High-Pressure Vapor−Liquid Equilibrium Data for (Carbon Dioxide + Cyclopentanol) and (Propane + Cyclopentanol)

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Isothermal vapor−liquid equilibrium (VLE) data are presented for (carbon dioxide + cyclopentanol) and (propane + cyclopentanol). Measurements were undertaken using a static analytic high-pressure cell at three temperatures ranging from (353.15 to 393.15) K for (propane + cyclopentanol) and at two temperatures (373.15 and 403.15) K for (carbon dioxide + cyclopentanol). The uncertainties in the measurements of temperature and pressure are ± 0.2 K and ± 0.0075 MPa, respectively, and less than 2 % for composition. The binary VLE data were regressed using the phi−phi (direct) method to obtain correlated thermodynamic model parameters. Data reductions using the Peng−Robinson cubic equation of state with the Stryjek−Vera alpha function, along with the Wong−Sandler mixing rule incorporating the NRTL activity coefficient model, satisfactorily represented both systems for all the measured isotherms. All the measured data sets were tested for thermodynamic consistency. The two tests used were the Chueh, Muirbrook, and Prausnitz area test and, probably the most rigorous and theoretically correct of all, the Christiansen and Fredenslund test. The results suggest that the data are consistent. For (propane + cyclopentanol), the latter test indicated a small bias in vapor composition for the 353.15 K isotherm. Henry's constants were also computed for both systems from the measured experimental data by application of the Krichevsky−Illinskaya equation.

Introduction

In previous HPVLE studies,[1−4] we have reported data for propane or carbon dioxide with toluene, methanol, or propanol at several isotherms, ranging from subambient (e.g., 263 K) to 393 K. Such data are scarce and find application in supercritical extraction procedures. A static analytical apparatus is used in our studies and, as a result of a complete thermodynamic data set measurement ($P-T-x-y$), permits thermodynamic consistency testing to evaluate data quality.

Data for (propane + cyclopentanol) measured at three temperatures, and for (carbon dioxide + cyclopentanol) measured at two temperatures, were modeled satisfactorily with the Peng−Robinson equation of state with the alpha function according to Stryjek and Vera.[5] The mixing rule utilized was the theoretically sound Wong−Sandler.[6]

Cyclopentanol is a useful intermediate for the production of cyclopentanone, e.g., from cyclopentene.[7] The ketone finds application in pesticides and perfume components.[7]

The Krichevsky−Illinskaya[8] procedure was used for determining Henry's law constants as functions of temperature.

Experimental Section

Materials. Carbon dioxide was supplied by Fedgas with a certified minimum mole fraction purity of 0.99995. The major impurities indicated were oxygen, nitrogen, water, sulfur dioxide, and some hydrocarbons, all of which were in less than 10 ppm quantities. GC analysis of the gas verified a mole fraction purity of greater than 0.9999. Instrument grade propane was supplied by Fedgas with a certified minimum mole fraction purity of 0.995. The major impurities were ethane, propylene, isobutane, and *n*-butane, all of which were in less than parts per million quantities. GC analysis of the gas verified a mole fraction purity of greater than 0.99. Cyclopentanol was supplied by Fluka with a mole fraction purity stated to be greater than 0.99. GC analysis verified a mole fraction purity of greater than 0.99 with no significant impurities. Cyclopentanol was used without further purification.

Experimental Apparatus. The high-pressure static equilibrium apparatus used in this study has been described in detail in previous publications.[1,2] The variable volume feature of the equilibrium cell, produced by a stepper-motor driven piston with a pressure-compensating mechanism, was useful for adjustment of the initial pressure to values higher than the supplied cylinder pressure (or that obtained from the specially designed propane compressor) and could also be used for measuring mixture second virial coefficients.[1] A schematic diagram of the cell is shown in Figure 1 with the equipment layout illustrated in Figure 2. A four-bladed flat impeller which is magnetically driven produced a strong vortex in the liquid with vapor bubbles drawn in and dispersed through the liquid. This circulating vapor flow also promoted uniformity of concentration in the vapor phase. The radial pressure gradient in the liquid was used to produce a substantial flow of representative liquid through a six-port high-temperature GC sampling valve. Sampling did not disturb the equilibrium, as verified by the monitored interior cell pressure. Both liquid and vapor samples were homogenized and diluted with carrier gas (Helium) in an evacuated static jet mixer before conveyance to a GC.

