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Isothermal Vapor–Liquid Equilibrium Data for the Binaries Propane–2-Propanol and Propylene–2-Propanol

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Vapor–liquid equilibria for the 2-propanol–propane and 2-propanol–propylene systems were measured in the temperature range of 313–370 K, and at pressures up to 40 bar. The results show no azeotrope formation in either of the systems studied. The data were correlated using the Soave–Redlich–Kwong (SRK) equation of state with local composition mixing rules, and a group contribution equation of state (GCEOS).

Introduction

The recovery of dehydrated alcohols from dilute aqueous solutions is a difficult separation problem. The distillation of these mixtures requires a large amount of energy per unit of product, and in the case of ordinary distillation, the dehydration is limited by the formation of azeotropes. For these reasons the use of alternative processes, such as supercritical extraction, has received considerable attention during the last decade.

Brignole et al. (*1*) have discussed the application of dual effect (extractant and entrainer) solvents, under near critical conditions, for the separation and dehydration of ethanol and 2-propanol from aqueous solutions. On the basis of vapor–liquid equilibrium (VLE) predictions from a group contribution equation of state (GCEOS) (*2*), the light hydrocarbons appear to be the most promising near critical fluid (NCF) solvents for these separations (*1*). However, the scarcity of VLE experimental data on mixtures of alcohols with light hydrocarbons hinders at present the development of such processes.

An experimental program has been undertaken to measure the vapor–liquid equilibria in binary and ternary mixtures of 2-propanol and water with light hydrocarbons. In the present work, VLE data for the binaries 2-propanol–propane and 2-propanol–propylene are reported.

Experimental Method and Apparatus

Figure 1 presents a diagram of the equilibrium cell. It is a static-type cell, 50 cm^3 capacity, built in brass, with a 20-mm wall thickness. As shown in the figure, the lid of the cell can be assembled with either a pressure transducer screwed to a brass support or a glass disk 20 mm thick for visual observations. A copper gasket allows a tight seal between the pressure transducer and the brass support. The cell is sealed via a Viton O-ring housed in a groove at the top of the equilibrium chamber. The brass support or the glass disk is pressed against the O-ring by a simple operation, i.e., just screwing by hand a brass pressing cylinder. When the cell is sealed with the glass lid, a Teflon washer is placed on top of the lid to avoid the glass from being broken by the action of the brass cylinder. A poly(vinyl chloride) (PVC) tube screwed to the brass pressing cylinder prevents the glass window or the pressure transducer connectors from coming into contact with the fluid in the thermostatic bath.

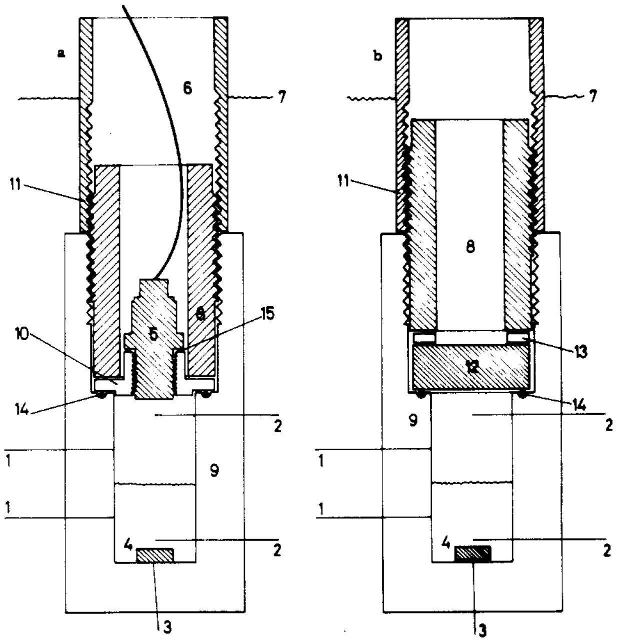

Figure 1. High-pressure equilibrium cell: (a) with pressure transducer lid; (b) with glass window: (1) feeding lines; (2) sampling lines; (3) purging line for liquid phase; (4) stirring magnet; (5) pressure transducer; (6) pressure transducer connectors; (7) thermostatic fluid level; (8) pressing cylinder; (9) cell body; (10) brass support for pressure transducer; (11) PVC tube; (12) glass window; (13) Teflon washer; (14) Viton O-ring; (15) copper gasket.

