Isobaric Vapor−Liquid Equilibria for Binary and Ternary Mixtures of Ethanol and 2-Propanol with 2-Butanone and Butyl Propionate at 101.3 kPa

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This paper presents vapor−liquid equilibrium (VLE) data at 101.3 kPa for the ternary systems ethanol + 2-butanone + butyl propionate and 2-propanol + 2-butanone + butyl propionate and some of their constituent binary systems: ethanol + butyl propionate and 2-butanone + butyl propionate. The ethanol + butyl propionate system exhibits positive deviation from Raoult's law and 2-butanone + butyl propionate does not present appreciable deviation from ideal behavior. The activity coefficients of the solutions were correlated as a function of mole fraction by the Wilson, nonrandom two-liquid, and universal quasichemical models. The binary VLE data measured in the present study passed the thermodynamic consistency test of Fredeslund et al. The ternary systems were very well-predicted from binary interaction parameters and passed the McDermott−Ellis consistency test. Butyl propionate can be considered an effective agent for the separation of the azeotropic mixtures ethanol + 2-butanone and 2-propanol + 2-butanone by extractive distillation.

Introduction

Nowadays, the use of traditional organic solvents remains still quite important in the chemical industry and especially in the petrochemical industry. The use of traditional solvents is still preferred over ionic liquids because of the high cost of ionic liquids.[1] The use of chlorinated and aromatic solvents has decreased, but other "friendly" solvents such as alcohols, esters, ketones, and ethers are still in use in many applications, especially as extraction or diluting agents.

The most rational use of solvents demands their recovery with a certain degree of purity for later use. In this way, the environmental impact can be minimal if the necessary investments are made to ensure reuse. For this reason, many industries have made remarkable progress in implementing "closed-loop systems" that reduce the environmental impact of the solvents and improve their ability to recycle.

In both consumer products and industrial applications, 2-butanone is frequently used as one of several components in a mixture of other solvents (alcohols). 2-Butanone is also used as an extraction solvent in the processing of foodstuffs and food ingredients, for example in the fractionation of fats and oils, decaffeination of tea and coffee, and extraction of flavors. In mixtures with other alcohols, 2-butanone is used as a cleaner agent for refrigeration pipelines[2] and also for the dispersion of TiO_2 powders in the fabrication of wide and flat sheets of ceramic materials.[3]

However, 2-butanone forms azeotropic mixtures with many alcohols, including ethanol and 2-propanol. Therefore, the purification of the ketone and recovery of the alcohol for recycling is impractical by ordinary distillation. However, these mixtures can be separated by enhanced distillation techniques, such as pressure-swing distillation[4] and extractive distillation.[5] At present, the separation of the azeotropic mixture is done by azeotropic distillation,[6,7] using entrainers such as amyl acetate, methyl formate, 2,2-dimethyl butane, or 2,3-dimethyl butane for the separation of ethanol + 2-butanone and 3-methylpentane, amyl ether, and acetonitrile for the separation of 2-propanol + 2-butanone.

Laboratory tests in distillation techniques are time-consuming and expensive because of the large number of parameters involved. It would be desirable to predict the experimental data with the help of available simulation programs, but unfortunately, their applicability to highly nonideal systems, such as those involved in these distillation techniques, is very limited, partially because of the low quality of the interaction parameters available in the literature, generally obtained from binary systems.

For a long time, our research group has been working on the separation of close-boiling mixtures and azeotropic mixtures using procedures related to vapor−liquid equilibrium (VLE). In a previous paper,[8] we reported VLE data for the azeotropic binary systems ethanol + 2-butanone and 2-propanol + 2-butanone at (20 and 101.3) kPa to investigate the pressure influence on the azeotropic composition and, in view of the results, showed that pressure-swing distillation could be a useful technique to break the binary azeotropes for both systems.

In this work, we have measured isobaric VLE data for the ternary systems ethanol + 2-butanone + butyl propionate and 2-propanol + 2-butanone + butyl propionate and some of their constituent binary systems: ethanol + butyl propionate and 2-butanone + butyl propionate at 101.3 kPa. The other binary systems have been determined in a previous work.[8] In a recent literature review[9] only isobaric VLE for the ethanol + butyl propionate system at atmospheric pressure has been found.

