Phase Equilibria Involved in Extractive Distillation of Dipropyl Ether + 1-Propyl Alcohol Using *N*,*N*-Dimethylformamide as Entrainer

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Consistent vapor−liquid equilibrium data for the binary and ternary systems dipropyl ether (1) + 1-propyl alcohol (2) + *N*,*N*-dimethylformamide (3) are reported at 101.3 kPa. The results indicate that dipropyl ether (1) + *N*,*N*-dimethylformamide (3) system exhibits a positive deviation from ideal behavior and that 1-propyl alcohol (2) + *N*,*N*-dimethylformamide (3) system deviates negatively from ideality. The activity coefficients of the solutions were correlated by the Wilson, NRTL, and UNIQUAC models. It is shown that these models allow a very good prediction of the phase equilibrium of the ternary system using the pertinent parameters of the binary systems. In addition, the Wisniak−Tamir relations were used for correlating bubble-point temperatures.

Introduction

The separation of ether + alcohol mixtures can be carried out by extractive distillation. This process requires the addition of a third component that modifies the relative volatilities of dipropyl ether (1) to 1-propyl alcohol (2). 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.

This work was undertaken as a part of the thermodynamic research on the separation of dipropyl ether (1) and 1-propyl alcohol (2) using different solvents. The mixture under study is formed by dipropyl ether (1), 1-propyl alcohol (2), and *N*,*N*-dimethylformamide (3). *N*,*N*-Dimethylformamide exhibits strongly varying interactions with different functional groups and may be useful as a solvent in enhancing relative volatility and/or breaking azeotropes in mixtures of compounds with certain functionalities. *N*,*N*-Dimethylformamide is a polar compound, which does not form any azeotropes with the original components in the mixture, its boiling temperature is higher than the dipropyl ether (1) and 1-propyl alcohol (2) boiling temperatures, and it is completely miscible with them in all proportion.[1]

In this work we measured isobaric VLE data for the ternary system dipropyl ether (1) + 1-propyl alcohol (2) + *N*,*N*-dimethylformamide (3) and two of the constituent binary systems dipropyl ether (1) + *N*,*N*-dimethylformamide (3) and 1-propyl alcohol (2) + *N*,*N*-dimethylformamide (3) at 101.3 kPa. In a recent literature review, only isobaric VLE for the 1-propyl alcohol + *N*,*N*-dimethylformamide system at (25.0 and 50.0) kPa has been found.[2] In a previous work,[3] we reported VLE data for the binary system dipropyl ether (1) + 1-propyl alcohol (2) at (20 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, NRTL, and UNIQUAC equations to relate activity coefficients with compositions.

Experimental Section

Chemicals. 1-Propyl alcohol ($w > 99.5$ %, analytical grade) was purchased from Panreac, dipropyl ether ($w = 90$ %, for synthesis) was supplied by Merck and *N*,*N*-dimethylformamide ($w > 99.9$ %, HPLC grade) was purchased from Aldrich Ltd. Dipropyl ether was purified to $w = 99.5$ % 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 ($w < 0.05$ %). Before measurements, the liquids were degassed and subsequently dried over molecular sieves (Union Carbide, type 4 Å, 0.0016 m 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 uncertainly in refractive index and density measurements are ± 0.0002 and ± 0.01 $kg \cdot m^{-3}$, 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 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 uncertainly is estimated to be ± 0.01 K. The temperature probe

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10.1021/je0604479 CCC: $37.00

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

	d (298.15 K)/kg·m^{-3}		n_D (298.15 K)		T_b (101.3 kPa)/K	
component	exptl	lit	exptl	lit	exptl	lit[b]
dipropyl ether (1)	741.81	742.00[a]	1.3784	1.3780[a]	363.16	362.79
1-propyl alcohol (2)	799.62	799.51[a]	1.3836	1.3837[a]	369.75	370.35
N,*N*-dimethylformamide (3)	948.72	948.69[b]	1.4265	1.4269[b]	425.63	425.15

[a] Ref 4. [b] Ref 5.

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 deviations in the liquid mole fraction were $\sigma_1 = 0.0010$ for the dipropyl ether (1) + *N*,*N*-dimethylformamide (3) system, $\sigma_2 = 0.0002$ for the 1-propyl alcohol (2) + *N*,*N*-dimethylformamide (3) system, and $\sigma_1 = 0.0008$ and $\sigma_2 = 0.0012$ for the dipropyl ether (1) + 1-propyl alcohol (2) + *N*,*N*-dimethylformamide (3) system.