During the experiments reported in the present paper, the glass lid was only used to determine an adequate stirring velocity inside the cell. The stirring was kept slow to avoid the physical entrainment of liquid drops in the vapor phase. A Teflon-coated bar, placed inside the cell and driven by a magnetic circuit immersed in the thermostatic bath, was used for this purpose.

The sampling valves for the liquid and vapor phases were made from brass, and have a configuration similar to that proposed by Laugier and Richon (*3*). They are connected to the cell through capillary tubings and allow the withdrawal of minute amounts of samples, in the microliter range. Teflon gaskets procure a tight seal of the cell between samplings.

Figure 2 shows a diagram of the experimental setup. The equilibrium cell is immersed in a thermostatic liquid bath, regulated to within 0.1 K by a proportional controller (YSI, Model 72, plus YSI-400 thermistor probe). A pressure transducer (Sedeme, Model MD20, MD100, or CMB200), suitable for the range of temperature and pressure measurements, is mounted on the lid of the cell and connected to a digital indicator (Daytronic-3370). This device was calibrated against a bourdon-type digital manometer (Heise-710A, range 0–60 bar). Measurements of pure propane and propylene

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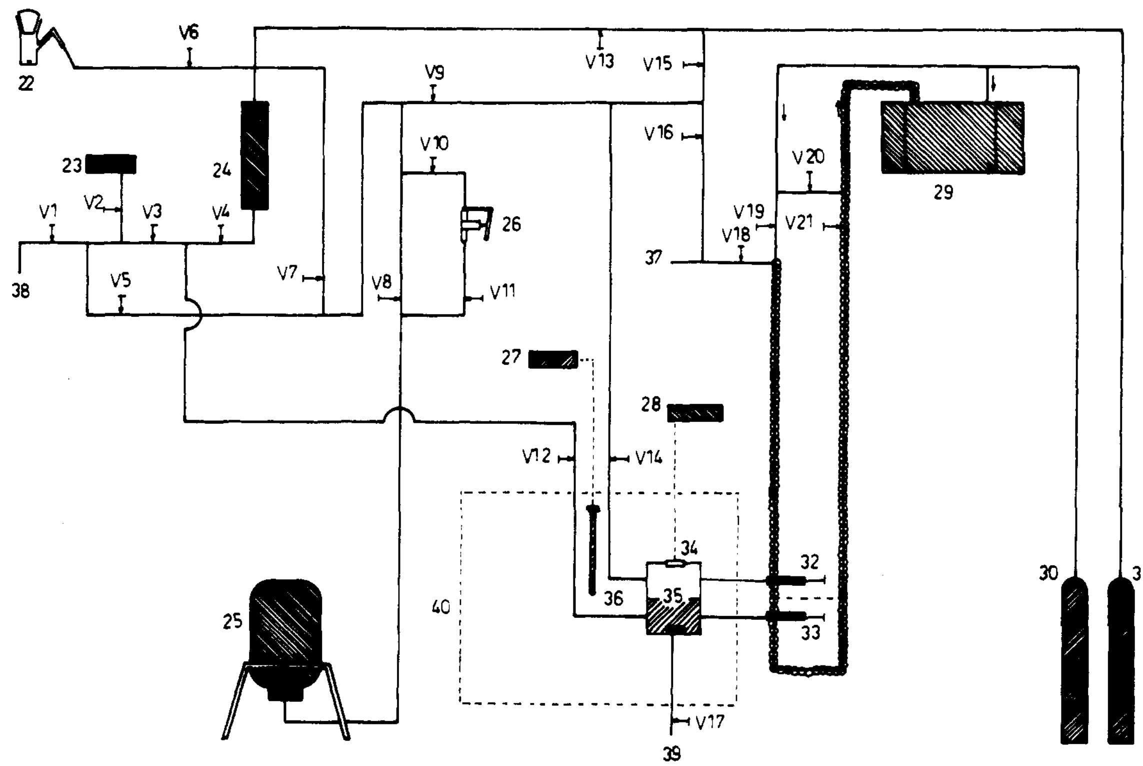

