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Isobaric Vapor−Liquid Equilibria for Binary and Ternary Mixtures of Dipropyl Ether, 1-Propyl Alcohol, and Butyl Propionate

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Consistent vapor−liquid equilibrium (VLE) data at 101.3 kPa have been determined for the ternary system dipropyl ether + 1-propyl alcohol + butyl propionate and two constituent binary systems: dipropyl ether + butyl propionate and 1-propyl alcohol + butyl propionate. The dipropyl ether + butyl propionate system exhibits ideal behavior, and the 1-propyl alcohol + butyl propionate system shows positive deviations from Raoult's law. No additional azeotropes are present. The activity coefficients of the solutions were correlated with its composition by the Wilson, NRTL, and UNIQUAC models. The ternary system is well-predicted from binary interaction parameters. Butyl propionate breaks the dipropyl ether/1-propyl alcohol binary azeotrope. However, the change of phase equilibria behavior is small; therefore, this solvent is not such an effective agent to this azeotrope mixture separation. In fact, the mean relative volatility on a solvent-free basis is 0.82 (close to unity).

Introduction

Ethers and alcohols have been traditionally used as blending agents in the formulation of unleaded gasolines for enhancing the octane number. Aliphatic ethers, used extensively as solvents, are obtained normally by dehydration of the corresponding alcohol. In many cases, the system formed by the ether and the homologous alcohol form an azeotropic mixture. This behavior is shown for the binary mixture dipropyl ether (1) and 1-propyl alcohol (2). Its separation by simple distillation is impossible. Extractive distillation[1] would be an attractive method for carrying out the separation of dipropyl ether from 1-propyl alcohol if adequate entrainers could be found.

As a part of a continuing program of work, we have identified a selection of possible solvents by means of Scheibels criterion,[2] which suggests selection among compounds of the same homologous series, and moreover by means of the calculation of the separation factor. In a previous work,[3] we have chosen 1-pentanol as an entrainer for the extractive distillation to separate the azeotropic mixture. It was verified that this solvent was an excellent solvent for the rupture of the dipropyl ether (1)/1-propyl alcohol (2) azeotropic mixture. In the present paper, the behavior of butyl propionate (3) as a possible entrainer is investigated, since by means of DISTIL v5.0 Hyprotech Ltd.[4] software it could verified that butyl propionate (3) could be a good solvent, although it reversed the relative volatility of dipropyl ether (1) to 1-propyl alcohol (2) (relative volatility on a solvent-free basis,[3] $\alpha_{12}{}^{S} = 0.42$).

Butyl propionate (3) has been recognized as a green solvent for its low vapor pressure, good mixing capability, high electrical resistance, and acceptable odor.[5] To increase the knowledge of the phase behavior of the original mixture, dipropyl ether (1) + 1-propyl alcohol (2) with butyl propionate (3) as entrainer, we measured isobaric VLE data for the ternary system dipropyl ether (1) + 1-propyl alcohol (2) + butyl propionate (3) and two constituent binary systems dipropyl ether (1) + butyl propionate (3) and 1-propyl alcohol (2) + butyl propionate (3) at 101.3 kPa. In a recent literature review, only isobaric VLE for 1-propyl alcohol (2) + butyl propionate (3) system at atmospheric pressure has been found.[6] In a previous work,[7] we reported VLE data for the binary system dipropyl ether (1) + 1-propyl alcohol (2) at two pressures (20 and 101.3 kPa).

Experimental Section

Chemicals. 1-Propyl alcohol (> 99.5 mass %, analytical grade) was purchased from Panreac, dipropyl ether (90 mass %, for synthesis) was supplied by Merck, and butyl propionate (> 99.0+ mass %, puriss. p.a. (GC)) was purchased from Aldrich Ltd. Dipropyl ether was purified to 99.5 mass % by batch distillation in a Fischer Spaltrohr column HMS-500, controlled by a Fischer system D301-C. The other 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 (< 0.05 mass %). 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 thermostated bath. The accuracy in refractive index and density measurements are ± 0.0002 and ± 0.01 $\text{kg}\cdot\text{m}^{-3}$, 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 in order 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 und Verfahrenstechnik (Germany). The apparatus is capable of handling pressures from (0.25 to 400) kPa, and temperatures up to 523.15 K. The Cottrell