Therefore, the aim of this work is to obtain experimental VLE data of the ternary systems and compare it with that predicted by the Wilson,[10] nonrandom two-liquid (NRTL),[11] and universal quasichemical (UNIQUAC)[12] models, using the binary interaction parameters of the constituent's binary systems and subse-

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Table 1. Density *d*, Refractive Index n_D, and Normal Boiling Temperature 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.[a]	exptl.	lit.[a]	exptl.	lit.[b]
ethanol	786.47	785.01	1.3594	1.3594	351.46	351.44
2-propanol	780.75	781.26	1.3754	1.3752	355.40	355.41
2-butanone	799.62	800.02	1.3761	1.3764	352.68	352.79
butyl propionate	870.88	871.40	1.3992	1.4000	418.69	419.75

[a] Taken from Thermodynamics Research Center (TRC) tables.[13] [b] Taken from Daubert and Danner.[14]

Table 2. Vapor Pressure Parameters

compound	eq[a]	A_i	B_i	C_i	D_i	E_i	ref
ethanol	(2)	74.475	−7164.30	−7.3270	$3.1340 \cdot 10^{-6}$	2	*b*
2-propanol	(2)	92.935	−8177.10	−10.031	$3.9988 \cdot 10^{-6}$	2	*b*
2-butanone	(2)	114.740	−7130.00	−15.184	$1.7234 \cdot 10^{-2}$	1	*b*
butyl propionate	(1)	14.440	3467.69	−65.630			*c*

[a] Vapor pressure equations: (1) $\ln P/\text{kPa} = A - B/[(T/\text{K}) + C]$; (2) $\ln P/\text{Pa} = A + B/(T/\text{K}) + C \ln(T/\text{K}) + D(T/\text{K})^E$. [b] Parameters taken from Daubert and Danner.[14] [c] Taken from Muñoz et al.[15]

Table 3. Experimental VLE Data for Ethanol (1) + Butyl Propionate (3) at 101.3 kPa

T/K	x_1	y_1	γ_1	γ_3
418.69	0.000	0.000		1.000
404.10	0.039	0.369	1.628	1.002
392.71	0.089	0.564	1.531	1.043
385.10	0.136	0.668	1.493	1.080
379.74	0.180	0.738	1.487	1.078
375.10	0.231	0.800	1.463	1.038
370.88	0.287	0.832	1.414	1.098
367.20	0.353	0.858	1.350	1.170
364.52	0.410	0.880	1.313	1.202
362.20	0.468	0.900	1.277	1.227
360.56	0.525	0.911	1.226	1.303
359.11	0.581	0.920	1.181	1.401
357.83	0.637	0.930	1.143	1.482
356.74	0.691	0.938	1.106	1.631
355.80	0.737	0.947	1.085	1.702
354.90	0.787	0.955	1.060	1.857
354.04	0.835	0.962	1.042	2.070
353.30	0.878	0.971	1.029	2.233
352.60	0.921	0.981	1.018	2.354
351.95	0.964	0.992	1.010	2.081
351.46	1.000	1.000	1.000	

Table 4. Experimental VLE Data for 2-Butanone (2) + Butyl Propionate (3) at 101.3 kPa

T/K	x_2	y_2	γ_2	γ_3
418.69	0.000	0.000		1.000
410.79	0.050	0.239	1.008	1.003
404.78	0.090	0.393	1.050	0.999
398.76	0.134	0.520	1.082	0.996
393.32	0.187	0.619	1.051	1.002
387.90	0.252	0.697	1.010	1.033
383.75	0.297	0.756	1.033	1.021
379.66	0.345	0.803	1.052	1.018
376.18	0.398	0.838	1.044	1.030
373.09	0.448	0.869	1.046	1.020
370.49	0.506	0.890	1.021	1.054
367.37	0.571	0.914	1.016	1.062
364.72	0.628	0.932	1.017	1.070
362.47	0.683	0.947	1.015	1.076
360.32	0.737	0.960	1.016	1.072
358.40	0.789	0.971	1.018	1.033
356.77	0.835	0.979	1.019	1.026
355.31	0.877	0.986	1.022	0.969
354.43	0.921	0.991	1.006	0.995
353.25	0.968	0.996	0.999	1.039
352.68	1.000	1.000	1.000	

quently to study the possibility of using the butyl propionate as an entrainer for the separation of the azeotropic mixtures ethanol + 2-butanone and 2-propanol + 2-butanone.

Experimental Section

Chemicals. 2-Butanone ($w \geq 99.7$ %, gas chromatography (GC) assay), butyl propionate ($w > 99.0$ %, grade GC), and 2-propanol (w = 99.9 %, GC assay) were purchased from Aldrich Ltd., and ethanol ($w \geq 99.5$ %, analytical grade) was purchased from Acros.

