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High-Pressure Vapor−Liquid Equilibria for Propane + 2-Butanol, Propylene + 2-Butanol, and Propane + 2-Butanol + 2-Propanol

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Vapor−liquid equilibria have been measured for propane + 2-butanol, propylene + 2-butanol, and propane + 2-butanol + 2-propanol in the temperature range of (328.1 to 368.1) K and at pressures up to 44.45 bar. The data were correlated using a group contribution equation of state for associating mixtures.

Introduction

The use of dual effect solvents (near critical extractant and high-pressure water entrainer), for the recovery and dehydration of alcohols from dilute aqueous solutions, has been proposed by Brignole et al. (1987). The present work is part of an experimental program undertaken to confirm the applicability of light hydrocarbons for this separation problem. Zabaloy et al. (1992, 1993a,b) have obtained experimental evidence which confirms the applicability of propane, propylene, and isobutane to the recovery of dehydrated 2-propanol. Additionally, Zabaloy et al. (1994) have shown that propane and isobutane are suitable solvents to recover and dehydrate ethanol and 1-propanol, respectively. However, isobutane is not recommended for dehydrating ethanol due to the formation of a binary azeotrope.

In the present work, experimental vapor−liquid equilibrium (VLE) data are reported for propane + 2-butanol and propylene + 2-butanol. The main objective is to establish whether any of these systems exhibit azeotropic behavior. Ternary data for the system propane + 2-butanol + 2-propanol are also reported.

Experimental Method and Apparatus

The experimental procedure and apparatus have been described in detail previously (Zabaloy et al., 1994), and only brief details are given below. A simplified diagram illustrating the concept of the experimental setup is shown in Figure 1.

A static equilibrium cell with a window for visual observations was used. Temperature control was performed by a solid thermostat. It consists of an aluminum shell, two heating resistances, a proportional controller (YSI Model 72), and a YSI 400 thermistor probe, placed inside a well machined on the aluminum shell. The temperature was measured within the liquid phase by a YSI 700 thermistor probe and read within ±0.1 K in a digital indicator (Cole Parmer Model 8502). The equilibrium pressure was directly measured with a Bourdon-type digital manometer (Heise-710A, range (0 to 60) bar). It was calibrated against atmospheric pressure with a mercury barometer. The accuracy of the pressure measurements was estimated by comparing our experimental vapor pressure data for propane and propylene with values obtained from the DIPPR correlation (Daubert and Danner, 1989). A relative deviation of less than 0.6% on average was found. The results are reported in Table 1.

Table 1. Comparison between Experimental and Calculated Vapor Pressures

T/K	*P*/bar (this work)[a]	*P*(lit.)/bar[b]	% rel dev[c]
	Propane[d]		
328.1	19.17	19.07	0.52
348.1	28.60	28.46	0.49
368.1	41.40	40.90	1.21
	Propylene[d]		
333.1	25.30	25.32	0.08
353.1	37.10	37.24	0.38

[a] P = experimental vapor pressure. [b] P(lit.) = vapor pressure from the DIPPR correlation (Daubert and Danner, 1989). [c] % rel dev = $100|P - P(\text{lit.})|/P$. [d] % rel dev of the DIPPR correlation <3%.

At a constant temperature, the pressure was modified by feeding alcohol or hydrocarbon into the cell, or purging some liquid or vapor from it. The difference in density of the liquid and vapor phases allowed a rapid phase separation. Clear phases were seen a few seconds after the cell was charged. The equilibration time was minimized by a magnetic stirrer. It was greater than 4 h for all the data presented here. Capillary tubes connected to commercial sampling valves were used to withdraw samples from the phases at equilibrium. A Rheodyne Model 7410 valve and a Valco C10 TX valve were used to remove samples of the liquid and vapor phases, respectively. Prior to each sample injection into the gas chromatograph, the sampling line was slowly purged. At least four samples were withdrawn from each phase after equilibration. Vapor and liquid compositions were measured by gas chromatography (Hewlett-Packard 5890 with an HP-3392A integrator). The TCD detector was calibrated by injecting known amounts of the pure components, via Hamilton syringes. A 2 m Porapak Q column was used. The oven temperature was 463.1 K.