A Sensotec Super TJE pressure transducer [(0 to 15) MPa absolute] was used to measure pressures in the equilibrium cell. The transducer was certified accurate to within ± 0.05 %. The pressure transducer was calibrated using an Ashcroft Modular Digital Indicator (MDI). The calibration module was traceable

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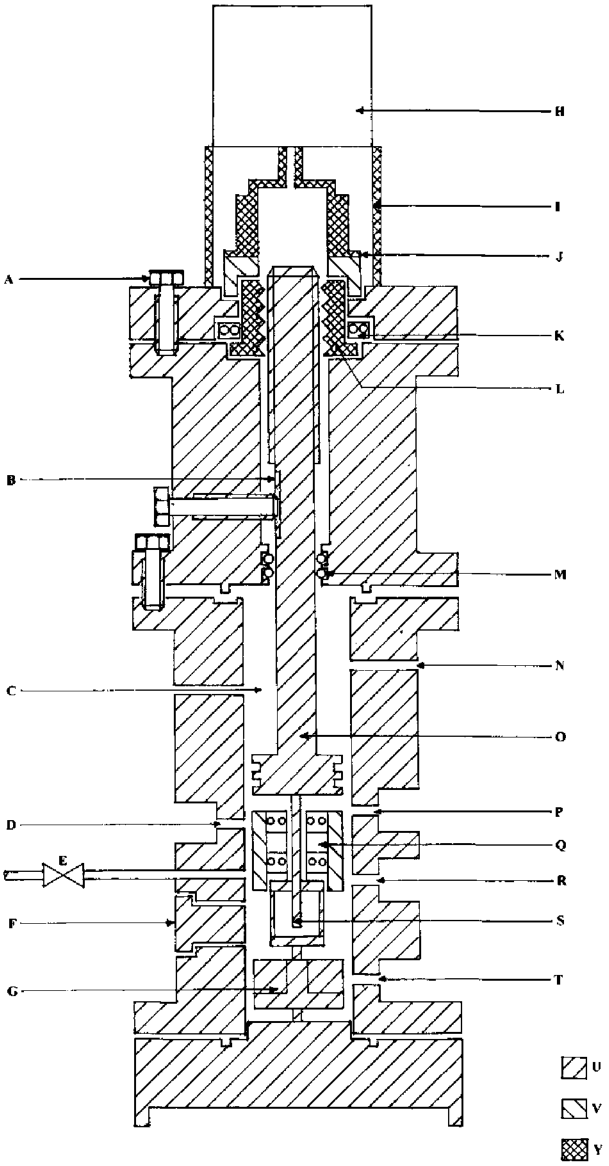

Figure 1. Schematic of the equilibrium cell assembly. A, 8 mm diameter SS bolts; B, slot; C, nitrogen space controlled pressure; D, to pressure transducer; E, fill/evacuate valve; F, two viewing windows; G, lower impellor; H, reversible stepper motor; I, brass stand; J, micrometer dial; K, high trust ball bearing; L, brass rotating nut; M, O-ring; N, to pressure transducer nitrogen and vent; O, piston; P, GC valve; Q, composite stirrer; R, GC valve; S, liquid manipulation device; T, GC valve; U, stainless steel; V, teflon; Y, brass.

to NIST. The resultant uncertainty in the equilibrium cell pressure is ± 0.0075 MPa.

Temperatures within the equilibrium cell and the air-bath were measured using platinum resistance thermometer probes (Pt-100) which were calibrated against a Hewlett-Packard 2804 A quartz thermometer with NIST traceability. The uncertainties in the temperature measurement are ± 0.2 K.

Sample analysis was undertaken by gas chromatography using a Chrompak CP 9000, fitted with a Porapak Q column employing both thermal conductivity and flame ionization detectors. For each component, a plot of the GC area versus the number of moles injected was determined as part of the detector calibration process. These average peak areas correspond to within ± 1.0 % for liquids and ± 1.5 % for gases. The uncertainties in the measured mole fractions are less than 2 %.

