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Liquid−Liquid Equilibrium for the Ethanol + Water + Propylene and 2-Propanol + Water + Propylene Systems from Subcritical to Near-Critical Conditions

Andres Rojas, Hernán P. Gros, Guillermo Mabe, and Esteban A. Brignole*

PLAPIQUI-UNS/CONICET, CC 717, 8000 Bahía Blanca, Argentina

Liquid−liquid equilibria have been measured for the systems ethanol + water + propylene, and 2-propanol + water + propylene, from subcritical to near-critical conditions (313−363 K), to investigate the applicability of propylene as a solvent for the extraction of alcohols from aqueous solutions. The favorable effect of temperature on the alcohol distribution coefficient is confirmed for both systems.

Introduction

The use of light hydrocarbons as extraction solvents, at near-critical conditions, for the recovery and dehydration of alcohols, has been the subject of several experimental and separation process studies (Brignole et al., 1987; Zabaloy et al., 1992; Horizoe et al., 1993; Gros et al., 1998). A main feature of light hydrocarbons as solvents is that the alcohol distribution coefficient increases with temperature at subcritical and supercritical conditions. This effect has been confirmed for several alcohols using propane (Horizoe et al., 1993). One of the solvents that has been proposed for this application is propylene. Horizoe et al. (1993) have measured a few tie lines for the system ethanol + water + propylene, which seems to confirm the expected increase in ethanol distribution coefficient with temperature. In the present work additional data are obtained for this system. Also the system 2-propanol + water + propylene is investigated at several temperatures.

Experimental Methods and Apparatus

The experimental apparatus is similar to the one described previously by Rojas et al. (1997). A static equilibrium cell, 150 cm^3 capacity, with a glass window for visual observations is used. Temperature control is performed by a solid aluminum thermostat. The temperature is measured inside 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 is directly measured with a Bourdon-type digital manometer (Heise-710A; range 0−60 bar). The manometer was calibrated using propane an a relative deviation of less than 0.2% of experimental vapor pressure values with literature data was obtained (Rojas et al., 1997). Capillary tubes connected to commercial sampling valves are used to withdraw samples from the phases at equilibrium. A Rheodyne Model 7410 valve and a Valco C10 TX valve are used to remove samples of the aqueous and the organic phase, respectively. Some modifications were introduced to the original apparatus to control independently the pressure and temperature of the cell. The control of pressure is achieved by connecting the cell to a pressure generator (High-Pressure Equipment Co., Model 62-6-10). In addition the light (propylene) phase was circulated with a double head reciprocating pump (Eldex Model AA-100) to speed up the mixing in the cell. The main components of the equilibrium cell are shown in Figure 1.

Table 1. High-Pressure Liquid−Liquid Equilibria for the Ternary System Ethanol (1) + Water (2) + Propylene (3) (Mass Fractions), at 60 Bar

aqueous phase			organic phase		
$100w_1$	$100w_2$	$100w_3$	$100w_1$	$100w_2$	$100w_3$
		T = 313.16 K			
1.69	97.65	0.66	0.12	0.06	99.82
11.68	87.50	0.82	1.42	0.07	98.51
25.16	73.73	1.17	4.94	0.10	94.96
57.68	33.61	8.71	15.10	1.32	83.58
		T = 343.16 K			
1.74	97.76	0.50	0.21	0.08	99.71
10.41	88.79	0.84	2.70	0.38	96.92
28.34	70.73	1.39	8.12	0.58	91.31
55.83	35.69	8.48	16.82	2.69	80.49
		T = 363.16 K			
1.78	97.62	0.60	0.60	0.09	99.31
10.47	88.81	0.72	3.98	0.46	95.56
22.53	76.06	1.41	8.97	0.70	90.33
48.55	39.71	11.74	17.09	4.42	78.49

The cell, connecting lines, and ancillary vessels are evacuated to remove noncondensable gases. Thereafter the cell is partially filled, at room temperature, with an aqueous mixture. The free space of the cell is filled with liquid propylene from a gas cylinder. Pure alcohol can be added to the cell using a pressure generator directly connected to the cell. The pressure generator is also used to control the system pressure. At the beginning the cell is charged with a dilute alcohol−water mixture and is filled with propylene. Thereafter, the cell is brought to the desired temperature and pure alcohol is introduced to the system to reach the operating pressure. The cell is mixed with a magnetic stirrer for 5 to 6 h, and finally the recirculating pump is turned on for 30 min. When the pump is turned off, the system is left to rest for 6 h, to ensure complete phase separation and equilibrium conditions.