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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}		n_D (298.15 K)		T_b (101.3 kPa)/K	
	exptl	lit[a]	exptl	lit[a]	exptl	lit[b]
dipropyl ether (1)	741.81	742.00	1.3784	1.3780	363.16	362.79
1-propyl alcohol (2)	799.62	799.51	1.3836	1.3837	369.75	370.35
butyl propionate (3)	870.88	871.40	1.3992	1.4000	418.69	419.75

[a] Ref 8. [b] Ref 9.

Table 2. Vapor Pressure Parameters

compound	A	B	C	D	E	ref
dipropyl ether (1)	106.260	−7557.00	−12.792	1.123110^{-5}	2	*a*
1-propyl alcohol (2)	88.134	−8498.60	−9.077	8.330310^{-18}	6	*a*
butyl propionate (3)	14.440	3467.69	−65.63			*b*

[a] Ref 9, $\ln(P_i^\circ/\mathrm{Pa}) = A + B/(T/\mathrm{K}) + C \ln(T/\mathrm{K}) + D\,(T/\mathrm{K})^E$. [b] Ref 11, $\ln(P_i^\circ/\mathrm{kPa}) = A - B/[(T/\mathrm{K}) + C]$.

Table 3. Experimental Vapor−Liquid Equilibrium Data for the Binary System Dipropyl Ether (1) + Butyl Propionate (3) at 101.3 kPa

T/K	x_1	y_1	γ_1	γ_3	T/K	x_1	y_1	γ_1	γ_3
418.69	0.000	0.000		1.000	382.40	0.470	0.837	1.031	0.947
414.60	0.032	0.132	1.085	1.006	379.61	0.524	0.865	1.030	0.963
411.00	0.067	0.252	1.073	0.998	377.39	0.577	0.889	1.022	0.964
407.34	0.104	0.362	1.080	0.987	375.10	0.635	0.909	1.012	0.994
403.83	0.144	0.460	1.077	0.971	372.70	0.695	0.930	1.012	0.999
400.63	0.189	0.545	1.049	0.953	370.75	0.752	0.946	1.006	1.019
397.01	0.229	0.610	1.059	0.962	368.77	0.808	0.961	1.008	1.024
394.02	0.270	0.666	1.056	0.957	366.83	0.871	0.976	1.005	1.009
391.00	0.313	0.715	1.056	0.957	365.00	0.935	0.988	1.001	1.075
387.75	0.372	0.766	1.035	0.957	363.16	1.000	1.000	1.000	
384.91	0.419	0.805	1.040	0.949					

Table 4. Experimental Vapor−Liquid Equilibrium Data for the Binary System 1-Propyl Alcohol (2) + Butyl Propionate (3) at 101.3 kPa

T/K	x_2	y_2	γ_2	γ_3	T/K	x_2	y_2	γ_2	γ_3
418.69	0.000	0.000		1.000	377.30	0.579	0.868	1.161	1.155
410.78	0.046	0.253	1.447	0.981	376.09	0.633	0.885	1.131	1.206
404.73	0.093	0.409	1.382	0.976	375.08	0.684	0.899	1.104	1.276
397.40	0.158	0.559	1.393	0.984	374.20	0.740	0.915	1.072	1.347
393.89	0.206	0.636	1.359	0.963	373.32	0.789	0.929	1.055	1.432
390.16	0.257	0.690	1.335	0.989	372.55	0.835	0.942	1.040	1.539
387.13	0.309	0.740	1.317	0.987	371.83	0.881	0.957	1.029	1.624
384.40	0.361	0.779	1.302	0.995	371.27	0.924	0.971	1.016	1.751
382.20	0.415	0.808	1.268	1.018	370.65	0.966	0.987	1.011	1.796
380.32	0.473	0.831	1.222	1.062	369.75	1.000	1.000	1.000	
378.69	0.525	0.851	1.195	1.100					