Figure 2. Experimental setup: (V1)–(V21) valves; (22) degassing cell; (23) pressure indicator (Heise); (24) alcohol reservoir; (25) gas cylinder (propane or propylene); (26) manual pump; (27) temperature indicator; (28) pressure indicator; (29) gas chromatograph; (30) helium cylinder; (31) nitrogen cylinder; (32) sampling vapor phase; (33) sampling liquid phase; (34) pressure transducer; (35) equilibrium cell; (36) thermistor; (37) vent or vacuum; (38) vacuum; (39) vent; (40) thermostatic bath.

vapor pressures in the temperature range of the binary VLE experiments showed a maximum difference of 0.35% with respect to literature values (*4*).

Vapor and liquid compositions were measured by gas chromatography (Hewlett-Packard-5890 with HP-3392A integrator). In order to assure a complete vaporization of the samples, the sampling valves and the carrier gas line connections to the gas chromatograph were kept at around 400 K by the use of heating tapes. The TCD detector response was calibrated against known amounts of pure components, injected via gas-tight syringes (Hamilton). The response coefficients were determined to within 3%. A Porapak Q column, 3 m long, was used for the separation at 433 K. The carrier gas was helium.

Before being fed to the cell, the 2-propanol is degassed in a glass, magnetically stirred, stripping cell, connected to a vacuum pump; the cell and the whole of the apparatus are also evacuated. The alcohol is then allowed to flow by gravity into a reservoir, where it is compressed by the hydrocarbon coming from the gas cylinder. The alcohol is fed to the equilibrium cell, by opening valve V4 in Figure 2. The hydrocarbon component is then charged into the cell by pumping it with a manual pump, until the pressure in the cell reaches the desired value. Further charges of alcohol can be accomplished by increasing the reservoir pressure through the manual pump.

The values of the total pressure and liquid phase level in the cell can be adjusted by feeding more alcohol and/or hydrocarbon into the cell, or by purging some liquid and/or vapor from it. For pressures close to the pure hydrocarbon vapor pressure at a given temperature, the vapor–liquid phase splitting is attained at a low alcohol global composition. Under these conditions, the gas is first loaded into the evacuated cell, until its vapor pressure is reached. At this point, having present two phases of the pure volatile component, a small amount of alcohol is charged into the cell.

Although a pressure close to the final equilibrium value was always reached after 2 or 3 h of having charged the cell, the normal practice was to wait no less than 12 h before measuring the equilibrium conditions. At this time, the cell pressure was recorded and samples from the vapor and liquid phases were injected directly into the carrier gas line, to be analyzed by gas chromatography. Pressure drops of no more than 0.25% were observed in the equilibrium cell after sampling.

The operating features of the experimental setup can be summarized as follows: the liquid and vapor phases can be easily purged, the components can be loaded independently of each other, the equilibrium conditions can be changed without losing the contents of the cell, and the equilibrium cell can be evacuated or filled with nitrogen, without altering the contents of the manifold.

The nitrogen supply to the apparatus served two purposes: first, to calibrate the cell pressure transducer at the temperature of interest, against the Heise manometer (always kept at room temperature); second, to test the sampling valves. Valves V19, V20, and V21 in Figure 2 allowed bypass of the sampling lines, whenever the gaskets of the sampling valves failed. In that case valve V18 allowed the discharge of the chemicals from the carrier line, avoiding the saturation of the chromatographic column.

The gases used for the experiments were propane (Phillips Co.) and propylene (polymerization grade), with purities of 99.98% and 99.95%, respectively. 2-Propanol (Merck, pro-analysis) was distilled and degassed prior to its use.