Sampling from the cell is carried out using the chromatographic sampling valves. First several samples of the aqueous phase are sent to the chromatograph until reproducible values are obtained. In the same way is made the sampling of the organic phase. The sample volumes are on the order of microliters and the sampling process did not change the equilibrium conditions. To measure another

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* To whom correspondence should be addressed. Fax: 54 2 91 4 861600.

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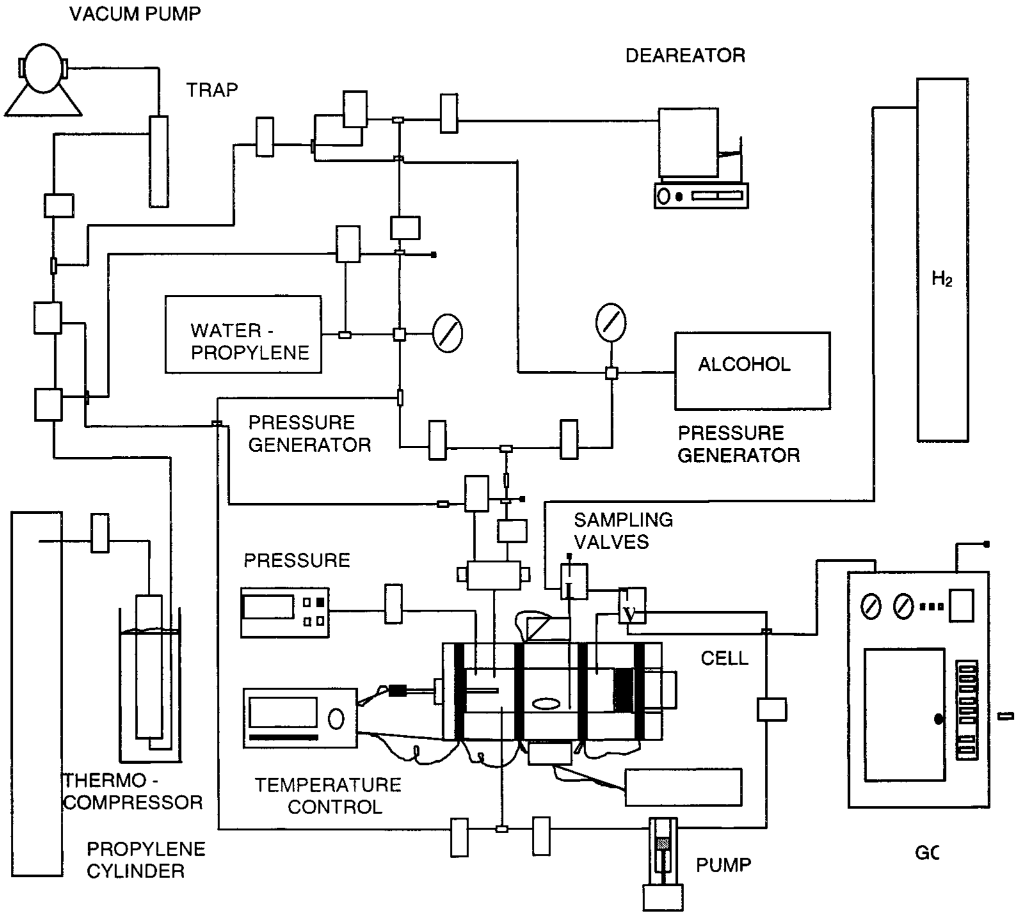

Figure 1. Equilibrium cell and ancillary equipment for high-pressure liquid−liquid equilibria.

tie line, a certain amount of mixture is withdrawn to a second pressure generator. Pure alcohol is then introduced, using the first pressure generator until the operating pressure is reached.

Phase compositions were measured by gas chromatography (Hewlett-Packard 5890 with an HP-3392A integrator). The compositions were obtained using the response factor method. The estimated accuracy in composition was within 5%. A 3.5 m long column packed with 15% Carbowax on Cromosorb P. Propylene was of polymerization grade, with purity of 99.5%. The ethanol and 2-propanol (certified minimum purity of 99.0%) were degassed prior to use.