The propane was from Matheson and the propylene was polymerization grade, with purities of 99.5% for both. The 2-propanol and 2-butanol (Merck, 99+% for both) were degassed prior to use.

Results

The VLE results for propane + 2-butanol at (328.1, 348.1, and 368.1) K and for propylene + 2-butanol at (333.1, 353.1, and 368.1) K are presented in Tables 2 and 3, respectively. x_1 and y_1 are the molar fractions of the light hydrocarbon in the liquid and vapor phases, respectively. At each temperature (T) and pressure (P), x_1 and y_1 result from averaging the values obtained for all the samples withdrawn from each phase. λ_{x_1} and λ_{y_1} are the normal distribution limits of error in the mean values of x_1 and y_1, respectively. They represent the absolute uncertainties in

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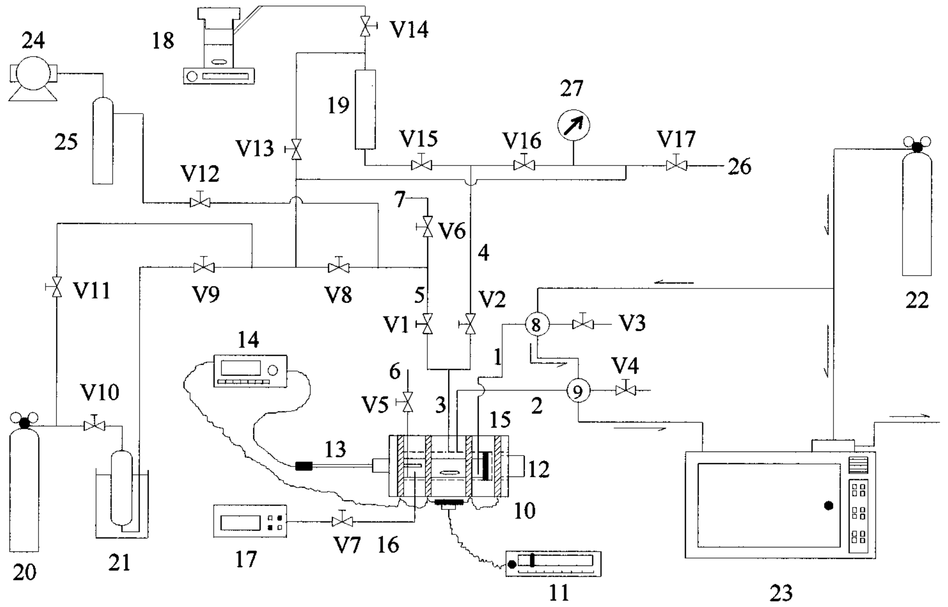

Figure 1. Experimental setup: (V1−V17) valves; (1) liquid-phase sampling line; (2) vapor-phase sampling line; (3) feeding line; (4) alcohol feeding line; (5) hydrocarbon feeding line; (6) liquid-phase purging line; (7) vapor-phase purging line; (8) four-way valve (liquid phase); (9) ten-way valve (vapor phase); (10) equilibrium cell; (11) magnetic stirrer; (12) glass window; (13) thermistor probe; (14) temperature controller and indicator; (15) solid thermostat; (16) pressure measurement line; (17) cell pressure indicator; (18) degassing cell; (19) alcohol reservoir; (20) hydrocarbon cylinder; (21) thermocondenser/thermocompressor; (22) carrier gas cylinder; (23) gas chromatograph; (24) vacuum pump; (25) vacuum trap; (26) vent; (27) pressure indicator.