The experimental procedure is described in detail in a previous publication.[2]

Data Reduction

The direct (equation of state) method was used for reduction of the measured $P-T-x-y$ data. The fugacity coefficients, expressed in eq 1, were calculated from the Peng−Robinson[9] EOS with the alpha correlation of Stryjek−Vera[5] (PRSV) and the Wong−Sandler[6] mixing rule.

$$\hat{f}_i^{\mathrm{L}} = x_i\hat{\varphi}_i^{\mathrm{L}}P = \hat{f}_i^{\mathrm{L}} = x_i\hat{\varphi}_i^{\mathrm{L}}P \tag{1}$$

The NRTL activity coefficient model was used to describe the liquid phase in the mixing rule. All parameter-optimization computations were undertaken using the least-squares fitting method of Marquardt[10] which performs an optimum interpolation between the Taylor series and the gradient methods. The parameters obtained from the VLE data by the above method were k_{ij} (the binary interaction parameters in the Wong−Sandler mixing rule) and the parameters Δg_{12} and Δg_{21} in the NRTL model for G^{E}.

For pure component properties, the κ_i parameter found in the Stryjek−Vera[5] alpha correlation was regressed using literature vapor pressure data. The objective function used in these computations was

$$S = \sum_{i=1}^{n}\left(\frac{P_i^{\mathrm{exp}} - P_i^{\mathrm{calc}}}{P_i^{\mathrm{exp}}}\right)^2 \tag{2}$$

The optimized values for the alpha correlation parameters are listed in Table 3. The deviations of the calculated pressures from the literature values are expressed as

$$\mathrm{AAD}\ \%\ (\Delta P) = \frac{100}{n}\sum_{i}^{n}\frac{|P_i^{\mathrm{exp}} - P_i^{\mathrm{calc}}|}{P_i^{\mathrm{exp}}} \tag{3}$$

The binary interaction and G^{E} model parameters in the binary VLE data reduction computations were determined by least-squares regression of the experimental $P-T-x-y$ data as described above. The objective function for the least-squares regression was

$$S = \left[\sum_{i=1}^{n}\left(\frac{P_i^{\mathrm{exp}} - P_i^{\mathrm{calc}}}{P_i^{\mathrm{exp}}}\right)^2 + \left(\frac{y_i^{\mathrm{exp}} - y_i^{\mathrm{calc}}}{y_i^{\mathrm{exp}}}\right)^2\right] \tag{4}$$

In eq 4, the sum of the errors between the calculated or predicted pressure and vapor phase compositions and the experimentally measured properties is minimized. The calculated pressure and vapor mole fractions were obtained using a bubble pressure computation in the direct method.

The optimized binary interaction and G^{E} model parameter values were used to predict the entire $P-x-y$ diagram for that specific isotherm.

The deviations of the experimental pressures and vapor compositions from the correlated or predicted values are expressed in terms of the absolute error, AE %

$$\mathrm{AE}\ \% = \frac{100}{n}\sum_{i}^{n}\left(\frac{|P_i^{\mathrm{exp}} - P_i^{\mathrm{calc}}|}{P_i^{\mathrm{exp}}}\right)^2 + \left(\frac{|y_i^{\mathrm{exp}} - y_i^{\mathrm{calc}}|}{y_i^{\mathrm{exp}}}\right)^2 \tag{5}$$

Thermodynamic Consistency Testing

Thermodynamic consistency tests were performed on all five isotherms measured in this study. The Chueh et al.[11] area test, an extension of the Redlich and Kister[12] test for low pressure isothermal VLE data, suffers, although to a lesser extent, from the same deficiencies as the latter and is more useful in a negative sense, i.e., permits rejection of data that are *not* consistent. The Christiansen and Fredenslund[13] test is a *model-free* test but is complex and involves considerable computation. It is based on fewer assumptions, and application of the test produces values of Henry's constant, H_{12}, for systems with a supercritical component, as in the present study. Details of the two tests are given in the above references and also in Naidoo[4] and Raal and Mühlbauer.[14]

Chueh et al. Consistency Test. The test requires comparisons between the sum of values calculated from eqs 6 and 7

$$\int_{x_2=0}^{x_2} \ln \frac{K_2}{K_1} \mathrm{d}x_2 + \int_{x_2=0}^{x_2} \ln \frac{\hat{\phi}_2^{\mathrm{V}}}{\hat{\phi}_1^{\mathrm{V}}} \mathrm{d}x_2 + \frac{1}{RT}\int_{x_2}^{x_2} V^{\mathrm{L}} \mathrm{d}P = \mathrm{LHS} \tag{6}$$

$$\mathrm{RHS} = \left[\ln K_1 + \ln \frac{\hat{\phi}_1^{\mathrm{V}} P}{\phi_1^{\mathrm{sat}} P_1^{\mathrm{sat}}} + x_2\left(\ln \frac{\hat{\phi}_2^{\mathrm{V}}}{\hat{\phi}_1^{\mathrm{V}}} + \ln \frac{K_2}{K_1}\right)\right]_{x_2=x_2} \tag{7}$$