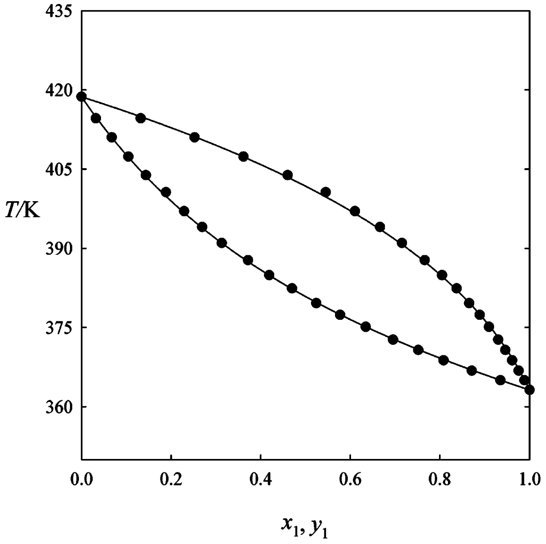

Figure 1. Experimental VLE data for the system dipropyl ether (1) + butyl propionate (3) at 101.3 kPa. ●, experimental data; —, smoothed data using the UNIQUAC model with the parameters given in Table 6.

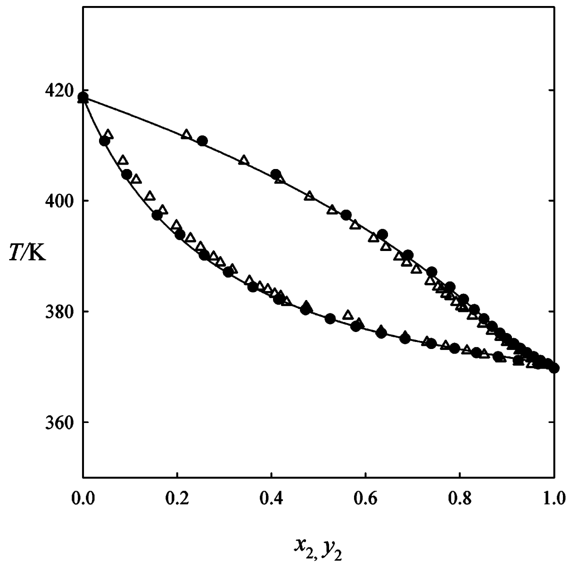

Figure 2. Experimental VLE data for the system 1-propyl alcohol (2) + butyl propionate (3) at 101.3 kPa. ●, experimental data; △, ref 6; —, smoothed data using the UNIQUAC model with the parameters given in Table 6.

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 accuracy 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.

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 30 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.

Analysis. The composition 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 column (DB-MTBE, J & Scientific). The GC response peaks were treated with Chrom-Card for Windows. Column, injector, and detector temperatures were (363, 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.

Table 5. Consistency Test for the Binary Systems Considered in VLE Measurement

system $i + j$	A_1[a]	A_2[a]	A_3[a]	AADy_i[b]	AADP[c]/kPa
dipropyl ether (1) + butyl propionate (3)	0.0651	0.0171	0.0204	0.0074	0.29
1-propyl alcohol (2) + butyl propionate (3)	0.5345	0.2643	0.0363	0.0048	0.33

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

Table 6. Parameters and Deviations between Experimental and Calculated Values for Different G^E Models

					buble point		
model	system $i + j$	A_{ij}/J·mol^{-1}	A_{ji}/J·mol^{-1}	α_{ij}	AADT[a]	AADy_1[b]	AADy_2[b]
Wilson[c]	(1) + (2)[d]	−346.22	4265.53		0.11	0.0035	
	(1) + (3)	458.52	−175.81		0.22	0.0062	
	(2) + (3)	1281.49	1603.80		0.22		0.0034
	(1) + (2) + (3)[e]				0.69	0.0081	0.0088
NRTL	(1) + (2)[d]	2495.24	1100.97	0.30	0.08	0.0040	
	(1) + (3)	2442.80	−1743.45	0.30	0.26	0.0056	
	(2) + (3)	5545.78	−2004.75	0.30	0.39		0.0034
	(1) + (2) + (3)[e]				0.48	0.0077	0.0057
UNIQUAC[f]	(1) + (2)[d]	2458.83	−834.19		0.09	0.0040	
	(1) + (3)	522.12	−401.13		0.16	0.0016	
	(2) + (3)	459.92	320.50		0.24		0.0031
	(1) + (2) + (3)[e]				0.70	0.0073	0.0078

[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 7. [e] Ternary prediction from binary parameters. [f] Volume and surface parameters from ref 13.