The reagents were used without further purification, except for drying, since impurities are smaller than the detection limit of the analytical method used. The water content, determined using a Karl Fischer volumetric automatic titrator (Metrohm, 701 KF Titrino), was small in all chemicals ($w < 0.05$ %).

To avoid the alteration and hydration of the reagents in the storage and in their handling, the reagents were kept under inert atmosphere and over molecular sieves (Union Carbide, type 4 Å, 1/16 in. pellets). Moreover, once the experiment was over, the equipment was kept under inert nitrogen atmosphere.

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 uncertainty 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 temperatures are given in Table 1 together with those given in the literature.

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 was 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 Pt100 probe Hart Scientific model 5622 calibrated at the ENAC-Spanish Instituto Nacional de Técnica Aeroespacial. The uncertainty is estimated to be ± 0.01 K. To guarantee the correct operation of the temperature probe, the boiling and the fusion temperature of distilled water were measured. 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 45 min or longer. To verify equilibrium conditions, the vapor and liquid were analyzed until the variation of the mole fraction of both liquid and vapor phase was less than 0.001. 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, after calibration with gravimetrically prepared standard mixtures. A flame ionization detector was used with a 30 m, 0.454 mm inner diameter

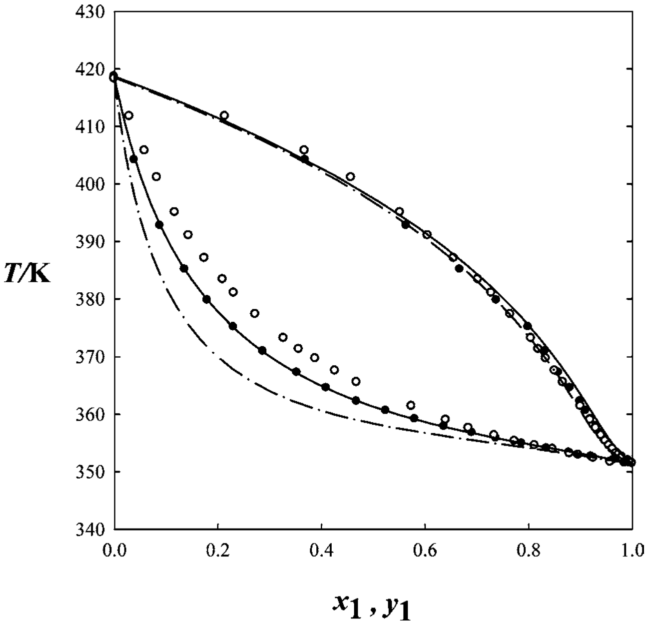

Figure 1. Experimental VLE data for the system ethanol (1) + butyl propionate (3) at 101.3 kPa: ●, experimental data; ○, ref 9; solid line, calculated using the Wilson model with the parameters given in Table 8; dotted−dashed line, predicted by UNIFAC method.

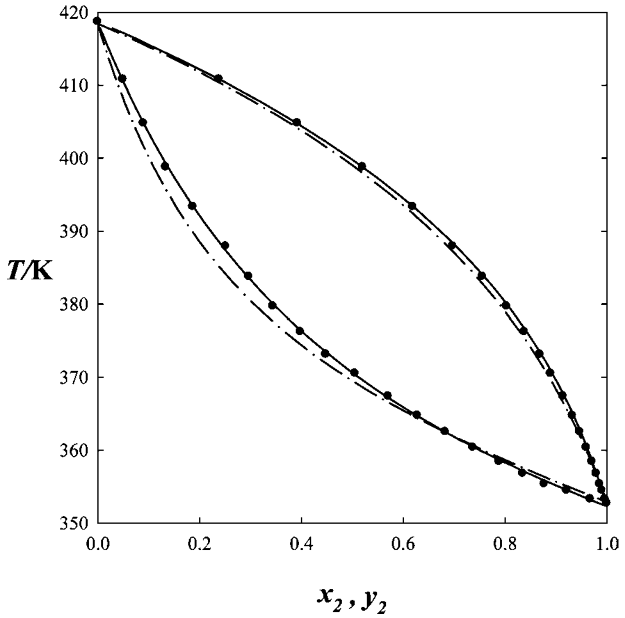

Figure 2. Experimental VLE data for the system 2-butanone (2) + butyl propionate (3) at 101.3 kPa: ●, experimental data; solid line, calculated using the Wilson model with the parameters given in Table 8; dotted−dashed line, predicted by UNIFAC method.

