Vapor−Liquid Equilibrium Data for Propylene + Ethanol, Propylene + MEK, and Propylene + MTBE

Andrés S. Rojas R., Hernán P. Gros,[†] and Esteban A. Brignole*

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

Vapor−liquid equilibria (VLE) for propylene + ethanol, propylene + methyl ethyl ketone (MEK), and propylene + methyl *tert*-butyl ether (MTBE) were measured in the temperature range of (333 to 368) K and at pressures up to 45.5 bar. The systems show no azeotrope formation.

Introduction

The successful application of near critical extraction to the recovery of organic oxychemicals from aqueous solutions requires no azeotrope formation between the near critical solvent and the oxychemical product, among other solvent properties (Brignole et al., 1987). The present work is part of an experimental program undertaken to confirm the applicability of light hydrocarbons as near critical solvents for this separation problem. Zabaloy et al. (1992, 1993a,b) have obtained experimental evidence that 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. Lately, Gros et al. (1996) have shown that propane and propylene can be used for recovering 2-butanol from dilute aqueous solutions.

In the present work, we extend the experimental program to oxychemicals other than alcohols, including ketones and ethers. Experimental VLE data are reported for propylene + ethanol, propylene + MEK, and propylene + MTBE. One objective is to establish if any of these systems exhibit the undesirable azeotropic behavior. Also, the data are required for the process development.

Experimental Method and Apparatus

The experimental procedure and apparatus have been described in detail previously (Zabaloy et al., 1994; Gros et al., 1996). A static equilibrium cell with a window for visual observations is used. Temperature control is performed by a solid thermostat. The temperature is measured within the liquid phase by a YSI 700 thermistor probe (accurate to ±0.1 K), and read in a digital indicator (Cole Palmer, Model 8502). The equilibrium pressure is directly measured with a Bourdon-type digital manometer (Heise-710A, range (0 to 60) bar, accurate to ±0.01 bar). The manometer was calibrated against atmospheric pressure with a mercury barometer. Our experimental vapor pressure data for propylene were compared with values from the DIPPR correlation (Daubert and Danner, 1989). A relative deviation of less than 0.2% on average was obtained. The results are reported in Table 1.

Table 1. Comparison between Experimental and Calculated Vapor Pressures for Propylene

T/K	*P*/bar (this work)[a]	*P*(lit.)/bar[b,c]	% rel. dev.[d]
333.1	25.37	25.32	0.20
353.1	37.31	37.24	0.18

[a] P = experimental vapor pressure. [b] P(lit.) = vapor pressure from DIPPR correlation. [c] % Relative deviation of the DIPPR correlation < 3%. [d] % Relative deviation = $100|P-P(\text{lit.})|/P$.

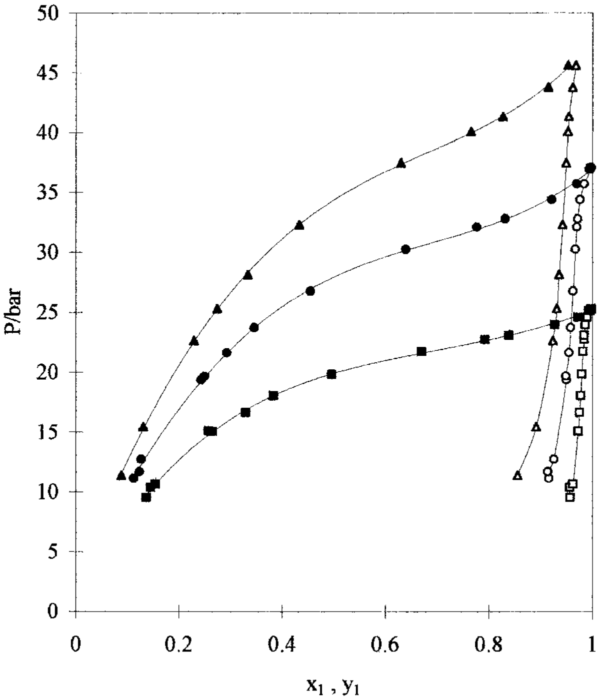

Figure 1. VLE for propylene (1) + ethanol (2). (■, □) 333.1 K, (●, ○) 353.1 K, (▲, △) 368 K. Full symbols, liquid phase; open symbols, vapor phase; (−) interconnecting line.