Results and Discussion

Pure Component Vapor Pressures. The pure component vapor pressure $P_i°$ for dipropyl ether (1), 1-propyl alcohol (2), and *N*,*N*-dimethylformamide (3) were determined experimentally and reported in previous papers.[3,6,7] 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 *N*,*N*-dimethylformamide (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 a larger temperature range.[5] The temperature dependence of dipropyl ether (1) and 1-propyl alcohol (2) pure component vapor pressures was calculated using

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

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

Table 2. Vapor Pressure Parameters

compound	*A*	*B*	*C*	*D*	*E*	ref
dipropyl ether (1)	106.260	−7557.00	−12.792	1.1231·10^{-5}	2	*a*
1-propyl alcohol (2)	88.134	−8498.60	−9.077	8.3303·10^{-18}	6	*a*
N,*N*-dimethyl-formamide (3)	14.820	3822.15	−51.001			*b*

[a] Ref 5, $\ln(P°_i/\mathrm{Pa}) = A + B/(T/\mathrm{K}) + C \ln(T/\mathrm{K}) + D(T/\mathrm{K})^E$. [b] Ref 7, $\ln(P°_i/\mathrm{kPa}) = A - B/[(T/\mathrm{K}) + C]$.

Table 3. Experimental Vapor−Liquid Equilibrium Data for the Binary System Dipropyl Ether (1) + *N*,*N*-Dimethylformamide (3) at 101.3 kPa

T/K	$x1$	y_1	γ_1	γ_3	T/K	$x1$	y_1	γ_1	γ_3
425.63	0.000	0.000		1.000	371.77	0.391	0.876	1.740	1.130
423.99	0.002	0.038	4.067	1.009	370.62	0.439	0.884	1.617	1.198
420.79	0.009	0.148	3.771	0.983	369.55	0.489	0.895	1.516	1.239
417.24	0.016	0.228	3.533	0.992	368.76	0.540	0.899	1.411	1.364
413.81	0.025	0.303	3.244	0.998	367.65	0.625	0.904	1.266	1.659
410.79	0.034	0.380	3.203	0.978	366.87	0.682	0.911	1.196	1.869
405.08	0.051	0.495	3.176	0.963	366.18	0.738	0.919	1.138	2.120
391.86	0.105	0.687	2.958	0.962	365.43	0.800	0.929	1.086	2.506
384.08	0.158	0.775	2.714	0.955	364.57	0.871	0.945	1.041	3.111
378.87	0.222	0.820	2.352	0.992	363.77	0.939	0.968	1.013	3.949
374.67	0.296	0.854	2.064	1.035	363.16	1.000	1.000	1.000	
373.08	0.340	0.865	1.904	1.082					

Table 4. Experimental Vapor−Liquid Equilibrium Data for the Binary System 1-Propyl Alcohol (2) + *N*,*N*-Dimethylformamide (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
425.63	0.000	0.000		1.000	383.06	0.603	0.919	0.963	0.755
419.92	0.064	0.218	0.693	0.979	380.85	0.656	0.937	0.975	0.732
414.90	0.115	0.372	0.757	0.959	378.82	0.707	0.952	0.988	0.704
409.78	0.172	0.500	0.787	0.948	377.02	0.755	0.965	1.000	0.654
405.38	0.226	0.602	0.821	0.922	375.40	0.802	0.975	1.009	0.613
401.23	0.285	0.686	0.841	0.895	373.95	0.847	0.982	1.015	0.603
397.57	0.338	0.742	0.860	0.891	372.69	0.892	0.988	1.016	0.596
394.27	0.391	0.790	0.879	0.876	371.58	0.933	0.993	1.017	0.584
390.98	0.445	0.833	0.906	0.852	370.71	0.969	0.997	1.016	0.559
388.02	0.499	0.869	0.930	0.817	369.75	1.000	1.000	1.000	
385.37	0.553	0.896	0.946	0.795					

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

$$\gamma_i = \frac{y_i P}{x_i P_i^{\circ}} \quad (2)$$

where y_i is the mole fraction of component i in vapor phase, x_i is the mole fraction of component i in liquid phase, γ_i is the activity coefficient of the component i in liquid phase, P is the total pressure, and $P_i°$ 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 experiments data makes these simplifications reasonable. The activity coefficients presented in Tables 3 and 4 indicate that the dipropyl ether (1) + *N*,*N*-dimethylformamide (3) system shows positive deviations from ideal behavior, that the 1-propyl alcohol (2) + *N*,*N*-