Results

Three isotherms at 313, 333, and 353 K were measured for the binary propane–2-propanol, and another three isotherms at 333, 353, and 370 K for the system propylene–2-propanol. A pressure range from 6 bar to the pure NCF vapor pressure at each subcritical temperature was covered. A pressure of

Table I. Experimental VLE Data for the System Propane (1)–2-Propanol (2)

T/K	P/bar	x_1	$\bar{\lambda}_{x_1}$	y_1	$\bar{\lambda}_{y_1}$
313.1	5.95	0.1497	0.0113		
313.1	7.94	0.2388	0.0110		
313.1	10.15	0.3851	0.0189		
313.1	11.35	0.5410	0.0164		
313.1	12.62	0.7822	0.0101		
313.1	13.34	0.9441	0.0046		
333.1	5.70	0.0944	0.0041	0.9202	0.0043
333.1	9.14	0.1922	0.0078	0.9491	0.0019
333.1	12.43	0.3322	0.0081	0.9699	0.0039[a]
333.1	14.74	0.4431	0.0085	0.9720	0.0014[a]
333.1	16.40	0.5413	0.0084	0.9779	0.0016[a]
333.1	18.22	0.7172	0.0095	0.9861	0.0012[a]
333.1	19.09	0.8184	0.0069	0.9937	0.0011[a]
333.1	19.82	0.9018	0.0040	0.9935	0.0012[a]
353.1	5.66	0.0683	0.0060	0.8556	0.0080
353.1	12.96	0.2045	0.0166	0.9401	0.0029
353.1	19.08	0.3708	0.0163		
353.1	22.36	0.5046	0.0233		
353.1	26.40	0.8125	0.0101	0.9794	0.0013

[a] Normal distribution limit of errors.

Table II. Experimental VLE Data for the System Propylene (1)–2-Propanol (2)

T/K	P/bar	x_1	$\bar{\lambda}_{x_1}$	y_1	$\bar{\lambda}_{y_1}$
333.1	6.74	0.1316	0.0081	0.9587	0.0016
333.1	10.59	0.2081	0.0089	0.9704	0.0019
333.1	13.29	0.3059	0.0109	0.9770	0.0014
333.1	15.36	0.3766	0.0168[a]		
333.1	17.02	0.4658	0.0267[a]	0.9839	0.0010
333.1	18.48	0.5572	0.0160		
333.1	20.52	0.6836	0.0136	0.9870	0.0014[a]
333.1	22.41	0.8395	0.0105[a]	0.9858	0.0045[a]
333.1	24.32	0.9429	0.0047[a]		
353.1	6.47	0.0843	0.0045	0.8548	0.0193[a]
353.1	12.96	0.1974	0.0084	0.9236	0.0046[a]
353.1	18.61	0.3301	0.0150		
353.1	22.88	0.4648	0.0139		
353.1	26.70	0.6083	0.0103		
353.1	29.15	0.7296	0.0084		
353.1	31.58	0.8414	0.0055	0.9769	0.0010
353.1	33.63	0.9197	0.0029	0.9772	0.0013
370.1	5.13	0.0435	0.0018	0.6587	0.0345[a]
370.1	9.08	0.0924	0.0048[a]	0.8003	0.0073
370.1	14.00	0.1553	0.0057	0.8649	0.0100[a]
370.1	17.14	0.2072	0.0090	0.8837	0.0046
370.1	23.51	0.3285	0.0121	0.9172	0.0086[a]
370.1	29.37	0.4753	0.0133		
370.1	37.08	0.7244	0.0117	0.9492	0.0068[a]
370.1	38.73	0.7798	0.0117	0.9558	0.0051[a]
370.1	40.87	0.8594	0.0073	0.9677	0.0030[a]

[a] Normal distribution limit of errors.

6 bar was the minimum cell pressure required for a good operation of the sampling devices. The T-P-x-y data sets are shown in Tables I and II and Figures 3 and 4. There are some data points for which no information is given on the experimental vapor-phase composition. Most of those points lie in the region of low alcohol concentration in the vapor phase. A bad chromatographic resolution or the lack of an acceptable level of reproducibility between consecutive vapor samplings made the value of the vapor-phase composition in those experiments rather uncertain.