K_i are the equilibrium constants (y_i/x_i) and V^{L} is the liquid molar volume, evaluated by assuming the partial molar volumes to be independent of pressure and composition. Chueh et al. suggest a percentage inconsistency (eq 8) of less than 5 % to be satisfactory, generally the uncertainties introduced by an (approximate) EOS.

$$\%\ \text{inconsistency} = \frac{|\mathrm{LHS} - \mathrm{RHS}|}{\dfrac{\mathrm{LHS} + \mathrm{RHS}}{2}} \cdot 100 \tag{8}$$

Christiansen and Fredenslund Test. The Christiansen and Fredenslund[13] test uses model-free equations to predict the vapor phase compositions, y_i, which can then be compared with the measured values over the full composition range. The method is applicable to both isobaric and isothermal data and requires simultaneous solution of one algebraic and two differential equations.[4]

Henry's Law Constant

The Krichevsky−Illinskaya[8] (KI) equation was used to represent the pressure effect on the solubility of carbon dioxide and propane in cyclopentanol. The KI model is given by

$$\ln \frac{\hat{f}_1}{x_1} = \ln H_{1,2}^{(P_2^{\mathrm{sat}})} + A(x_2^2 - 1) + \bar{V}_1^{\infty} \frac{(P - P_2^{\mathrm{sat}})}{RT} \tag{9}$$

where component 1 refers to the light component and 2 to the heavy liquid. $H_{1,2}^{(P_2^{\mathrm{sat}})}$ is Henry's law constant at the vapor pressure of the heavy component, P_2^{sat}. A is the Margules constant, and $\bar{V}_1^{\infty}$ is the partial molar volume of the light component at infinite dilution. In this study, $\bar{V}_1^{\infty}$ was estimated from

$$\bar{V}_1 = -\left[\frac{\left(\dfrac{\partial P}{\partial n_1}\right)_{T,V,n_2}}{\left(\dfrac{\partial P}{\partial V}\right)_{T,n_1,n_2}}\right] \tag{10}$$

The Peng−Robinson (PR) EOS with the van der Waals mixing rules was used in the calculation of $\bar{V}_1$ at the system temperature in a manner similar to that of Prausnitz and Chueh.[15] The fugacity of the light component in the vapor phase $\hat{f}_1$ was computed from

$$\hat{f}_1 = \hat{f}_1^{\mathrm{V}} = y_1 \hat{\phi}_1^{\mathrm{V}} P \tag{11}$$

Results

Propane + Cyclopentanol System. The experimental data points for the 353.15 K, 373.15 K, and 393.15 K isotherms are listed in Table 1. A graphical illustration of the experimental data points for each isotherm is shown in Figure 3. The (propane + cyclopentanol) isotherms represent new data.

Carbon Dioxide + Cyclopentanol System. The experimental data points for the 373.15 K and 403.15 K isotherms are listed in Table 2. A graphical illustration of the experimental data points for each isotherm is shown in Figure 4. The (carbon dioxide + cyclopentanol) isotherms represent new data.

Data Reduction. The regressed κ_i parameters for the pure components are tabulated in Table 3. The model predictions using the correlated parameters for (propane + cyclopentanol) isotherms are included in Figure 3. The regressed model parameters for the system are provided in Table 4. Good modeling of the data was achieved with the PRSV EoS with the Wong−Sandler mixing rule. For (carbon dioxide + cyclopentanol), the model predictions using the correlated parameters for the two isotherms are included in Figure 4. The model parameters are provided in Table 5. Good modeling was also achieved for this system with the PRSV EoS with the Wong−Sandler mixing rule.