Results and Discussion

Pure Component Vapor Pressures. The pure component vapor pressure $P_i°$ for dipropyl ether (1), 1-propyl alcohol (2), and butyl propionate (3) were determined experimentally and reported in previous papers.[7,10,11] However, we measured the vapor pressures of dipropyl ether (1) and 1-propyl alcohol (2) up to about the normal boiling point of the respective pure components, which are lower than the butyl propionate (3) boiling point. So, to avoid excessive extrapolations of the Antoine equation for the two more volatile components (dipropyl ether and 1-propyl alcohol), we have decided to use in this work other equations to estimate these vapor pressures that are applicable in larger temperature range.[9] The temperature dependence of dipropyl ether (1) and 1-propyl alcohol (2) pure component vapor pressures was calculated using

$$\ln(P_i°/\mathrm{Pa}) = A_i + \frac{B_i}{(T/\mathrm{K})} + C_i \ln(T/\mathrm{K}) + D_i(T/\mathrm{K})^{E_i} \qquad (1)$$

whose parameters A_i, B_i, C_i, D_i, and E_i are reported in Table 2.

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 dipropyl ether (1) + butyl propionate (3) and 1-propyl alcohol (2) + butyl propionate (3) are reported in Tables 3 and 4 and plotted in Figures 1 and 2. The activity coefficients γ_i for these systems were calculated from the following equation:

$$\gamma_i = \frac{y_i P}{x_i P_i°} \qquad (2)$$

where P is the total pressure. 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 experiments data makes these simplifications reasonable.

The activity coefficients presented in Tables 3 and 4 indicate that the dipropyl ether (1) + butyl propionate (3) system exhibits ideal behavior and that the 1-propyl alcohol (2) + butyl propionate (3) system shows positive deviations from Raoult's law, and no additional azeotropes are present.

Table 7. 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	AADT[a]/K	RMSD[b]/K
1 + 2[c]	−31.08	5.61	−17.57	0.07	0.06
1 + 3	−40.17	17.11	−6.56	0.12	0.08
2 + 3	−59.41	41.87	−16.00	0.18	0.10

system $i + j + k$	A	B	C	D	AADT/K	RMSD/K
1 + 2 +3	−33.69	21.82	19.47	44.31	0.37	0.07

[a] Average absolute deviation in temperature. [b] Root-mean-square deviation: $1/N\cdot\{\Sigma(T_{\mathrm{exptl}} - T_{\mathrm{calc}})^2\}^{0.5}$. [c] Ref 7.

The Fredenslund et al.[12] test was applied to the binary experimental data to test thermodynamic consistency. In Table 5, 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):

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

and are reported in Table 6, 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]

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

In this equation, $T_i°$ is the boiling point of the pure component i and m is the number of terms used in the series expansion of (x_i - x_j), usually 2. The various constants of eq 4 are reported in

Table 8. Experimental Vapor−Liquid Equilibrium Data for Dipropyl Ether (1) + 1-Propyl Alcohol (2) + Butyl Propionate (3) at 101.3 kPa