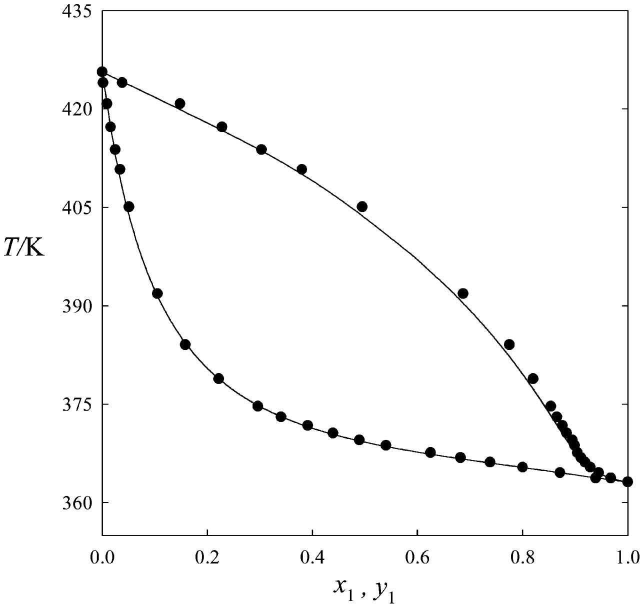

Figure 1. Experimental VLE data for the system dipropyl ether (1) + *N*,*N*-dimethylformamide (3) at 101.3 kPa: ●, experimental data; —, smoothed data using the Wilson model with the parameters given in Table 6.

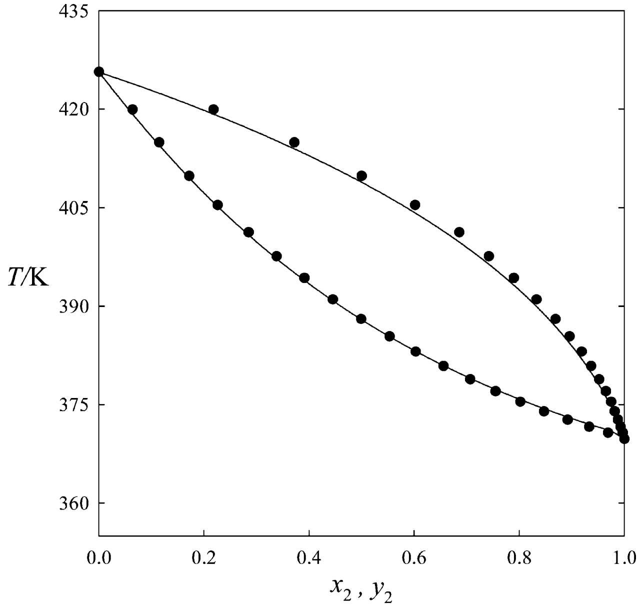

Figure 2. Experimental VLE data for the system 1-propyl alcohol (2) + *N*,*N*-dimethylformamide (3) at 101.3 kPa: ●, experimental data; —, smoothed data using the Wilson model with the parameters given in Table 6.

dimethylformamide (3) system exhibits negative deviation from ideal behavior, and that no additional azeotropes are present.

The test of Fredenslund[8] 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):

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

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:[10]

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

In this equation T_i^0 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 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) + *N*,*N*-dimethylformamide (3) are reported in Table 8. Figure 3 shows the vapor-phase mole fractions deviations calculated with the Wilson model with the parameters given in Table 6. The ternary data were found to be thermodynamically consistent by the Wisniak and Tamir[11] modification of the McDermott−Ellis[12] test ($D < D_{\max}$ at all data points) and the Wisniak L-W test[13] ($0.92 < L_i/W_i < 1.10$). A complete description of these tests is given in the Appendix.

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, representing the data successfully. Thus, 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 Wilson model are presented in Figure 4.