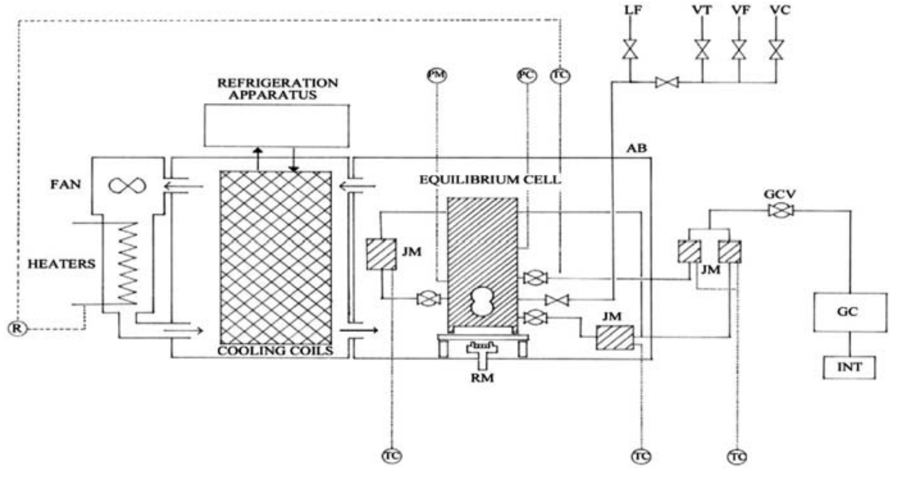

Figure 2. Layout of the experimental apparatus. AB, air bath; GC, gas chromatograph; GCV, gas chromatograph valve; INT, integrator; JM, jet mixer; LF, liquid feed; PC, pressure controller; PM, pressure measurement; R, relay; RM, rotating magnet; TC, temperature sensor; VF, vapor feed; VC, vacuum; VT, vent.

Table 1. Experimental Data for {Propane (1) + Cyclopentanol (2)}

$T = 353.15$ K			$T = 373.15$ K			$T = 393.15$ K		
P/MPa	x_1	y_1	P/MPa	x_1	y_1	P/MPa	x_1	y_1
0.288	0.0435	0.9517	0.216	0.0279	0.8860	0.579	0.0502	0.9083
0.550	0.0838	0.9705	0.405	0.0502	0.9478	0.841	0.0797	0.9307
0.994	0.1653	0.9891	0.565	0.0707	0.9592	0.994	0.0917	0.9396
1.016	0.1663	0.9868	0.987	0.1264	0.9731	1.227	0.1206	0.9431
1.307	0.2245	0.9877	1.438	0.1794	0.9772	1.539	0.1459	0.9502
1.583	0.2733	0.9870	2.027	0.2782	0.9798	1.983	0.1949	0.9522
1.874	0.3363	0.9858	2.543	0.3582	0.9780	2.441	0.2682	0.9546
2.238	0.4302	0.9887	2.689	0.3808	0.9775	2.667	0.2920	0.9573
2.601	0.6120	0.9915	2.987	0.4839	0.9858	3.183	0.3753	0.9624
			3.030	0.4803	0.9827	3.561	0.4415	0.9613
						4.116	0.6098	0.9581

Thermodynamic Consistency Tests. Propane + Cyclopentanol. The Chueh et al.[11] consistency test results for the system at three temperatures are summarized in Table 6. The overall percentage inconsistency for all isotherms of the (propane + cyclopentanol) ranges from (0.167 to 1.762) %. The measured HPVLE data comfortably passed the Chueh et al. consistency test.

The deviations between the calculated and measured vapor compositions for the (propane + cyclopentanol) system for the Christiansen and Fredenslund consistency test are tabulated in Table 7. For the 353.15 K isotherm, these deviations lie between $-16.4 \cdot 10^{-3}$ and $-2.31 \cdot 10^{-3}$, all of which lie in the negative quadrant, indicating a small bias in the vapor compositions.

For the 373.15 K isotherm, there is a good scatter of the deviations about the zero axis which indicates good consistency. These values ranged from $-1.30 \cdot 10^{-2}$ to $8.62 \cdot 10^{-3}$.

For the 393.15 K isotherm, these deviations lie between $-3.38 \cdot 10^{-3}$ and $-6.59 \cdot 10^{-2}$. Although these values lie in the negative quadrant, the deviation range is quite small, and hence the data can be assumed to be consistent.