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 liquid and the vapor phase, respectively. 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 thermal conductivity detector was calibrated by injecting known volumes of the pure components, via Hamilton syringes. A 2 m Porapak Q column was used. The oven temperature was 413 K for propylene + ethanol

---

* Corresponding author. FAX: (54) (91) 883764.

[†] E-mail: hgros@criba.edu.ar.

S0021-9568(97)00122-2 CCC: $14.00

Table 2. Experimental VLE for Propylene (1) + Ethanol (2)

P/bar	$\lambda_{(p)}$/bar	x_1	$\lambda_{(x_1)}$	y_1	$\lambda_{(y_1)}$	P/bar	$\lambda_{(p)}$/bar	x_1	$\lambda_{(x_1)}$	y_1	$\lambda_{(y_1)}$
T/K = 333.1											
9.51	0.03	0.1369	0.0015	0.9576	0.0010	21.73	0.02	0.6703	0.0025	0.9818	0.0001
10.33	0.01	0.1451	0.0009	0.9567	0.0002	22.72	0.01	0.7926	0.0006	0.9834	0.0004
10.64	0.06	0.1546	0.0020	0.9625	0.0004	23.07	0.01	0.8385	0.0011	0.9845	0.0004
15.04	0.03	0.2655	0.0010	0.9720	0.0004	23.93	0.02	0.9275	0.0004	0.9867	0.0001
15.10	0.06	0.2580	0.0030	0.9727	0.0004	24.56	0.01	0.9721	0.0004	0.9905	0.0001
16.63	0.05	0.3297	0.0021	0.9756	0.0004	25.10	0.03	0.9935	0.0001	0.9961	0.0004
18.03	0.04	0.3840	0.0008	0.9774	0.0004	25.25	0.02	0.9968	0.0001	0.9977	0.0004
19.82	0.02	0.4963	0.0030	0.9795	0.0001	25.37		1.0000		1.0000	
T/K = 353.1											
11.12	0.02	0.1126	0.0004	0.9160	0.0004	30.28	0.02	0.6397	0.0007	0.9670	0.0001
11.67	0.01	0.1234	0.0020	0.9135	0.0016	32.12	0.02	0.7767	0.0004	0.9697	0.0001
12.71	0.09	0.1272	0.0012	0.9255	0.0001	32.81	0.03	0.8312	0.0006	0.9715	0.0007
19.34	0.05	0.2438	0.0014	0.9501	0.0004	34.39	0.02	0.9212	0.0001	0.9763	0.0004
19.66	0.03	0.2501	0.0013	0.9489	0.0001	35.73	0.01	0.9697	0.0004	0.9844	0.0001
21.62	0.06	0.2934	0.0009	0.9550	0.0004	36.93	0.02	0.9938	0.0004	0.9959	0.0001
23.69	0.04	0.3466	0.0021	0.9579	0.0004	37.08	0.02	0.9966	0.0004	0.9980	0.0001
26.79	0.03	0.4551	0.0010	0.9623	0.0008	37.31		1.0000		1.0000	
T/K = 368.0											
11.38	0.05	0.0884	0.0005	0.8550	0.0014	37.48	0.03	0.6294	0.0009	0.9493	0.0001
15.43	0.04	0.1311	0.0013	0.8915	0.0007	40.09	0.04	0.7652	0.0005	0.9525	0.0001
22.62	0.04	0.2291	0.0007	0.9236	0.0005	41.34	0.02	0.8266	0.0001	0.9546	0.0001
25.29	0.05	0.2740	0.0005	0.9307	0.0004	43.78	0.02	0.9146	0.0004	0.9615	0.0001
28.17	0.05	0.3336	0.0035	0.9357	0.0006	45.62	0.04	0.9529	0.0001	0.9679	0.0011
32.32	0.07	0.4333	0.0009	0.9420	0.0040						

Table 3. Experimental VLE for Propylene (1) + MEK (2)