The boiling points of the ternary system were correlated by the equation proposed by Wisniak and Tamir:[10]

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

where T_i^0 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. In order to carry out the separation of the azeotropic mixture of dipropyl ether (1) + 1-propyl alcohol (2)

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

system *i* + *j*	A_1[a]	A_2[a]	A_3[a]	A_4[a]	AADy_i[b]	AADP[c]/kPa
dipropyl ether (1) + *N*,*N*-dimethylformamide (3)	1.4203	0.2237	0.0394	0.0514	0.0073	0.40
1-propyl alcohol (2) + *N*,*N*-dimethylformamide (3)	−0.3981	0.1135	0.0245	0.0450	0.0095	0.41

[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 for the System Dipropyl Ether (1) + 1-Propyl Alcohol (2) + *N*,*N*-Dimethylformamide (3)

					bubble 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	253.93	5600.70		0.29	0.0064	
	2 + 3	389.87	−1502.48		0.29		0.0096
	1 + 2 + 3[e]				0.43	0.0119	0.0078
NRTL	1 + 2[d]	2495.24	1100.97	0.30	0.08	0.0040	
	1 + 3	3430.78	1755.95	0.30	0.25	0.0070	
	2 + 3	−2021.71	1255.59	0.30	0.59		0.0115
	1 + 2 + 3[e]				0.43	0.0069	0.0119
UNIQUAC[f]	1 + 2[d]	2458.83	−834.19		0.09	0.0040	
	1 + 3	2745.67	−756.90		0.27	0.0072	
	2 + 3	−1730.56	1710.18		0.30		0.0053
	1 + 2 + 3[e]				0.25	0.0141	0.0094

[a] Average absolute deviation in temperature. [b] Average absolute deviation in vapor-phase composition. [c] Molar liquid volumes of pure components from ref 9. [d] Ref 3. [e] Ternary prediction from binary parameters. [f] Volume and surface parameters from ref 9.

Table 7. Coefficients in Correlation of Boiling Points (eqs 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]	−31.08	5.61	−17.57		0.07	0.06
1 + 3	−96.70	85.98	−116.07	106.47	0.62	0.18
2 + 3	−40.11	6.14	−2.61		0.10	0.07

system $i + j + k$	A	B	C	D	AADT[a]/K	rmsd[b]/K
1 + 2 + 3	−30.13	−117.66	−6.79	52.43	0.44	0.14

[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 3.

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

T/K	x_1	x_2	y_1	y_2	γ_1	γ_2	γ_3
359.12	0.404	0.550	0.354	0.637	1.363	1.310	1.891
359.51	0.188	0.772	0.230	0.754	1.872	1.093	3.518
360.26	0.599	0.360	0.459	0.537	1.138	1.629	1.031
360.27	0.296	0.613	0.281	0.698	1.412	1.245	1.940
360.83	0.507	0.400	0.403	0.585	1.154	1.572	1.098
361.49	0.185	0.696	0.199	0.767	1.521	1.159	2.350
362.16	0.058	0.878	0.086	0.878	2.046	1.032	4.434
362.28	0.104	0.787	0.129	0.829	1.700	1.083	3.054
362.69	0.300	0.507	0.261	0.704	1.174	1.407	1.443
362.70	0.402	0.403	0.328	0.644	1.099	1.622	1.133
363.73	0.702	0.203	0.564	0.428	1.040	2.072	0.590
364.02	0.507	0.295	0.411	0.565	1.037	1.868	0.884
364.24	0.102	0.696	0.110	0.830	1.368	1.156	2.183
364.42	0.208	0.530	0.187	0.759	1.135	1.380	1.495
365.05	0.302	0.403	0.254	0.697	1.032	1.636	1.176
365.28	0.585	0.221	0.487	0.491	1.011	2.089	0.803
365.88	0.404	0.295	0.335	0.623	0.983	1.945	0.988
366.06	0.092	0.594	0.094	0.830	1.203	1.282	1.661
366.52	0.049	0.642	0.057	0.862	1.331	1.215	1.790
366.92	0.212	0.418	0.183	0.750	0.983	1.603	1.219
367.46	0.799	0.094	0.716	0.273	1.002	2.555	0.623
368.02	0.304	0.304	0.259	0.679	0.931	1.934	1.015
368.04	0.504	0.196	0.444	0.516	0.963	2.274	0.848
368.30	0.092	0.482	0.088	0.823	1.037	1.467	1.318
368.40	0.899	0.047	0.833	0.162	0.998	2.954	0.605
370.17	0.211	0.310	0.185	0.732	0.882	1.920	1.023
370.27	0.044	0.442	0.050	0.851	1.125	1.562	1.138
370.36	0.401	0.196	0.369	0.570	0.919	2.347	0.900
370.73	0.091	0.368	0.086	0.810	0.933	1.762	1.106
371.39	0.569	0.121	0.560	0.401	0.948	2.594	0.705
373.27	0.300	0.193	0.292	0.627	0.873	2.418	0.846
373.40	0.702	0.045	0.759	0.208	0.966	3.415	0.666
374.31	0.097	0.263	0.094	0.785	0.841	2.161	0.953
375.13	0.209	0.203	0.205	0.687	0.822	2.396	0.898
377.58	0.394	0.101	0.469	0.446	0.913	2.926	0.753
378.53	0.052	0.213	0.054	0.796	0.771	2.402	0.885
379.66	0.501	0.046	0.655	0.270	0.930	3.688	0.693
380.27	0.100	0.180	0.110	0.737	0.764	2.512	0.870
384.31	0.183	0.109	0.271	0.568	0.896	2.854	0.805
388.08	0.097	0.120	0.136	0.652	0.744	2.715	0.843
388.31	0.289	0.047	0.485	0.355	0.888	3.762	0.743
406.24	0.055	0.053	0.131	0.477	0.710	2.875	0.769