Table 2. Experimental VLE Data for Propane (1) + 2-Butanol (2)

P/bar	λ_P/bar	x_1	λ_{x_1}	y_1	λ_{y_1}
		T/K = 328.1			
10.10	0.02	0.286	0.001	0.9872	0.0004
12.51	0.01	0.407	0.002	0.989	0.001
14.28	0.01	0.5232	0.0004	0.9908	0.0006
15.54	0.01	0.6365	0.0009	0.9922	0.0002
16.49	0.01	0.7389	0.0002	0.9928	0.0003
17.28	0.01	0.8356	0.0005	0.9938	0.0001
17.81	0.01	0.904	0.001	0.9944	0.0003
18.23	0.01	0.9461	0.0008	0.9955	0.0001
18.55	0.00	0.9719	0.0003	0.9965	0.0002
18.77	0.01	0.9856	0.0002	0.9977	0.0001
18.97	0.01	0.9946	0.0001	0.9990	0.0001
19.17	0.01	1.0000		1.0000	
		T/K = 348.1			
13.65	0.01	0.2858	0.0007	0.9728	0.0001
17.09	0.01	0.3983	0.0008	0.9777	0.0001
19.75	0.01	0.5125	0.0002	0.9806	0.0001
21.87	0.01	0.6306	0.0004	0.9825	0.0003
23.48	0.01	0.7368	0.0003	0.9842	0.0001
24.83	0.01	0.8319	0.0002	0.9860	0.0001
25.83	0.01	0.901	0.001	0.9881	0.0001
26.72	0.01	0.9469	0.0002	0.9907	0.0001
27.39	0.01	0.9718	0.0001	0.9934	0.0001
27.86	0.01	0.9853	0.0001	0.9960	0.0001
28.24	0.01	0.9946	0.0001	0.9983	0.0001
28.60		1.0000		1.0000	
		T/K = 368.1			
17.03	0.01	0.2745	0.0007	0.9459	0.0008
22.25	0.01	0.3953	0.0007	0.9566	0.0002
26.20	0.01	0.5114	0.0009	0.9617	0.0001
29.26	0.01	0.6240	0.0004	0.9648	0.0001
31.93	0.01	0.735	0.001	0.9677	0.0001
34.04	0.01	0.8265	0.0002	0.9706	0.0001
35.94	0.01	0.8975	0.0004	0.9746	0.0002
37.76	0.01	0.9462	0.0002	0.9802	0.0001
39.03	0.00	0.9713	0.0002	0.9866	0.0001
40.00	0.00	0.9856	0.0001	0.9920	0.0001
40.82	0.01	0.9946	0.0003	0.9967	0.0001
41.40		1.0000		1.0000	

Table 3. Experimental VLE Data for Propylene (1) + 2-Butanol (2)

P/bar	λ_P/bar	x_1	λ_{x_1}	y_1	λ_{y_1}
		T/K = 333.1			
11.20	0.01	0.305	0.001	0.9839	0.0002
15.37	0.01	0.479	0.001	0.9885	0.0008
17.74	0.01	0.5911	0.0003	0.9901	0.0004
19.05	0.01	0.6625	0.0009	0.9914	0.0003
20.55	0.01	0.7451	0.0009	0.9926	0.0002
22.12	0.01	0.8540	0.0004	0.9939	0.0003
22.96	0.01	0.9130	0.0007	0.9946	0.0001
23.53	0.01	0.9401	0.0003	0.9954	0.0002
24.16	0.01	0.9648	0.0005	0.9963	0.0001
24.52	0.01	0.9793	0.0006	0.9970	0.0001
24.88	0.01	0.9901	0.0008	0.9984	0.0003
25.30		1.0000		1.0000	
		T/K = 353.1			
14.51	0.01	0.2953	0.0008	0.9665	0.0001
20.34	0.01	0.464	0.002	0.9752	0.0002
23.79	0.01	0.568	0.001	0.9792	0.0001
26.11	0.01	0.6481	0.0007	0.9807	0.0001
28.37	0.01	0.7318	0.0008	0.9827	0.0001
31.04	0.01	0.8369	0.0003	0.9854	0.0001
32.58	0.01	0.8926	0.0007	0.9872	0.0003
33.62	0.01	0.9259	0.0004	0.9893	0.0002
34.59	0.01	0.9540	0.0008	0.9920	0.0001
35.81	0.01	0.9755	0.0002	0.9961	0.0001
36.23	0.01	0.988	0.001	0.9978	0.0001
37.10		1.0000		1.0000	
		T/K = 368.1			
18.05	0.01	0.293	0.001	0.9452	0.0008
24.35	0.01	0.442	0.002	0.9581	0.0002
28.66	0.00	0.5403	0.0004	0.9633	0.0001
32.08	0.02	0.629	0.002	0.9671	0.0006
34.92	0.01	0.7020	0.0005	0.9702	0.0002
38.76	0.01	0.8137	0.0007	0.9744	0.0002
41.17	0.01	0.8889	0.0003	0.9770	0.0001
42.74	0.01	0.9314	0.0002	0.9791	0.0003
44.45	0.01	0.9626	0.0004	0.9824	0.0004