T/K	x_1	x_2	y_1	y_2	γ_1	γ_2	γ_3
359.71	0.676	0.269	0.682	0.313	1.122	1.765	0.620
360.13	0.468	0.478	0.567	0.427	1.331	1.333	0.806
360.86	0.597	0.303	0.643	0.345	1.156	1.653	0.834
361.14	0.492	0.406	0.580	0.407	1.254	1.435	0.902
361.19	0.703	0.199	0.718	0.271	1.084	1.952	0.780
361.90	0.387	0.512	0.515	0.470	1.384	1.277	0.992
362.05	0.277	0.672	0.443	0.549	1.655	1.129	1.089
362.77	0.892	0.053	0.891	0.103	1.012	2.608	0.625
362.77	0.802	0.096	0.820	0.167	1.035	2.338	0.796
363.31	0.277	0.619	0.434	0.547	1.559	1.163	1.099
364.17	0.492	0.300	0.592	0.376	1.166	1.592	0.922
364.32	0.596	0.198	0.679	0.290	1.100	1.850	0.917
364.46	0.387	0.409	0.516	0.451	1.283	1.385	0.960
365.10	0.183	0.713	0.344	0.635	1.773	1.091	1.217
365.28	0.287	0.509	0.431	0.531	1.413	1.267	1.074
365.89	0.696	0.098	0.789	0.177	1.044	2.148	0.925
367.32	0.504	0.193	0.638	0.307	1.118	1.790	0.964
367.51	0.399	0.291	0.536	0.407	1.180	1.564	0.962
367.58	0.091	0.805	0.222	0.754	2.134	1.042	1.242
367.97	0.142	0.655	0.282	0.672	1.720	1.125	1.167
368.22	0.298	0.388	0.441	0.500	1.274	1.398	0.975
368.56	0.032	0.926	0.124	0.870	3.324	1.007	0.627
370.71	0.645	0.044	0.838	0.098	1.040	2.209	0.964
371.04	0.040	0.751	0.114	0.830	2.254	1.078	1.234
371.17	0.396	0.198	0.571	0.344	1.138	1.690	0.965
371.42	0.295	0.296	0.453	0.462	1.205	1.501	0.949
371.53	0.096	0.594	0.202	0.721	1.650	1.162	1.134
372.18	0.197	0.399	0.336	0.574	1.312	1.345	0.984
372.95	0.495	0.092	0.714	0.193	1.083	1.910	0.976
374.62	0.287	0.212	0.477	0.402	1.190	1.621	0.980
375.16	0.052	0.543	0.115	0.772	1.566	1.191	1.105
375.19	0.190	0.312	0.340	0.537	1.259	1.440	0.983
376.60	0.102	0.397	0.203	0.664	1.345	1.327	1.006
377.45	0.443	0.061	0.721	0.148	1.077	1.872	0.970
379.63	0.209	0.194	0.396	0.431	1.183	1.582	0.980
380.78	0.299	0.104	0.563	0.260	1.136	1.712	0.970
383.43	0.052	0.309	0.112	0.679	1.208	1.371	0.973
388.12	0.101	0.175	0.232	0.493	1.139	1.497	0.962
390.27	0.228	0.052	0.533	0.166	1.099	1.595	0.986
394.30	0.107	0.092	0.276	0.332	1.093	1.562	1.014
403.13	0.058	0.051	0.194	0.239	1.143	1.544	1.000

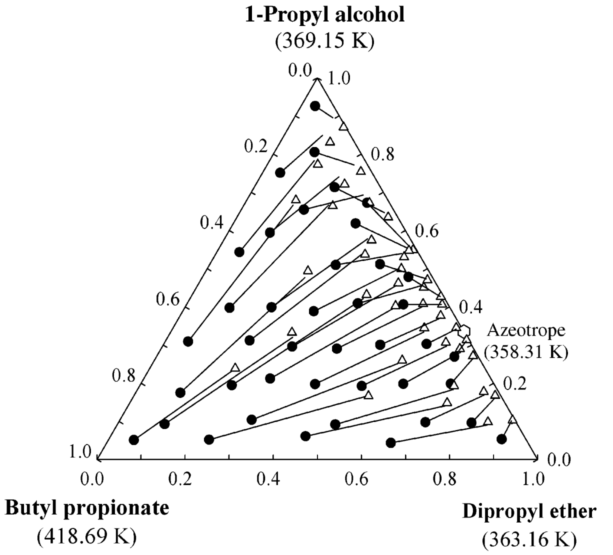

Figure 3. Diagram of VLE for the ternary system dipropyl ether (1) + 1-propyl alcohol (2) + butyl propionate (3) at 101.3 kPa: ●, liquid-phase mole fraction; △, vapor-phase mole fraction; Smoothed lines calculated with the UNIQUAC equation with the parameters given in Table 6.