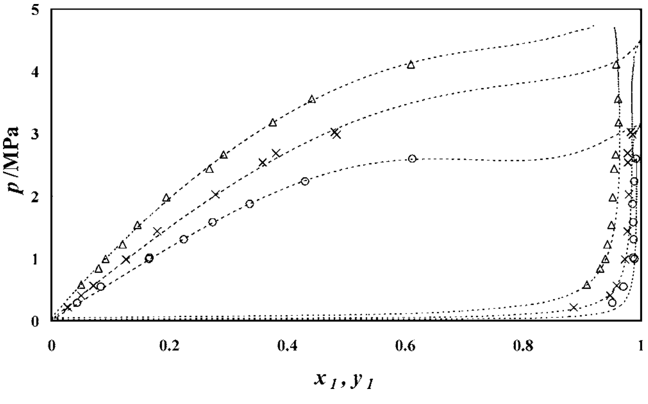

Figure 3. Experimental data for the propane (1) + cyclopentanol (2) system (○, $T = 353.15$ K; ×, $T = 373.15$ K; Δ, $T = 393.15$ K; ----, model).

Table 2. Experimental Data for {Carbon Dioxide (1) + Cyclopentanol (2)}

$T = 373.15$ K			$T = 403.15$ K		
P/MPa	x_1	y_1	P/MPa	x_1	y_1
0.914	0.0177	0.9752	1.248	0.0291	0.9264
1.154	0.0243	0.9770	3.401	0.0726	0.9716
3.154	0.0743	0.9879	4.521	0.0978	0.9715
3.852	0.0951	0.9870	5.627	0.1211	0.9678
5.191	0.1279	0.9870	5.743	0.1249	0.9743
5.787	0.1471	0.9891	7.402	0.1617	0.9691
6.747	0.1776	0.9868	8.914	0.2076	0.9681
8.005	0.2245	0.9874	10.980	0.2578	0.9656
9.089	0.2601	0.9878			
11.838	0.3942	0.9837			

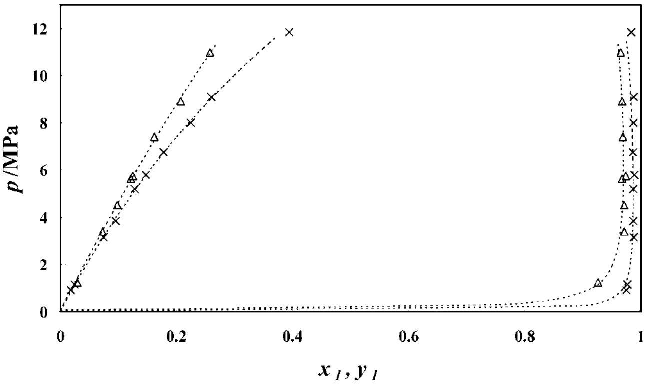

Figure 4. Experimental data for the carbon dioxide (1) + cyclopentanol (2) system (×, $T = 373.15$ K; Δ, $T = 403.15$ K; -----, model).

Table 3. Pure Component κ_1 Values Regressed Using the Peng−Robinson EoS with Stryjek−Vera Alpha Function, as Well as Critical Properties and Acentric Factors (ω)[16]

			T_C	P_C	V_C	
components	κ_1	AAD % (ΔP)	K	MPa	$\text{cm}^3 \cdot \text{mol}^{-1}$	ω
CO_2	0.0430	0.79	304.1	7.38	93.9	0.239
propane	0.0210	0.35	369.8	4.25	203	0.153
cyclopentanol	0.4527	0.47	619.5	4.90	280.1[a]	0.442

[a] Ambrose estimation method for critical properties.[16]

Table 4. Model Parameters for Propane (1) + Cyclopentanol (2) for the Peng−Robinson EoS with the Stryjek−Vera Alpha Function Using the Wong−Sandler Mixing Rules Encorporating the NRTL Activity Coefficient Model

		Δg_{12}[a]	Δg_{21}[a]	
T/K	k_{ij}	$\text{J} \cdot \text{mol}^{-1}$	$\text{J} \cdot \text{mol}^{-1}$	AE %
353.15	0.127	4484.6	−129.5	0.160
373.15	0.123	3712.1	−272.0	0.093
393.15	0.166	7212.5	−230.3	0.068

[a] NRTL: $\Delta g_{12} = g_{12} - g_{22}$, $\Delta g_{21} = g_{21} - g_{11}$, $\alpha_{12} = 0.3$.