the compositions reported, in the presence of random errors only (Shoemaker et al., 1967). Otherwise, they describe the precision of the experiments. Lower values indicate a better reproducibility. The values of pressure reported result from averaging all the values read before each sampling, from the first liquid-phase analysis to the last vapor-phase one. The symbol λ_p represents the absolute

Table 4. Experimental VLE Data for Propane (1) + 2-Butanol (2) + 2-Propanol (3)($x_2/x_3 \approx 5$)

P/bar	λ_P/bar	x_1	λ_{x_1}	x_2	λ_{x_2}	y_1	λ_{y_1}	y_2	λ_{y_2}
T/K = 328.1									
15.85	0.01	0.6676	0.0003	0.2750	0.0002	0.9912	0.0001	0.0060	0.0001
17.06	0.01	0.8058	0.0003	0.1594	0.0002	0.9926	0.0001	0.0051	0.0001
17.96	0.00	0.9174	0.0002	0.0714	0.0002	0.9943	0.0001	0.0044	0.0001
T/K = 348.1									
22.48	0.01	0.6638	0.0003	0.2783	0.0002	0.9812	0.0001	0.0135	0.0001
24.54	0.01	0.8020	0.0004	0.1627	0.0004	0.9838	0.0002	0.0117	0.0002
26.24	0.01	0.9150	0.0002	0.0737	0.0002	0.9878	0.0001	0.0095	0.0001
T/K = 368.1									
30.42	0.01	0.6647	0.0003	0.2776	0.0003	0.9630	0.0003	0.0276	0.0003
33.66	0.00	0.7974	0.0003	0.1667	0.0003	0.9667	0.0003	0.0250	0.0003
36.77	0.01	0.9152	0.0001	0.0734	0.0001	0.9744	0.0001	0.0209	0.0001