Table 7, with information indicating the goodness of the correlation fit.

Ternary System. VLE data for the ternary system dipropyl ether (1) + 1-propyl alcohol (2) + butyl propionate (3) are reported in Table 8 and Figure 3. The activity coefficients γ_i were again calculated from eq 2. The ternary data were found to be thermodynamically consistent by the Wisniak and Tamir[15] modification of the McDermott−Ellis[16] test ($D < D_{\max}$ at all data points) and the Wisniak $L - W$ test[17] ($0.92 < L_i/W_i < 1.10$).

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 6 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. Therefore, the models can be used to calculate boiling points from liquid-phase compositions at the system pressure. As an applied example, boiling isotherms calculated with the UNIQUAC model are presented in Figure 4.

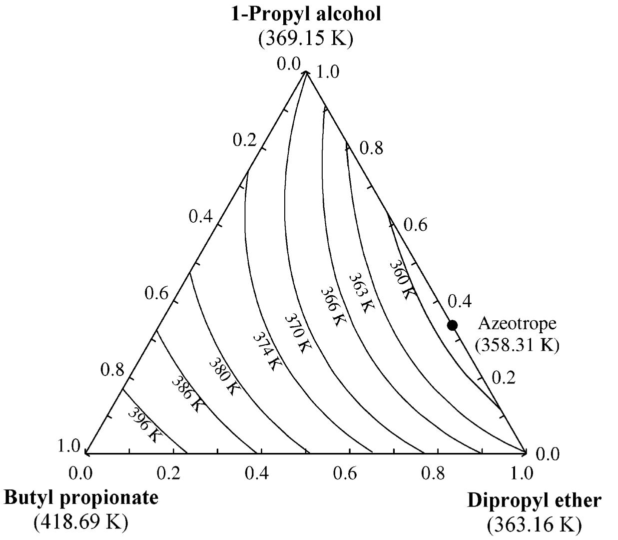

Figure 4. Boiling isotherms (K) for the ternary system dipropyl ether (1) + 1-propyl alcohol (2) + butyl propionate (3) at 101.3 kPa calculated with the UNIQUAC model with the parameters given in Table 6. ●, azeotrope.

The boiling points of the ternary system were correlated by the equation proposed by Wisniak and Tamir:[15]

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

where T_i° is the boiling point of the pure component 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 7, 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 for the residue curves as they approach the pure solvent vertex.[18] In Figure 5, residue curves simulated by DISTIL using the UNIQUAC model with the experimental parameters reported in Table 6 are shown. As can

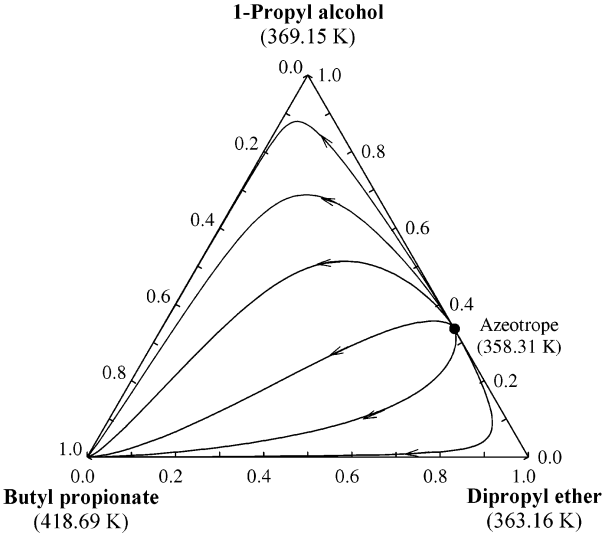

Figure 5. Residual curve map for the ternary dipropyl ether (1) + 1-propyl alcohol (2) + butyl propionate (3). Continuous lines simulated by DISTIL using UNIQUAC model with the parameters given in Table 6. ●, azeotrope.