P/bar	$\lambda_{(p)}$/bar	x_1	$\lambda_{(x_1)}$	y_1	$\lambda_{(y_1)}$	P/bar	$\lambda_{(p)}$/bar	x_1	$\lambda_{(x_1)}$	y_1	$\lambda_{(y_1)}$
T/K = 333.3											
7.13	0.02	0.2205	0.0032	0.9424	0.0014	20.90	0.01	0.8558	0.0004	0.9840	0.0015
9.71	0.02	0.3433	0.0003	0.9560	0.0017	22.50	0.01	0.9188	0.0004	0.9897	0.0006
11.89	0.04	0.4380	0.0021	0.9671	0.0007	24.01	0.01	0.9662	0.0001	0.9934	0.0004
13.96	0.03	0.5223	0.0004	0.9730	0.0004	24.80	0.01	0.9869	0.0001	0.9973	0.0004
15.82	0.03	0.6087	0.0009	0.9757	0.0009	25.08	0.01	0.9890	0.0004	0.9979	0.0001
18.22	0.01	0.7287	0.0004	0.9800	0.0013	25.29	0.01	0.9960	0.0001	0.9990	0.0001
19.98	0.01	0.8113	0.0001	0.9820	0.0001	25.37		1.0000		1.0000	
T/K = 353.4											
9.16	0.01	0.2208	0.0024	0.9051	0.0023	28.95	0.01	0.8294	0.0004	0.9753	0.0005
12.79	0.04	0.3267	0.0005	0.9306	0.0035	32.05	0.01	0.9105	0.0001	0.9822	0.0005
14.99	0.06	0.3948	0.0003	0.9426	0.0041	34.77	0.02	0.9630	0.0001	0.9904	0.0001
18.52	0.04	0.4976	0.0005	0.9547	0.0000	36.18	0.01	0.9846	0.0004	0.9953	0.0001
21.32	0.04	0.5848	0.0005	0.9616	0.0011	36.45	0.01	0.9868	0.0001	0.9959	0.0004
25.33	0.02	0.7170	0.0010	0.9682	0.0012	37.06	0.01	0.9950	0.0004	0.9982	0.0001
27.92	0.01	0.7974	0.0001	0.9729	0.0004	37.31		1.0000		1.0000	
T/K = 368.2											
10.60	0.05	0.2056	0.0020	0.8704	0.0110	31.34	0.04	0.7073	0.0004	0.9559	0.0001
14.82	0.06	0.3059	0.0005	0.9084	0.0010	34.40	0.02	0.7813	0.0004	0.9606	0.0006
17.37	0.06	0.3656	0.0004	0.9170	0.0065	35.20	0.03	0.8006	0.0001	0.9623	0.0005
22.14	0.05	0.4770	0.0004	0.9372	0.0007	40.26	0.03	0.9012	0.0001	0.9708	0.0005
25.64	0.03	0.5633	0.0010	0.9455	0.0004	44.13	0.02	0.9588	0.0001	0.9811	0.0001

Table 4. Experimental VLE for Propylene (1) + MTBE (2)