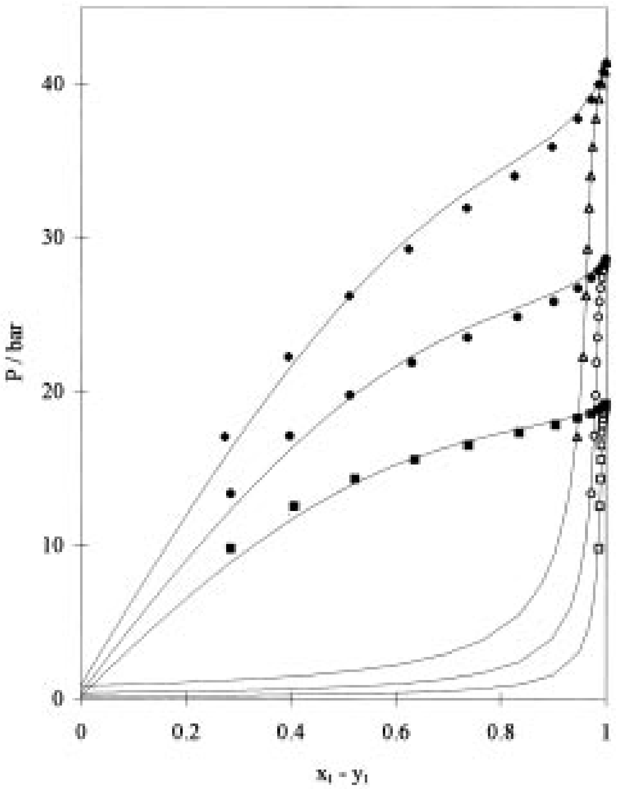

Figure 2. VLE for propane (1) + 2-butanol (2): (■, □) 328.1 K, (●, ○) 348.1 K, (◆, △) 368.1 K, (—) GCA-EOS predictions.

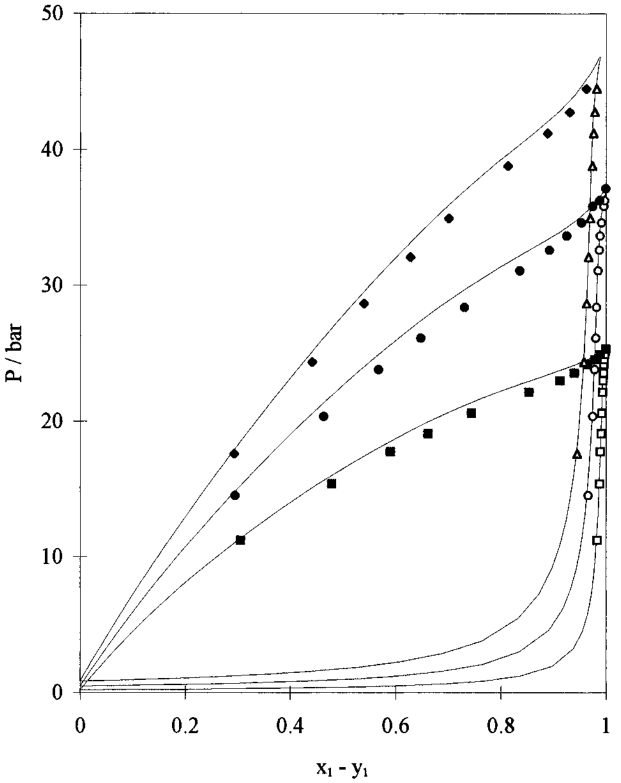

Figure 3. VLE for propylene (1) + 2-butanol (2): (■, □) 333.1 K, (●, ○) 353.1 K, (◆, △) 368.1 K, (—) GCA-EOS predictions.

fluctuation in pressure around the mean value.

Propane + 2-butanol and propylene + 2-butanol $T-P-x-y$ data are plotted in Figures 2 and 3, respectively. Both systems exhibit similar phase behavior. Under the experimental conditions of this work, there is no azeotrope formation for the binary systems studied.

VLE results for the ternary system propane + 2-butanol + 2-propanol at (328.1, 348.1, and 368.1) K are reported in Table 4. Figure 4 shows the distribution coefficient ($K = y/x$) values for 2-butanol in the binary propane + 2-butanol and the ternary system. It can be seen that under our experimental conditions, the presence of 2-propanol does not affect the distribution of 2-butanol between the vapor and liquid phases. Similar behavior is observed for the pressure and K values for propane.

Data Correlation

The pressure−temperature conditions covered in the present work require the use of a thermodynamic model with the PVT flexibility of an equation of state. Considering the highly nonideal interactions between nonpolar and polar associating components, the group contribution associating equation of state (GCA-EOS) proposed by Gros et al. (1995) was used to correlate the experimental VLE data presented in this work. This approach combines the repulsive and attractive dispersive contributions of the original GC-EOS (Skjold-Jorgensen, 1984, 1988) with the associating contribution proposed by Chapman et al. (1990) based on the statistical associating fluid theory (Wertheim, 1984a,b, 1986a,b).