by extractive distillation, we have studied the influence on the phase equilibria behavior of that azeotropic mixture of three different solvents: 1-pentanol,[14] butyl propionate,[15] and *N*,*N*-dimethylformamide (in this paper).

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.[16] In Figure 5, residue curves simulated by DISTIL v5.0 Hyprotech Ltd[17] using the Wilson model with the experimental parameters (Table 6) are shown. As can be seen in this figure, all residue curves approaching the *N*,*N*-dimethylformamide (solvent) vertex are inflected toward the *N*,*N*-dimethylformamide + 1-propyl alcohol face, with the result that 1-propyl alcohol + *N*,*N*-dimethylformamide will be recovered in the bottom and dipropyl ether in the distillate. 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, the three solvents studied eliminate the dipropyl ether + 1-propyl alcohol azeotrope, allowing the separation of pure dipropyl ether from 1-propyl alcohol by rectification when they are employed as solvents in extractive distillation. *N*,*N*-Dimethylformamide and 1-pentanol enhance the relative volatility of dipropyl ether to 1-propyl alcohol, but *N*,*N*-dimethylformamide brings about a larger enhancement of the relative volatility ($\alpha_{12}^S = 4.37$ with *N*,*N*-dimethylformamide and $\alpha_{12}^S = 1.67$ with 1-pentanol, where α_{12}^S is the relative volatility between dipropyl ether (1) and 1-propyl alcohol (2) in the presence of the solvent). On the contrary, butyl propionate enhances the relative volatility of 1-propyl alcohol to dipropyl ether ($\alpha_{12}^S = 0.82$). Therefore, Figure 6 confirms that thus far *N*,*N*-dimethylformamide is the best promising entrainer of the tree solvents studied for the separation of dipropyl ether and 1-propyl alcohol azeotropic mixture by extractive distillation.