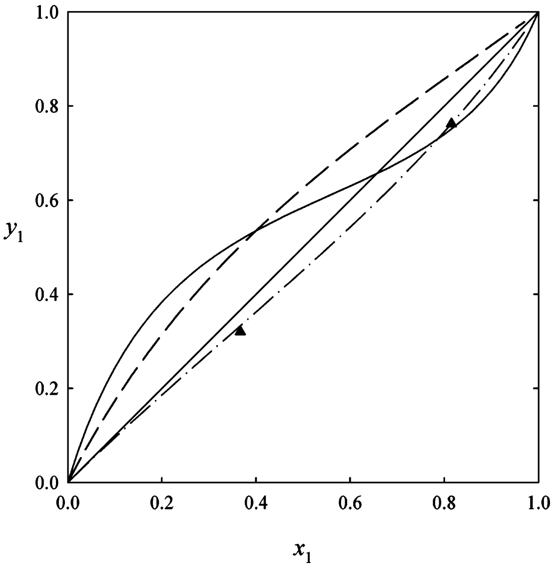

Figure 6. VLE data plotted on a solvent free basis for the system dipropyl ether (1) + 1-propyl alcohol (2) + solvent (3) at 101.3 kPa. Continuous line for $x_3 = 0.00$, ref 6. Dashed lines calculated using the UNIQUAC equation with the parameters given in Table 6 for $x_3 = 0.70$: ---, with 1-pentanol[3]; −•−, with butyl propionate. Experimental data: ▲, with butyl propionate.

be seen in this figure, all residue curves approaching the butyl propionate (solvent) vertex are inflected toward the butyl propionate−dipropyl ether face, with the result that dipropyl ether (1) + butyl propionate (3) will be recovered in the bottom and 1-propyl alcohol (2) in the distillate, as it were expected after the simulated results obtained in the previous work.[3] Nevertheless, although the simulation by means of DISTIL software with the parameters estimated using UNIFAC group-contribution method predicted a good separation of the original mixture ($\alpha_{12}^S = 0.42$; simulated[3]), it has been able to verified that this effect is not so accused as it would expected ($\alpha_{12}^S = 0.82$; experimental). Therefore, this fact confirms the necessity of the determination of experimental vapor−liquid data for the design of separation processes.

In order to carry out the separation of the azeotropic mixture of dipropyl ether (1) + 1-propyl alcohol (2) by extractive distillation, we studied the influence on the phase equilibria behavior of that azeotropic mixture with butyl propionate (3). In Figure 6, the VLE of the ternary mixture, on a solvent-free basis together with the experimental points obtained with 1-pentanol (4) as entrainer[3] were plotted. As can be seen in this figure, the two solvents eliminate the dipropyl ether (1)/1-propyl alcohol (2) azeotrope but in a different way. Butyl propionate (3) reverses the volatility of the original mixture, that is, enhances the relative volatility of 1-propyl alcohol (2) to dipropyl ether (1) in such a way that 1-propyl alcohol (2) would be obtained as the overhead product in the extractive column, with dipropyl ether (1) and butyl propionate (3) being the bottom product. Otherwise, 1-pentanol (4) enhances the relative volatility of dipropyl ether (1) to 1-propyl alcohol (2), in the natural way. Figure 6 confirms that 1-pentanol (4) brings about a larger enhancement of the relative volatility; so, for the moment, 1-pentanol (4) is a more promising entrainer than butyl propionate (3) for the separation of the dipropyl ether (1) and 1-propyl alcohol (2) azeotropic mixture by extractive distillation.

Conclusions

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

The experimental results revealed that the presence of butyl propionate reverses the relative volatility of dipropyl ether (1) to 1-propyl alcohol (2), which is reaffirmed in the residue curve map. Furthermore, the relative volatility on a solvent-free basis ($\alpha_{12}^S = 0.82$) confirms that butyl propionate breaks the azeotropic mixture, although 1-pentanol[3] is the most promising entrainer studied, for the time being.

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