P/bar	$\lambda_{(p)}$/bar	x_1	$\lambda_{(x_1)}$	y_1	$\lambda_{(y_1)}$	P/bar	$\lambda_{(p)}$/bar	x_1	$\lambda_{(x_1)}$	y_1	$\lambda_{(y_1)}$
T/K = 333.3											
5.08	0.01	0.2155	0.0010	0.8122	0.0028	22.52	0.01	0.9216	0.0005	0.9888	0.0001
8.59	0.01	0.3825	0.0004	0.8987	0.0011	23.14	0.02	0.9331	0.0001	0.9905	0.0001
11.63	0.02	0.5114	0.0004	0.9321	0.0004	24.35	0.01	0.9714	0.0004	0.9955	0.0004
15.68	0.02	0.6782	0.0001	0.9591	0.0001	24.91	0.02	0.9907	0.0004	0.9983	0.0004
18.11	0.01	0.7731	0.0005	0.9710	0.0005	25.06	0.02	0.9935	0.0004	0.9984	0.0004
20.49	0.02	0.8543	0.0012	0.9809	0.0004	25.37		1.0000		1.0000	
T/K = 353.4											
6.98	0.01	0.1956	0.0004	0.7392	0.0016	31.71	0.02	0.9038	0.0006	0.9763	0.0001
10.99	0.03	0.3410	0.0004	0.8414	0.0005	33.33	0.02	0.9299	0.0001	0.9819	0.0004
15.08	0.02	0.4709	0.0017	0.8950	0.0006	35.39	0.01	0.9689	0.0001	0.9905	0.0005
21.55	0.03	0.6586	0.0006	0.9351	0.0004	36.72	0.03	0.9926	0.0004	0.9972	0.0001
25.14	0.03	0.7534	0.0005	0.9514	0.0005	37.12	0.02	0.9987	0.0004	0.9993	0.0004
28.67	0.03	0.8375	0.0004	0.9654	0.0004	37.31		1.0000		1.0000	
T/K = 368.2											
7.97	0.01	0.1606	0.0001	0.6457	0.0004	35.64	0.03	0.8247	0.0001	0.9467	0.0001
13.57	0.04	0.3282	0.0003	0.7997	0.0005	36.31	0.07	0.8397	0.0005	0.9477	0.0015
18.61	0.03	0.4605	0.0011	0.8634	0.0001	42.20	0.02	0.9260	0.0001	0.9678	0.0005
25.62	0.05	0.6235	0.0004	0.9057	0.0010	45.45	0.03	0.9683	0.0001	0.9797	0.0004
30.72	0.05	0.7330	0.0001	0.9283	0.0005						

and 463 K for propylene + MEK and propylene + MTBE. The estimated uncertainty of the equilibrium compositions results lower than ±0.0001 in mole fraction.

The propylene was of polymerization grade, with a purity of 99.5%. The ethanol, MEK, and MTBE (certified minimum purity of 99.0%) were degassed prior to use.

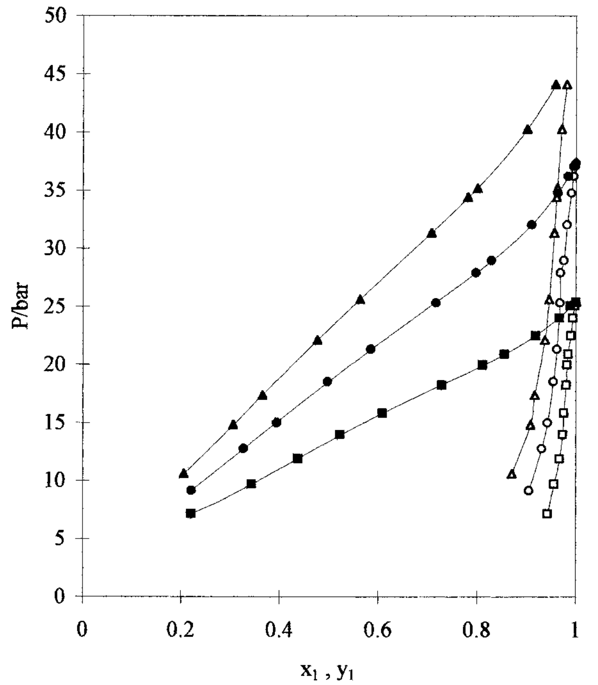

Figure 2. VLE for propylene (1) + MEK (2). (■, □) 333.3 K, (●, ○) 353.4 K, (▲, △) 368.2 K. Full symbols, liquid phase; open symbols, vapor phase; (—) interconnecting line.

