} \right| + |y_i^{\mathrm{exptl}} - y_i^{\mathrm{calcd}}| \right) \tag{3}$$

and are reported in Table 7, together with the pertinent statistics of each VLE correlation.

The boiling point temperatures of each binary system at 101.3 kPa were well correlated with mole fractions by the equation proposed by Wisniak and Tamir[14]

$$T = x_i T_i^0 + x_j T_j^0 + x_i x_j \sum_{k=0}^{m} C_k (x_i - x_j)^k \tag{4}$$

In this equation T_i^0 is the boiling point of the pure components i, and m is the number of terms used in the series expansion of $(x_i - x_j)$. The various constants of eq 4 are reported in Table 8, with information indicating the goodness of the correlation fit.

Ternary System. VLE data for the ternary system diisopropyl ether (1) + 2-propyl alcohol (2) + 3-methyl-1-butanol (3) are reported in Table 9. Figure 4 shows the plot of the vapor-phase mole fraction calculated with the Wilson model with the parameters given in Table 7 against the experimental vapor-phase composition. The ternary data were found to be thermodynamically consistent by the Wisniak and Tamir[11] modification of the McDermott−Ellis[15] test ($D < D_{\max}$ at all data points) and the Wisniak $L-W$ test[16] ($0.92 < L_i/W_i < 1.10$).

VLE data for the ternary system have been predicted using the Wilson, NRTL, and UNIQUAC equations with the binary interaction parameters obtained from the regression of binary data. Table 7 lists the mean absolute deviations between experimental and calculated temperature and vapor-phase mole fractions. From these results, it can be concluded that the binary contributions allow a good prediction of the ternary system, representing the data successfully. Thus, the models can be used to calculate boiling points from liquid-phase compositions at the system pressure.

The boiling points of the ternary system were correlated by the equation proposed by Wisniak and Tamir.[17]

$$T = \sum_{i=1}^{3} x_i T_i^0 + \sum_{j>i=1}^{3} \left[x_i x_j \sum_{k=0}^{m} C_k (x_i - x_j)^k \right] + x_1 x_2 x_3 [A + B(x_1 - x_2) + C(x_1 - x_3) + D(x_2 - x_3)] \tag{5}$$

where T_i^0 is the boiling point of the pure components i; m is the number of terms considered in the series expansion of $(x_i - x_j)$; and C_k is the binary constant, whereas A, B, C, and D are ternary constants. The constants of eq 5 are reported in Table 8, with information indicating the quality of the correlation.

Solvent Effects. Several methods are available for determining whether the lower- or higher-boiling pure component will be recovered in the distillate. A very simple method is to examine the shape and inflection of the residue curves as they approach the pure solvent vertex.[18] In Figure 5, residue curves simulated by AspenSplit v2006 Aspentech Ltd.[19] using the Wilson model with the experimental parameters (Table 7) are shown. As can be seen in this figure, all residue curves approaching the 3-methyl-1-butanol (solvent) vertex are inflected toward the 3-methyl-1-butanol + 2-propyl alcohol face, with the result that 2-propyl alcohol + 3-methyl-1-butanol will be recovered in the bottom and diisopropyl ether in the distillate, as can be expected in view of the activity coefficients of the binary systems (Tables 4 and 5). Another useful alternative is the study of the solvent influence on the phase behavior of the azeotropic mixture, on a solvent-free basis. As can be observed in Figure 6, 3-methyl-1-butanol and 2-ethoxyethanol (studied in a previous paper[5]) eliminate the diisopropyl ether-2-propyl alcohol azeotrope, allowing the separation of pure diisopropyl ether from 2-propyl alcohol by rectification when they are employed as solvents in extractive distillation. 3-Methyl-1-butanol and 2-ethoxyethanol enhance the relative volatility of diisopropyl ether to 2-propyl alcohol, but 2-ethoxyethanol brings about a larger enhancement of the relative volatility ($\alpha_{12}^S = 3.48$ with 2-ethoxyethanol and $\alpha_{12}^S = 2.00$ with 3-methyl-1-butanol; αij^S is relative volatility in the presence of the solvent).

Conclusions

Consistent VLE data at 101.3 kPa have been determined for the binary systems diisopropyl ether (1) + 3-methyl-1-butanol (3) and 2-propyl alcohol (2) + 3-methyl-1-butanol (3) and the ternary system diisopropyl ether (1) + 2-propyl alcohol (2) + 3-methyl-1-butanol (3). The Wilson, NRTL, and UNIQUAC models were capable of correlating all the binary systems and yielded reasonable predictions for the ternary system.

The experimental results revealed that the presence of 3-methyl-1-butanol enhances the relative volatility of diisopropyl ether (1) to 2-propyl alcohol (2). The relative volatility on a solvent-free basis ($\alpha_{12}^S = 2.00$) confirms that 3-methyl-1-butanol (3) breaks the azeotropic mixture, although 2-ethoxyethanol[5] is the most promising entrainer studied, for the time being.

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