Table 5. Model Parameters for Carbon Dioxide (1) + Cyclopentanol (2) for the Peng−Robinson EoS with the Stryjek−Vera Alpha Function Using the Wong−Sandler Mixing Rules Encorporating the NRTL Activity Coefficient Model

		Δg_{12}[a]	Δg_{21}[a]	
T/K	k_{ij}	$\text{J} \cdot \text{mol}^{-1}$	$\text{J} \cdot \text{mol}^{-1}$	AE %
373.15	0.623	543.9	443.3	0.206
403.15	0.476	2839.0	−18.6	0.240

[a] NRTL: $\Delta g_{12} = g_{12} - g_{22}$, $\Delta g_{21} = g_{21} - g_{11}$, $\alpha_{12} = 0.3$.

Table 6. Chueh et al. Thermodynamic Consistency Test Results

system	T/K	inconsistency/%
propane + cyclopentanol	353.15	0.17 to 0.78
	373.15	0.61 to 1.76
	393.15	0.67 to 0.81
carbon dioxide + cyclopentanol	373.15	2.85 to 3.25
	403.15	0.009 to 0.29

Carbon Dioxide + Cyclopentanol. Experimental HPVLE data for (carbon dioxide + cyclopentanol) were measured at two isotherms, 373.15 K and 403.15 K. The Chueh et al. consistency test results for the system at these temperatures are summarized in Table 6. The 373.15 K isotherm has larger inconsistencies ranging from (2.848 to 3.254) %. These values are still well within the 5 % recommendation; therefore these measured data are not inconsistent. The percentage inconsistency for the 403.15 K isotherm varied from (0.009 to 0.288) %, which is also well within the percent error for the consistency test.

Table 7. Christiansen and Fredenslund Thermodynamic Consistency Test Results

system	T/K	$\Delta y = y^{\mathrm{exp}} - y^{\mathrm{calc}}$
propane + cyclopentanol	353.15	$-16.4 \cdot 10^{-3}$ to $-2.31 \cdot 10^{-3}$
	373.15	$-1.3 \cdot 10^{-3}$ to $8.62 \cdot 10^{-3}$
	393.15	$-3.38 \cdot 10^{-3}$ to $-6.59 \cdot 10^{-2}$
carbon dioxide + cyclopentanol	373.15	$-2.156 \cdot 10^{-2}$ to $2.49 \cdot 10^{-4}$
	403.15	$-4.82 \cdot 10^{-3}$ to $2.017 \cdot 10^{-2}$

Table 8. Henry's Constants from the Krichevsky−Illinskaya Procedure[a]

		$H_{12}^{(P_2^{\mathrm{sat}})}$	AE	A
system	T/K	kPa	%	$\mathrm{J \cdot mol^{-1}}$
propane (1) + cyclopentanol (2)	353.15	77 ± 0.9	0.022	2968.8
	373.15	96 ± 2.2	0.093	2777.6
	393.15	118 ± 1.9	0.042	3598.5
carbon dioxide (1) + cyclopentanol (2)	373.15	459 ± 9.8	0.107	3227.2
	403.15	463 ± 10.9	0.092	1820.4

[a] AE % indicates the quality of the fitting and A (of eq 9), the Margules constant obtained from regression.

The data measured at 403.15 K also passed the Chueh et al. consistency test.

The consistency results for the Christiansen and Fredenslund test for (carbon dioxide + cyclopentanol) are shown in Table 7. For the 373.15 K isotherm, all deviations lie below the zero axis, excluding one point. These values ranged from $-2.156 \cdot 10^{-2}$ to $2.49 \cdot 10^{-4}$. These errors seem reasonable.

For the 403.15 K isotherm, there is a small scatter of the data about the zero axis, with errors between $-4.82 \cdot 10^{-3}$ and $2.017 \cdot 10^{-2}$. These values are considered satisfactory.

Henry's Constants. Henry's constants obtained from the Krichevsky llinskaya equation are shown in Table 8. The increase in H_{12} with temperature confirms the decrease in solubility of both propane and carbon dioxide in cyclopentanol with temperature for the pressure range studied.

Conclusion

High-pressure vapor−liquid equilibrium data have been measured for (propane + cyclopentanol) at temperatures of (353.15, 373.15, and 393.15) K and for (carbon dioxide + cyclopentanol) at temperatures of (373.15 and 403.15) K. These represent new data. The two high-pressure thermodynamic consistency tests used to check the data indicated data sets to be not inconsistent. Henry's constants, calculated using the Krichesky−Illinskaya procedure, are considered reliable. Satisfactory modeling was obtained for both systems.

Supporting Information Available:

Experimental data summary. This material is available free of charge via the Internet at http://pubs.acs.org.

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