Experimental Results

Two ternary systems were studied in the present work: (i) ethanol + water + propylene and (ii) 2-propanol + water + propylene. The system water + ethanol + propylene has been studied by Horizoe et al. (1993) and was chosen to compare the present results with literature data. Therefore, some experimental data were obtained under liquid−liquid equilibrium conditions similar to those used by Horizoe et al. (1993). The experimental data for the ternaries ethanol + water + propylene and 2-propanol + water + propylene are given in Tables 1 and 2. In Figure 2 the ethanol distribution coefficient (mass basis), between the propylene and the aqueous phase, is compared with the Horizoe et al. (1993) data. The present data of distribution coefficients, for the 313.16 K isotherm, are in good agreement with the values reported by these authors. In Figure 3 are reported the 2-propanol distribution coefficients (weight basis) at two

Table 2. High-Pressure Liquid−Liquid Equilibria for the Ternary System: 2-Propanol (1) + Water (2) + Propylene (3) (Mass Fractions)

aqueous phase			organic phase		
$100w_1$	$100w_2$	$100w_3$	$100w_1$	$100w_2$	$100w_3$
P = 16 bar					
T = 313.16 K					
1.63	98.03	0.34	0.80	0.00	99.20
8.14	91.41	0.45	6.74	0.00	93.26
12.71	86.77	0.52	15.32	0.00	84.68
13.69	85.68	0.63	17.38	0.30	82.32
18.35	80.52	1.13	23.36	0.98	75.66
20.57	78.67	0.76	33.96	2.14	63.90
29.46	69.28	1.26	48.63	10.21	41.16
34.43	64.05	1.52	50.41	20.48	29.12
T = 353.16 K					
P = 37 bar					
2.70	96.78	0.52	2.17	0.06	97.71
3.22	96.63	0.42	2.56	0.11	97.33
8.26	90.82	0.92	8.41	0.26	91.33
11.38	87.55	1.08	14.13	0.34	85.53
12.30	86.95	0.75	18.73	1.24	79.83
15.91	82.81	1.18	26.12	1.63	72.24
26.17	71.70	2.14	43.34	12.54	44.12
T = 363.16 K					
P = 60 bar					
1.83	97.67	0.50	2.23	0.03	97.73
3.60	95.85	0.55	4.14	0.06	95.80
8.44	90.43	1.13	11.18	0.11	88.71
10.52	88.56	0.92	16.05	0.45	83.50
13.09	86.03	0.88	25.66	1.64	72.70
16.94	81.91	1.15	32.85	3.95	63.20
20.07	78.54	1.39	40.14	9.18	50.68

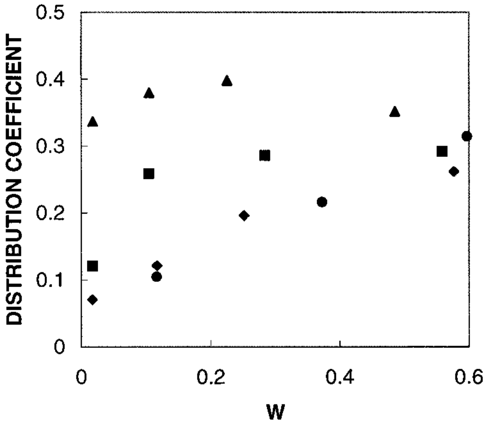

Figure 2. Ethanol distribution coefficient (mass basis) between the aqueous and the propylene phase as a function of the ethanol mass fraction in the aqueous phase: 313.16 K; (■) 343.16 K; (▲) 363.16 K (this work); (●) 313. 16 K. At 99 bar, Horizoe et al. (1993).

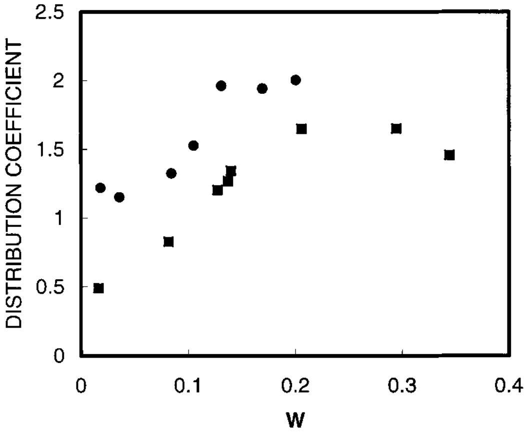

Figure 3. 2-Propanol distribution coefficient (mass basis) between the aqueous and the propylene phase as a function of the 2-propanol mass fraction in the aqueous phase: (■) 313.16 K, 16 bar; (●) 363.16 K, 60 bar.

temperatures: 313.16 and 363.16 K. In the case of 2-propanol, the mass basis distribution coefficient is greater than 1, indicating a good solvent power of propylene for this application. The distribution coefficients for ethanol and 2-propanol between propylene and the aqueous phase increase strongly with temperature at all concentrations. This behavior favors the use of hot propylene for the recovery and dehydration of alcohols from aqueous solutions. The distribution coefficients of 2-propanol between propylene and water increase with the alcohol concentration in the alcohol dilute range but level off at higher alcohol concentrations.

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