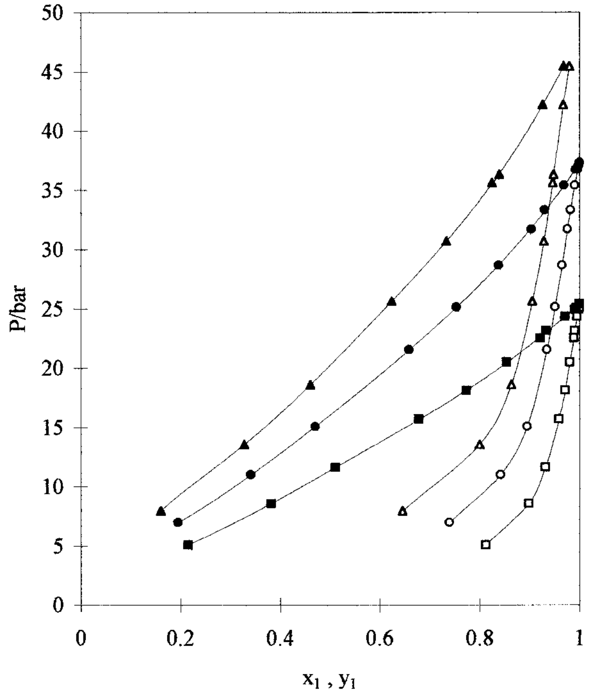

Figure 3. VLE for propylene (1) + MTBE (2). (■, □) 333.3 K, (●, ○) 353.4 K, (▲, △) 368.2 K. Full symbols, liquid phase; open symbols, vapor phase; (—) interconnecting line.

Results

The VLE data for propylene + ethanol, propylene + MEK, and propylene + MTBE at (333, 353, and 368) K, are presented in Tables 2, 3, and 4, respectively. x_1 and y_1 are the mole fractions of the light hydrocarbon in the liquid and vapor phase, 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. $\lambda_{(x_1)}$ and $\lambda_{(y_1)}$ are the normal distribution limits of error in the mean values of x_1 and y_1, respectively. They represents the precision of the experiments (Shoemaker et al., 1967). 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 $\lambda_{(p)}$ represents the absolute fluctuation in pressure around the mean value.

Propylene + ethanol, propylene + MEK, and propylene + MTBE T−P−x−y data are plotted in Figures 1, 2, and 3, respectively. It can be seen that under the experimental conditions, there is no azeotrope formation for the binary systems studied.

Conclusions

In this work, VLE data were measured for the binaries propylene + ethanol, propylene + MEK, and propylene + MTBE over a temperature range of (333 to 368) K and at pressures up to 45.5 bar. Nonazeotropic behavior was found for those systems. In principle, propylene could be a suitable near critical solvent for recovering those organic oxychemicals from dilute aqueous solutions.

Literature Cited

Brignole, E. A.; Andersen, P. M.; Fredenslund, Aa. Supercritical Fluid Extraction of Alcohols from Water. *Ind. Eng. Chem. Res.* **1987**, *26*, 254−261.

Daubert, T. E.; Danner, R. P. *Physical and Thermodynamic Properties of Pure Chemicals. Data Compilation*; Taylor and Francis: Bristol, PA, 1989.

Gros, H. P.; Zabaloy, M. S.; Brignole, E. A. High-Pressure Vapor−Liquid Equilibria for Propane + 2-Butanol, Propylene + 2-Butanol, and Propane + 2-Butanol + 2-Propanol. *J. Chem. Eng. Data* **1996**, *41*, 335−338.

Shoemaker, D.; Garland, C. W. *Experiments in Physical Chemistry*, 2nd ed.; McGraw-Hill: New York, 1967; Chapter II.

Zabaloy, M. S.; Mabe, G. D. B.; Bottini, S. B.; Brignole, E. A. The Application of High Water-Volatilities Over Some Liquefied Near-Critical Solvents as a Means of Dehydrating Oxychemicals. *J. Supercrit. Fluids* **1992**, *5*, 186−191.

Zabaloy, M. S.; Mabe, G. D. B.; Bottini, S. B.; Brignole, E. A. Isothermal Vapor−Liquid Equilibrium Data for the Binaries Propane−2-Propanol and Propylene−2-Propanol. *J. Chem. Eng. Data* **1993a**, *38*, 40−43.

Zabaloy, M. S.; Mabe, G. D. B.; Bottini, S. B.; Brignole, E. A. Vapor Liquid Equilibria in Ternary Mixtures of Water-Alcohol-Non Polar Gases. *Fluid Phase Equilib.* **1993b**, *83*, 159−166.

Zabaloy, M. S.; Gros, H. P.; Bottini, S. B.; Brignole, E. A. Isothermal Vapor−Liquid Equilibrium Data for the Binaries Isobutane−Ethanol, Isobutane−1-Propanol and Propane−Ethanol. *J. Chem. Eng. Data* **1994**, *39*, 214−218.

Received for review May 15, 1997. Accepted August 12, 1997.[⊗]

JE970122F

[⊗] Abstract published in *Advance ACS Abstracts,* October 1, 1997.