Table 6. Experimental VLE Data for Ethanol (1) + 2-Butanone (2) + Butyl Propionate (3) at 101.3 kPa

T/K	x_1	x_2	y_1	y_2	γ_1	γ_2	γ_3
348.70	0.412	0.537	0.471	0.529	1.276	1.106	0.022
348.97	0.571	0.368	0.595	0.402	1.149	1.215	0.578
349.83	0.210	0.755	0.286	0.714	1.462	1.029	0.031
349.84	0.505	0.391	0.566	0.423	1.196	1.169	1.069
350.28	0.306	0.593	0.409	0.586	1.400	1.052	0.564
350.45	0.687	0.202	0.727	0.258	1.100	1.355	1.487
351.40	0.893	0.050	0.911	0.082	1.023	1.677	1.231
351.67	0.797	0.100	0.838	0.143	1.042	1.461	1.894
352.13	0.403	0.398	0.542	0.431	1.309	1.088	1.302
352.22	0.200	0.659	0.314	0.676	1.527	1.028	0.677
352.40	0.499	0.298	0.629	0.341	1.215	1.142	1.409
352.85	0.599	0.196	0.722	0.245	1.140	1.229	1.554
352.87	0.099	0.791	0.182	0.817	1.740	1.013	0.111
352.88	0.303	0.489	0.455	0.520	1.422	1.043	1.138
354.74	0.391	0.309	0.599	0.355	1.349	1.064	1.353
355.01	0.494	0.203	0.702	0.249	1.238	1.130	1.379
355.16	0.690	0.047	0.873	0.072	1.096	1.393	1.794
355.50	0.303	0.391	0.507	0.449	1.429	1.038	1.234
355.63	0.591	0.099	0.809	0.135	1.165	1.224	1.513
355.96	0.094	0.684	0.201	0.776	1.794	1.011	0.879
356.55	0.193	0.501	0.373	0.583	1.592	1.017	1.164
357.46	0.376	0.216	0.664	0.270	1.400	1.062	1.265
358.26	0.299	0.295	0.572	0.365	1.470	1.028	1.193
359.00	0.094	0.588	0.223	0.731	1.781	1.010	1.053
359.52	0.468	0.050	0.838	0.081	1.314	1.307	1.204
359.73	0.188	0.403	0.415	0.516	1.613	1.019	1.189
360.77	0.361	0.119	0.747	0.171	1.451	1.104	1.093
360.85	0.048	0.629	0.128	0.826	1.843	1.008	0.993
362.60	0.092	0.490	0.246	0.682	1.749	1.014	1.103
363.45	0.176	0.305	0.465	0.440	1.676	1.026	1.132
364.46	0.214	0.218	0.570	0.324	1.632	1.028	1.105
366.60	0.089	0.394	0.272	0.624	1.729	1.028	1.096
367.63	0.167	0.210	0.532	0.343	1.745	1.029	1.057
368.19	0.243	0.056	0.759	0.104	1.672	1.151	1.008
370.02	0.050	0.427	0.154	0.724	1.539	0.997	1.126
371.54	0.084	0.300	0.303	0.552	1.716	1.038	1.074
371.91	0.159	0.114	0.620	0.218	1.833	1.071	1.000
376.81	0.083	0.209	0.363	0.442	1.742	1.028	1.038
382.69	0.080	0.112	0.449	0.288	1.854	1.070	0.993
382.79	0.043	0.222	0.208	0.546	1.591	1.021	1.017
401.84	0.030	0.039	0.275	0.164	1.672	1.094	0.984

capillary column (DB-MTBE, J & Scientific). The GC response peaks were analyzed with a Chrom-Card for Windows. Column, injector, and detector temperatures were (453.15, 473.15, and 498.15) 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 mole fractions 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 components vapor pressure P_i° for 2-propanol, 2-butanone, and butyl propionate have been measured and reported in previous papers.[8,15] However, in these papers, the vapor pressures of 2-propanol and 2-butanone were measured up to about the normal boiling temperature of the respective pure components, which are lower than the butyl propionate boiling temperature. So, to avoid excessive extrapolations of the Antoine equation for the more volatile components (ethanol, 2-propanol, and 2-butanone), we decided to use in this work equations to