Conclusions

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

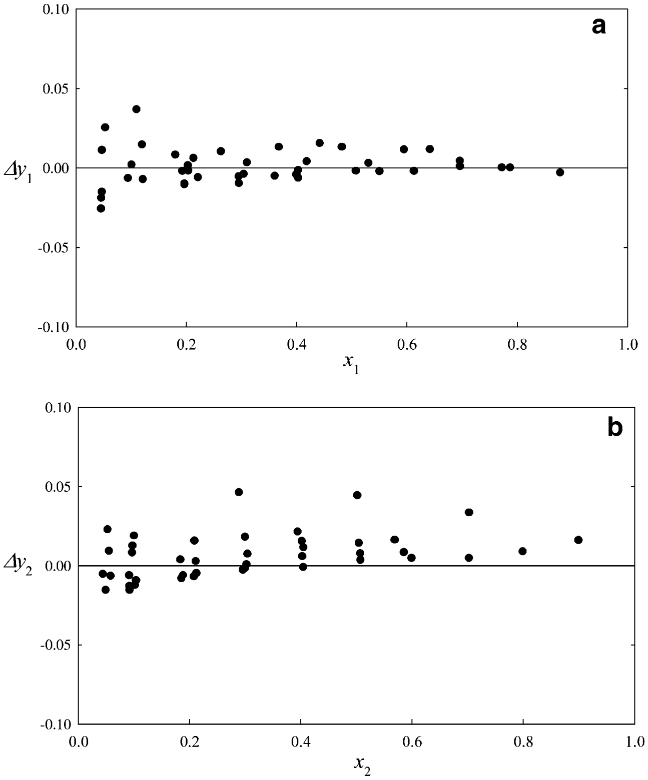

Figure 3. Vapor-phase mole fraction deviations $\Delta y_i = y_i^{\text{expt}} - y_i^{\text{calc}}$ for the system dipropyl ether (1) + 1-propyl alcohol (2) + *N,N*-dimethylformamide (3) at 101.3 kPa.

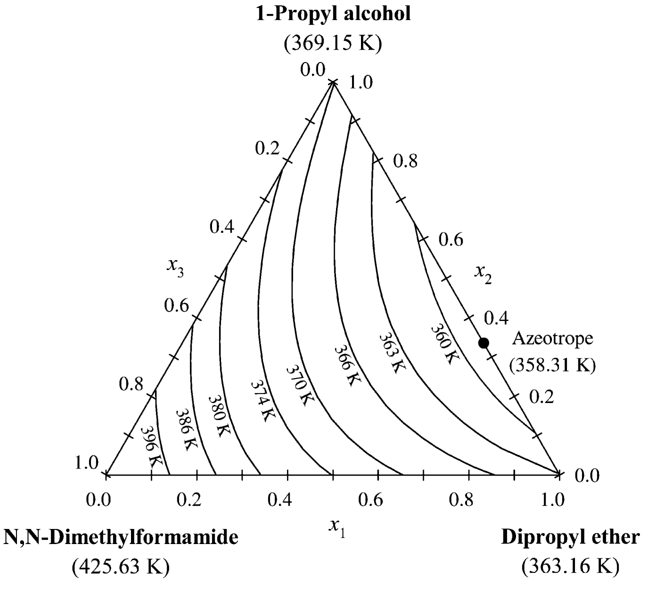

Figure 4. Boiling isotherms (K) for the ternary system dipropyl ether (1) + 1-propyl alcohol (2) + *N,N*-dimethylformamide (3) at 101.3 kPa calculated with the Wilson model with the parameters given in Table 6: ●, azeotrope.

general, for the three systems, the Wilson model is more adequate for correlation of the VLE data obtained.

According to the equilibrium diagrams, it is more suitable to use *N,N*-dimethylformamide as entrainer because it has a more distant equilibrium line from the diagonal line than the others, thus resulting in a small number of plates and/or minor reflux ratio in the distillation column, so the separation of the primary azeotropic mixture (dipropyl ether + 1-propyl alcohol) can be economically feasible.

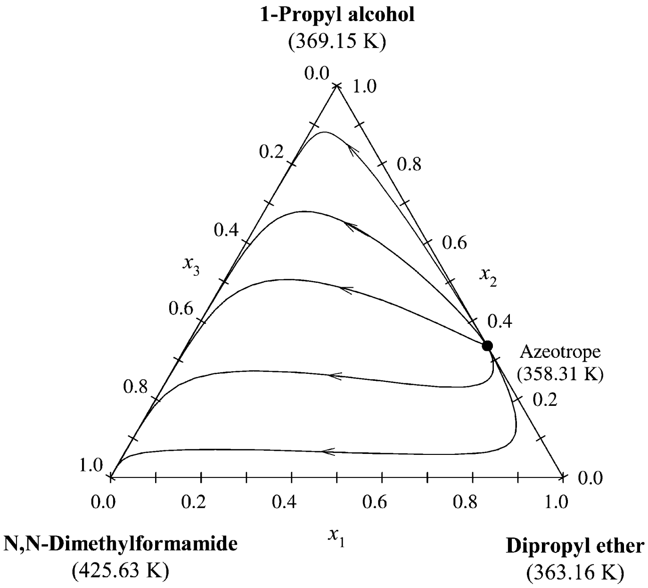

Figure 5. Residual curve map for the ternary dipropyl ether (1) + 1-propyl alcohol (2) + *N,N*-dimethylformamide (3). Continuous lines simulated by DISTIL using Wilson model with the parameters given in Table 6: ●, azeotrope.