Also given in Tables I and II are the estimated absolute uncertainties ($\bar{\lambda}_{x_1}$ and $\bar{\lambda}_{y_1}$) in the mean values of the equilibrium liquid and vapor compositions reported in this work. They were estimated through the errors associated with the chromatographic calibration and analysis. During calibration of the detector, at least five injections were performed for each known amount of pure component. On the other hand, a minimum of four samples per phase were analyzed for each equilibrium point. The uncertainties reported in Tables I and II correspond to the maximum between the $\bar{\lambda}$ value obtained from an analysis of the propagation of errors (*5*) and that corresponding to a normal distribution around the mean composition. An italic a by the uncertainty value in Tables I and II corresponds to a normal distribution maximum. For these experimental points, the uncertainty value is indicating the presence of other errors on top of the chromatographic ones (most probably in the sampling line).

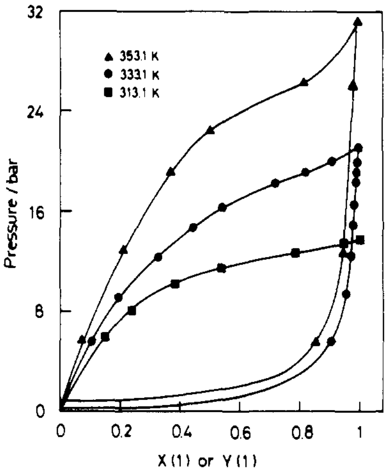

Figure 3. Vapor–liquid equilibrium data for propane (1)–2-propanol (2).

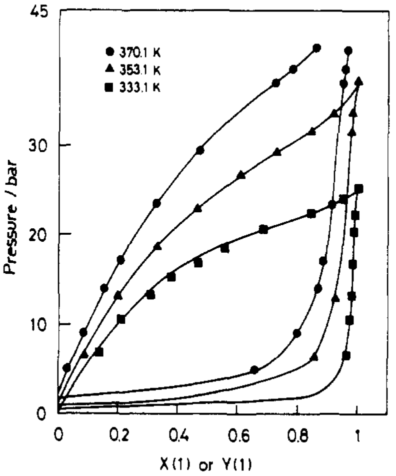

Figure 4. Vapor–liquid equilibrium data for propylene (1)–2-propanol (2).

Data Correlation

The thermodynamic model representing the type of mixtures studied in this work should be able to describe the properties of solutions of polar molecules in a dense gas phase. The large variations in density with temperature and pressure, together with the highly nonideal interactions between polar and nonpolar components, favor the use of a thermodynamic model that combines the PVT predictive capability of an equation of state with the flexibility provided by the activity coefficient models. On these bases, the Soave–Redlich–Kwong (SRK) (*6*) equation of state, with the mixing rules suggested by Huron and Vidal (*7*), and the group contribution equation of state (GCEOS) (*2*) were used to correlate experimental VLE data from this work and from the literature (*8–16*) on mixtures of alcohols with nonpolar gases. The SRK equation of state with the traditional quadratic mixing rules was also used for comparison.

Prior to the VLE data reduction, a fit of the models to the pure component vapor pressures was performed. The fitting