Table 5. Consistency Test for the Experimental Systems Considered in VLE Measurements

system	P kPa	L_1[a]	L_2[a]	L_3[a]	AADy_1[b]	AADP[c] kPa
ethanol (1) + butyl propionate (3)	101.3	0.7174	0.2410	0.0588	0.0096	0.39
2-butanone (2) + butyl propionate (3)	101.3	0.0673	0.0844		0.0042	0.83

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

Table 7. Experimental VLE Data for 2-Propanol (1) + 2-Butanone (2) + Butyl-Propionate (3) at 101.3 kPa

T/K	x_1	x_2	y_1	y_2	γ_1	γ_2	γ_3
352.07	0.407	0.541	0.424	0.568	1.199	1.058	1.429
352.14	0.207	0.747	0.245	0.752	1.357	1.011	0.676
352.87	0.599	0.344	0.585	0.407	1.090	1.161	1.379
353.19	0.054	0.893	0.076	0.921	1.535	1.002	0.554
353.39	0.298	0.595	0.355	0.639	1.302	1.037	0.526
353.68	0.492	0.399	0.533	0.464	1.167	1.114	0.276
354.25	0.100	0.789	0.140	0.850	1.478	1.013	0.786
354.53	0.208	0.648	0.276	0.710	1.386	1.021	0.837
354.90	0.682	0.210	0.714	0.283	1.077	1.241	0.299
355.69	0.874	0.063	0.892	0.097	1.018	1.388	1.448
356.11	0.775	0.107	0.834	0.157	1.055	1.297	0.669
356.16	0.402	0.392	0.503	0.473	1.225	1.067	0.991
356.51	0.490	0.303	0.593	0.386	1.169	1.113	0.830
357.23	0.588	0.202	0.696	0.278	1.111	1.180	0.965
357.61	0.091	0.689	0.146	0.824	1.495	1.012	1.070
359.21	0.202	0.503	0.322	0.637	1.385	1.022	1.019
359.23	0.398	0.299	0.561	0.391	1.227	1.055	1.148
359.41	0.287	0.401	0.440	0.517	1.320	1.034	1.007
359.53	0.683	0.067	0.853	0.104	1.073	1.248	1.237
359.59	0.492	0.212	0.665	0.292	1.157	1.100	1.063
360.45	0.584	0.110	0.782	0.167	1.111	1.176	1.159
361.23	0.082	0.595	0.153	0.794	1.497	1.015	1.106
361.40	0.045	0.637	0.090	0.858	1.609	1.017	1.089
362.70	0.389	0.206	0.629	0.300	1.234	1.061	1.108
362.79	0.286	0.306	0.498	0.434	1.324	1.028	1.066
362.94	0.196	0.405	0.361	0.574	1.392	1.023	1.027
364.93	0.488	0.062	0.807	0.107	1.162	1.172	1.107
365.58	0.085	0.483	0.184	0.740	1.484	1.023	1.007
366.43	0.290	0.210	0.566	0.344	1.296	1.070	0.989
366.58	0.385	0.108	0.714	0.183	1.226	1.100	1.112
367.34	0.192	0.301	0.414	0.488	1.386	1.031	1.023
370.04	0.087	0.385	0.217	0.671	1.453	1.025	1.018
371.61	0.038	0.429	0.104	0.772	1.516	1.013	1.054
373.41	0.174	0.195	0.474	0.379	1.412	1.039	0.988
373.64	0.284	0.062	0.707	0.131	1.281	1.130	1.038
375.05	0.088	0.289	0.258	0.587	1.443	1.039	0.992
379.48	0.173	0.097	0.560	0.228	1.364	1.068	0.990
381.11	0.088	0.196	0.315	0.467	1.435	1.034	0.977
384.13	0.041	0.232	0.163	0.587	1.448	1.015	0.997
388.07	0.087	0.126	0.390	0.301	1.422	0.867	1.000
403.38	0.039	0.039	0.270	0.174	1.402	1.113	0.940

estimate these vapor pressures which are applicable in a larger temperature range. We took them from Daubert and Danner,[14] and the parameters are reported in Table 2.

Binary Systems. The temperature T, the liquid-phase x_i, and vapor-phase y_i mole fractions at 101.3 kPa for the systems ethanol (1) + butyl propionate (3) and 2-butanone (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:

$$\gamma_i = \frac{y_i P}{x_i P_i^\circ} \tag{1}$$

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 1, 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 1 was selected because the low pressure used in the present experiments makes these simplifications reasonable.

The activity coefficients presented in Tables 3 and 4 indicate that the ethanol (1) + butyl propionate (3) system shows positive deviations from ideal behavior and 2-butanone (2) + butyl propionate (3) does not show an appreciable deviation from ideal behavior.