Pure compound vapor pressure information and the binary VLE data obtained in this work were used to fit the GCA-EOS adjustable parameters. The isofugacity criterion for the volatile component (propane or propylene) was set as the objective function. Details on the model and parameter fitting procedure are described by Gros et al. (1995).

The GCA-EOS binary correlation results are presented in Table 5 and shown in Figures 2 and 3. The experimental data are correlated with acceptable accuracy. The GCA-EOS ternary prediction results are presented in Table 6. The predictions are in good agreement with the experimental data.

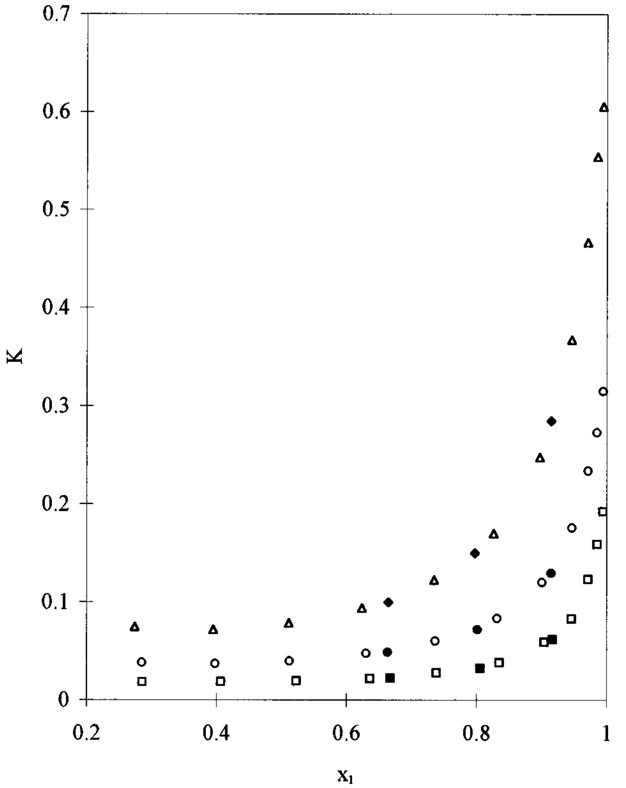

Figure 4. *K* values for 2-butanol: (■, ●, ◆) ternary system propane (1) + 2-butanol (2) + 2-propanol (3) at (328.1, 348.1, and 368.1) K. (□, ○, △) binary system propane (1) + 2-butanol (2) at (328.1, 348.1, and 368.1) K.

Table 5. Binary VLE Correlation Using the GCA-EOS Model

binary system	% AAD (P)[a]	% AAD (y_1)[a]	% AAD (y_2)[a]
propane (1) + 2-butanol (2)	3.70	0.20	9.10
propylene (1) + 2-butanol (2)	3.01	0.14	15.40

[a] Average absolute deviation = $100[\sum_i^{\text{no. points}}(\text{calc}_i/\text{exp}_i - 1)^2/\text{no. points}]^{1/2}$.

Table 6. Propane (1) + 2-Butanol (2) + 2-Propanol (3) VLE Prediction Using the GCA-EOS Model

% AAD (P)	% AAD (y_1)	% AAD (y_2)	% AAD (y_3)
2.20	0.05	3.80	5.50

Conclusions

The successful application of near critical fluid extraction to the recovery of alcohols from aqueous solutions requires the final product to be dehydrated. An adequate near critical solvent should exhibit no azeotrope formation with the recovered product. In this work, nonazeotropic behavior was found for the binaries propane + 2-butanol and propylene + 2-butanol. In conclusion, propane and propylene can be used for the near critical extraction and dehydration of 2-butanol. Additionally, ternary data were obtained to check the GCA-EOS predictive capability in multicomponent systems.

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