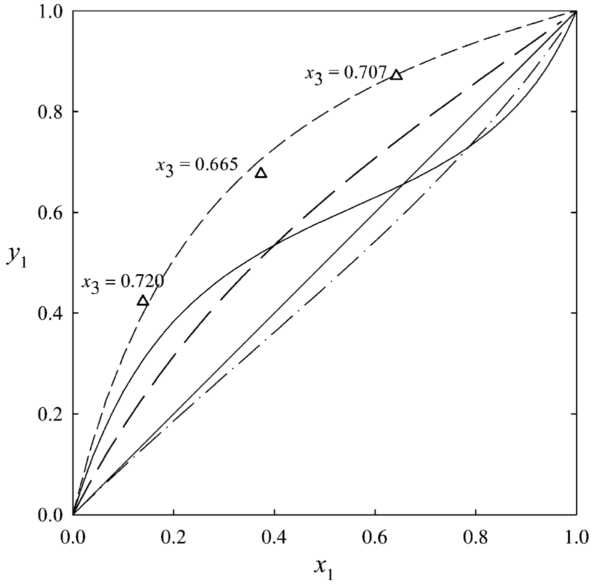

Figure 6. VLE data plotted on a solvent-free basis for the system dipropyl ether (1) + 1-propyl alcohol (2) + solvent (3) at 101.3 kPa. Continuous line[3] for $x_3 = 0.00$. Dashed line calculated using the Wilson equation with the parameters given in Table 6 for $x_3 = 0.70$: - - - , with 1-pentanol;[14] -•-, with butyl propionate;[15] and — —, with *N,N*-dimethylformamide (in this work). Experimental points: △, *N,N*-dimethylformamide.

Appendix

McDermott−Ellis Test. According with the McDermott−Ellis test, D is the local deviation, which is expressed as

$$D = \sum_{i=1}^{N_c} \{(x_{ia} + x_{ib})\cdot(\ln \gamma_{ib} - \ln \gamma_{ia})\} \qquad \text{(A1)}$$

and $D_{\max}$ is the maximum deviation. Wisniak and Tamir[11] propose the following expression for the maximum local deviation:

$$D_{\max} = \sum_{i=1}^{N_c} (x_{ia} + x_{ib})\left(\frac{1}{x_{ia}} + \frac{1}{x_{ib}} + \frac{1}{y_{ia}} + \frac{1}{y_{ib}}\right)\Delta x + 2\sum_{i=1}^{N_c} |\ln \gamma_{ib} - \ln \gamma_{ia}|\Delta x + \sum_{i=1}^{N_c} (x_{ia} + x_{ib})\frac{\Delta P}{P} + \sum_{i=1}^{N_c} (x_{ia} + x_{ib})B_i \times \left\{\frac{1}{(T_a + C_i)^2} + \frac{1}{(T_b + C_i)^2}\right\}\Delta T \quad \text{(A2)}$$

where B_i and C_i are the Antoine constants; Δx, ΔP, and ΔT are the uncertainties of mole fraction, pressure, and temperature, respectively; and T_a, T_b, y_{ia}, and y_{ib} are the temperature and vapor mole fraction of points a and b.

Wisniak L-W Test. This test is based on the Clausius−Clapeyron equation. For each data point *i* at system temperature T_i, we compute two functions L_i and W_i:

$$L_i = \sum_i^C T_i^0 x_i \frac{\Delta s_i^{\,0}}{\Delta s} - T = \frac{G^{\mathrm{E}}}{\Delta s} - RT\frac{\omega}{\Delta s} = W_i \qquad \text{(A3)}$$

For every species *i*, at the system pressure, there is a pure-component boiling point T_i^0, a liquid mole fraction x_i, and an entropy of vaporization $\Delta s°$. Then

$$\Delta s = \sum_i^C x_i \Delta s^0 \qquad \text{(A4)}$$

$$\omega = \sum_i^C x_i \ln \frac{y_i}{x_i} \qquad \text{(A5)}$$

We performed the point test by computing the ratio of L_i and W_i. Consistent data contain ratio values $0.92 < L_i/W_i < 1.10$.

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Received for review October 10, 2006. Accepted November 22, 2006. Financial support from the Ministerio de Ciencia y Tecnología of Spain, through Project CTQ2004-04477/PPQ, the FEDER European Program, and the Conselleria de Cultura, Educació i Esport (Generalitat Valenciana) of Valencia (Spain) are gratefully acknowledged.

JE0604479