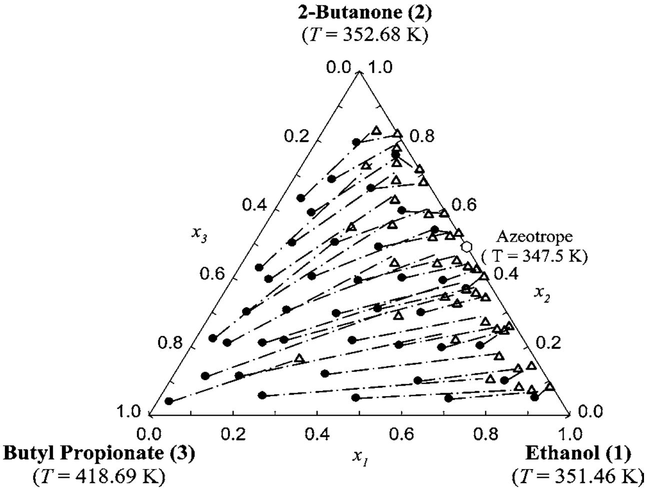

Figure 3. Diagram of VLE for the ternary system ethanol (1) + 2-butanone (2) + butyl propionate (3) at 101.3 kPa: ●, liquid-phase mole fraction; Δ, vapor-phase mole fraction; ○, azeotrope.[8] Smoothed lines calculated with the Wilson equation with the parameters given in Table 8.

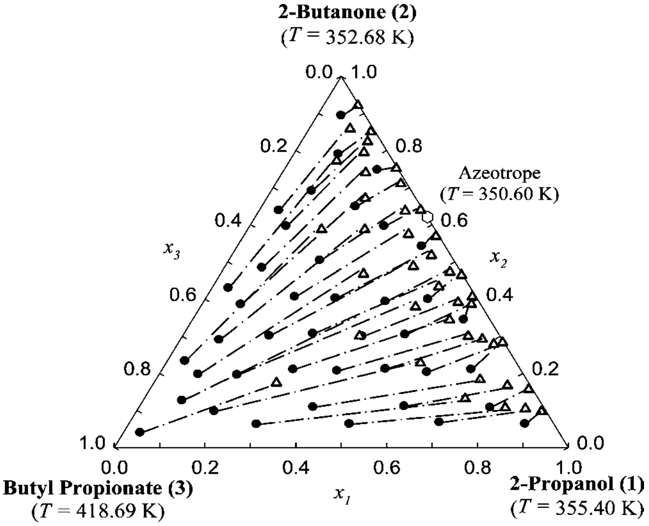

Figure 4. Diagram of VLE for the ternary system 2-propanol (1) + 2-butanone (2) + butyl propionate (3) at 101.3 kPa: ●, liquid-phase mole fraction; Δ, vapor-phase mole fraction; ○, azeotrope.[8] Smoothed lines calculated with the Wilson equation with the parameters given in Table 9.

The test of Fredenslund et al.[16] 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,[10] NRTL,[11] and UNIQUAC[12] equations. The parameters of these equations were obtained by minimizing the following objective function (OF):

$$\mathrm{OF} = \sum_{i=1}^{N}\left(\left|\frac{T_i - T_i^{\mathrm{calc}}}{T_i}\right| + |y_i - y_i^{\mathrm{calc}}|\right) \tag{2}$$

where T_i^{calc} and y_i^{calc} are the temperature and vapor fraction calculated using the thermodynamic models. The binary pa-

Table 8. Parameters and Deviations between Experimental and Calculated Values for Different G^E Models for the System Ethanol (1) + 2-Butanone (2) + Butyl Propionate (3) at 101.3 kPa

model	system $i + j$	A_{ij} J·mol^{-1}	A_{ji} J·mol^{-1}	α_{ij}	AADT[a] K	AADy_1[b]	AADy_2[b]
Wilson[c]	1 + 2[d]	2007.31	93.88		0.05		0.0024
	1 + 3	2486.10	601.12		0.10	0.0088	
	2 + 3	434.11	255.28		0.23	0.0029	
	1 + 2 + 3[e]				0.53	0.0111	0.0103
NRTL	1 + 2[d]	1322.91	698.55	0.30	0.05		0.0025
	1 + 3	4552.18	−1358.71	0.30	0.08	0.0092	
	2 + 3	1484.10	−1022.99	0.30	0.29	0.0034	
	1 + 2 + 3[e]				0.59	0.0125	0.0114
UNIQUAC[f]	1 + 2[d]	−445.40	1545.31		0.06		0.0026
	1 + 3	−242.27	1586.47		0.12	0.0088	
	2 + 3	96.43	96.59		0.24	0.0031	
	1 + 2 + 3[e]				0.54	0.0113	0.0105

[a] Average absolute deviation in temperature. [b] Average absolute deviation in vapor phase composition. [c] Molar liquid volumes of pure components from ref 17. [d] Ref 8. [e] Ternary prediction from binary parameters. [f] Volume and surface parameters from ref 17.