Table III. Correlation of VLE Data with Equations of State

system	equation	parameter	Δx_1/ %	Δy_2/ %
propane–2-propanol[b]	GCEOS	k_{12} = 1.0177 k'_{12} = 0.283 65 α_{12} = 0.754 13	10	8.7
	SRK	k_{12} = 0.075	5.6	14.1
	SRK–Vidal	$C_{12}{}^{a}$ = 45 275.7 $C_{21}{}^{a}$ = 2859.7 α_{12} = 0.248	4.7	11.6
propylene–2-propanol[c]	GCEOS	k_{12} = 0.945 47 k'_{12} = 0.00 α_{12} = 1.2277	5.0	9.9
	SRK	k_{12} = 0.068	4.4	21.1
	SRK–Vidal	$C_{12}{}^{a}$ = 16 310.9 $C_{21}{}^{a}$ = 926.57 α_{12} = 0.434	5.6	21.8
propane–methanol[d]	GCEOS	k_{12} = 0.8597 k'_{12} = −0.1535 α_{12} = 0.257 91	18.2	12.5
	SRK	k_{12} = 0.065	16.8	14.0
	SRK–Vidal	$C_{12}{}^{a}$ = 9131.6 $C_{21}{}^{a}$ = 4641.8 α_{12} = 0.405	2.0	9.6
propane–ethanol[e]	GCEOS	k_{12} = 1.0414 k'_{12} = 0.1711 α_{12} = 0.5261	6.9	16.0
	SRK	k_{12} = 0.022	3.8	12.3
	SRK–Vidal	$C_{12}{}^{a}$ = 981.1 $C_{21}{}^{a}$ = 1289.4 α_{12} = −2.95	3.9	16.8
CO_2–ethanol[f]	GCEOS	k_{12} = 1.00 k'_{12} = 0.012 56 α_{12} = 0.1929	4.8	28.4
	SRK	k_{12} = 0.107	4.2	27.5
	SRK–Vidal	$C_{12}{}^{a}$ = 4556.9 $C_{21}{}^{a}$ = 1984.4 α_{12} = 0.760	1.6	25.6
CO_2–methanol[g]	GCEOS	k_{12} = 0.958 11 k'_{12} = 0.034 981 α_{12} = 0.1364	4.9	1.7
	SRK	k_{12} = 0.038	6.7	13.8
	SRK–Vidal	$C_{12}{}^{a}$ = 5183.7 $C_{21}{}^{a}$ = −366.1 α_{12} = 0.375	3.0	11.4

[a] J/(mol g). [b] This work; T/K = 313–353; P/bar = 5–26.4. [c] This work; T/K = 333–370; P/bar = 5–40.3. [d] References 9 and 14; T/K = 311–373; P/bar = 2.1–42.8. [e] References 10 and 12; T/K = 325–350; P/bar = 0.3–30. [f] Reference 15; T/K = 304–349; P/bar = 37–129. [g] References 8, 11, 13, and 16; T/K = 313–353; P/bar = 5–26.4.

parameters were the hard-sphere diameter in the GCEOS equation and the slope of the energy parameter temperature dependence in the SRK equation of state.

Table III shows the results of the VLE data reduction. The isofugacity criterion for the volatile component (propane, propylene, or CO_2) was set as the objective function for the data reduction. The GCEOS parameters reported in Table III correspond to the interactions between molecular species. The nonrandomness parameter (α_{12}) in this model was considered to be symmetric. The k_{ij} values for the SRK equation are the classical binary interaction coefficients for its energy parameter. Finally, the parameters for the SRK–Vidal model correspond to the nonrandom two-liquid (NRTL) equation (*17*), as applied to the mixing rule of the energy parameter. The values under Δx_1/% and Δy_2/% represent the percentage differences between the predicted and the experimental compositions of the volatile component in the liquid phase and of the alcohol in the vapor phase, respectively. As can be inferred from Table III, the three models gave a similar correlation of the experimental data. The representation of the VLE data is not very good. The models seem to be lacking a molecular association term, to take into account the hydrogen bonding effect in these systems.

Conclusions

The successful application of supercritical fluid extraction to the recovery of oxichemicals from aqueous solutions requires the final products to be dehydrated. Brignole et al. (*1*) have proposed the following criteria for the selection of near critical fluids (NCF): (a) water entrainment property; (b) critical temperature in the range 350–450 K; (c) no azeotrope formation with the recovered products. The experimental data obtained in this work show that both propane and propylene comply with this last requirement. On the other hand, the binary VLE data, together with some experimental results for the ternaries water–alcohol–NCF, show both solvents to present the water entrainment property (*18*). From these results it can be concluded that propane and propylene are adequate solvents for the recovery of alcohols from aqueous solutions, by supercritical extraction.

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