Table 9. Parameters and Deviations between Experimental and Calculated Values for Different G^E Models for the System 2-Propanol (1) + 2-Butanone (2) + Butyl Propionate (3) at 101.3 kPa

model	system $i + j$	A_{ij} J·mol^{-1}	A_{ji} J·mol^{-1}	α_{ij}	AADT[a] K	AADy_1[b]	AADy_2[b]
Wilson[c]	1 + 2[d]	1166.62	302.25		0.03		0.0012
	1 + 3[e]	783.98	2261.08		0.15	0.0028	
	2 + 3	434.11	255.28		0..23	0.0029	
	1 + 2 + 3[f]				0.21	0.0083	0.0077
NRTL	1 + 2[d]	513.48	917.86	0.30	0.03		0.0012
	1 + 3[e]	5362.53	−2260.07	0.30	0.17	0.0029	
	2 + 3	1484.10	−1022.99	0.30	0.29	0.0034	
	1 + 2 + 3[f]				0.25	0.0105	0.0098
UNIQUAC[g]	1 + 2[d]	−126.60	688.53		0.03		0.0011
	1 + 3[e]	200.49	489.37		0.27	0.0014	
	2 + 3	96.43	96.59		0.24	0.0031	
	1 + 2 + 3[f]				0.17	0.0079	0.0070

[a] Average absolute deviation in temperature. [b] Average absolute deviation in vapor phase composition. [c] Molar liquid volumes of pure components from ref 17. [d] Ref 8. [e] Ref 20. [f] Ternary prediction from binary parameters. [g] Volume and surface parameters from ref 17.

rameters are reported in Tables 8 and 9, together with the pertinent statistics of each VLE correlation.

The experimental data were compared with those predicted by the UNIFAC group contribution method, and the quality of the prediction can be observed in Figures 1 and 2. Moreover, in these figures the calculated data using the Wilson model and the VLE bibliographic data[9] are presented.

Ternary Systems. VLE data for the ternary systems ethanol (1) + 2-butanone (2) + butyl propionate (3) and 2-propanol (1) + 2-butanone (2) + butyl propionate (3) are reported in Tables 6 and 7 and plotted in Figures 3 and 4, respectively. These figures show the plot of the vapor and liquid mole fractions calculated with the Wilson model with the parameters given in Tables 8 and 9, respectively, against the experimental vapor and liquid phase composition. The ternary data were found to be thermodynamically consistent by the Wisniak and Tamir[18] modification of the McDermott−Ellis[19] test ($D < D_{\max}$ at all data points).

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. Tables 8 and 9 list 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 systems, representing the data successfully.

Solvent Effects. In the distillation of ideal or nonazeotropic mixtures, the component with the lowest boiling temperature is always recovered first in the distillate, while the highest boiler is recovered in the bottom. The situation is not as straightforward for an extractive distillation. With some solvents, the component with the lower boiling point will be recovered in the distillate as in ordinary distillation. For other solvents, the expected order is reversed, and the component with the higher boiling point will be recovered in the distillate. The possibility that the expected relative volatility may be reversed by the addition of solvent is entirely a function of the way the solvent interacts with each component of the binary mixture.

Several methods are available for determining whether the lower- or higher-boiling pure component will be recovered in the distillate. One useful alternative is the study of the solvent influence on the phase equilibria behavior of the azeotropic mixture, on a solvent free basis. As can be observed in Figures 5 and 6, the solvent, butyl propionate, enhances the relative volatility of alcohols (ethanol and 2-propanol, respectively) to 2-butanone in the natural way. So, the alcohol would be obtained as the overhead product in the extractive distillation column, in both cases, while the 2-butanone and butyl propionate would be obtained as the bottom products. In addition, the calculated volatility for the ternary systems on a solvent free basis, using the Wilson model with the parameters given in Tables 8 and 9 is 1.77 for the ethanol + 2-butanone and 1.36 for the 2-propanol + 2-butanone mixture, slightly lower than the value obtained in a preliminary solvent screening using Aspen ComThermo software with the UNIFAC model ($\alpha^S_{12} = 2.077$, $\alpha^S_{12} = 1.64$).

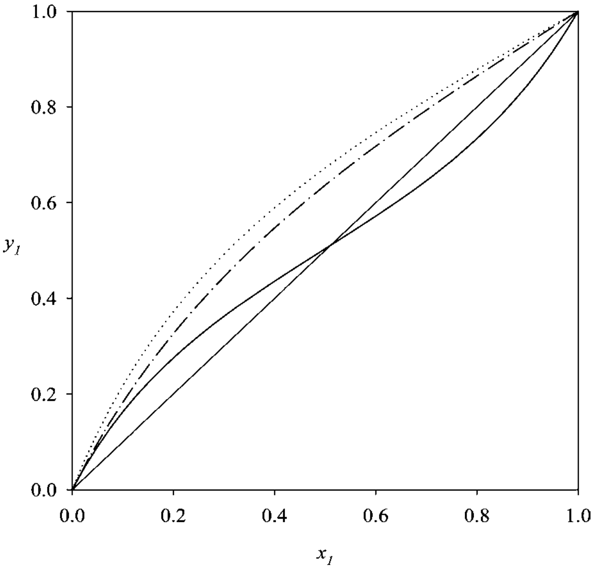

Figure 5. VLE data plotted on a solvent free basis for the system ethanol (1) + 2-butanone (2) + butyl propionate (3) at 101.3 kPa. Continuous line[8] for $x_3 = 0.00$; dotted−dashed line, calculated using the Wilson equation with the parameters given in Table 8 for $x_3 = 0.70$; dotted line, calculated using the UNIFAC model for $x_3 = 0.70$.

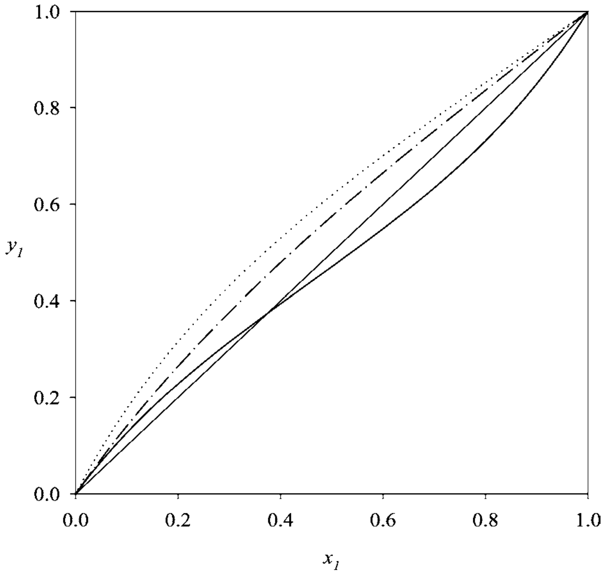

Figure 6. VLE data plotted on a solvent free basis for the system 2-propanol (1) + 2-butanone (2) + butyl propionate (3) at 101.3 kPa. Continuous line[8] for $x_3 = 0.00$; dotted−dashed line, calculated using the Wilson equation with the parameters given in Table 9 for $x_3 = 0.70$; dotted line, calculated using the UNIFAC model for $x_3 = 0.70$.

Conclusions

Consistent VLE data at 101.3 kPa have been determined for the binary systems ethanol (1) + butyl propionate (3) and 2-butanone (2) + butyl propionate (3) and the ternary systems ethanol (1) + 2-butanone (2) + butyl propionate (3) and 2-propanol (1) + 2-butanone (2) + butyl propionate (3). Although the Wilson, NRTL, and UNIQUAC models were capable of correlating all of the binary systems and yielded good predictions for the ternary systems, the correlation with the Wilson equation gives the best results for all systems.

The experimental results revealed that the presence of butyl propionate enhances the relative volatility of ethanol and 2-propanol to 2-butanone. The relative volatility on a solvent-free basis is $\alpha_{12}^{S} = 1.77$ and $\alpha_{12}^{S} = 1.36$, respectively. The change of phase equilibria behavior due to solvent is significant for both ternary systems; therefore, this solvent can be considered an effective agent for the separation of the azeotropic mixture ethanol + 2-butanone and 2-propanol + 2-butanone by extractive distillation.

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