High-Pressure Vapor−Liquid Equilibria in the System Carbon Dioxide and 2-Propanol at Temperatures from 293.25 K to 323.15 K

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Isothermal (P, T, x, y) data have been measured for the binary system carbon dioxide + 2-propanol at temperatures from (293 to 323) K. The pressure range under investigation was between (0.68 and 8.6) MPa. The new experimental data are correlated with the Soave−Redlich−Kwong (SRK) equation of state coupled with the HVID mixing rules. A correlation of the HVID parameters with temperature is proposed by using all reliable published data and those of this study.

Introduction

Vapor−liquid equilibria (VLE) at high pressure are required for practical applications such as supercritical fluid extraction (SFE). Supercritical extraction provides an attractive technique for highly efficient separation processes, with lower energy requirements. The importance of the carbon dioxide + alcohol systems as model mixtures of interest in the pharmaceutical and the food industries has motivated new studies of phase equilibria.[1]

Several papers have presented experimental vapor−liquid equilibrium data for the binary system carbon dioxide + 2-propanol.[2−5] For this system, some equations of state predicted vapor−liquid−liquid equilibria (VLLE) phase separations for high mole fractions of carbon dioxide. Therefore, in this work we made new measurements using a static-analytical method, in a high-pressure visual cell, for carbon dioxide + 2-propanol systems at (293, 298, 308, 316, and 323) K up to 8.6 MPa. VLLE phase separation was not observed in the present experiments.

The phase equilibria data obtained in this study were correlated with the Soave−Redlich−Kwong[6] (SRK) equation of state coupled with the HVID (Huron-Vidal infinit dilution) mixing rules.[7,8] A correlation of the HVID parameters with temperature is proposed by using all reliable published data and those of this study.

Experimental Section

Materials. Carbon dioxide (mass fraction purity > 0.997) was provided by Linde Gaz Romania, Bucharest, Romania, and 2-propanol (mass fraction purity > 0.997) was bought from SC Comchim SA, Bucharest, Romania. The chemicals were used as supplied.

Apparatus and Procedure. The experimental method used in this work is a static-analytical method with liquid and vapor phase sampling. A schematic diagram of the high-pressure equilibrium apparatus (NWA GmbH, Loerrach, Germany) is shown in Figure 1. The main part of the equipment is a visual cell with two sapphire windows and variable volume. One of the sapphire windows acts as a piston and allows a volume change between (25 and 60) cm^3. The apparatus is designed to operate at pressures below 30 MPa and temperatures between (273 and 353) K. The temperature in the cell is measured with a Ni−Cr−Ni thermocouple (accuracy ± 0.1 K). The pressure is measured with a pressure gauge (Type S 10, WIKA, Germany; accuracy 0.5% within (0 to 25) MPa). The cell is heated electrically, and its temperature is controlled by a circulating thermostat connected to the heating jacket. A controlled-speed stirrer, which allows achieving phase equilibrium quickly, is mounted into the cell.

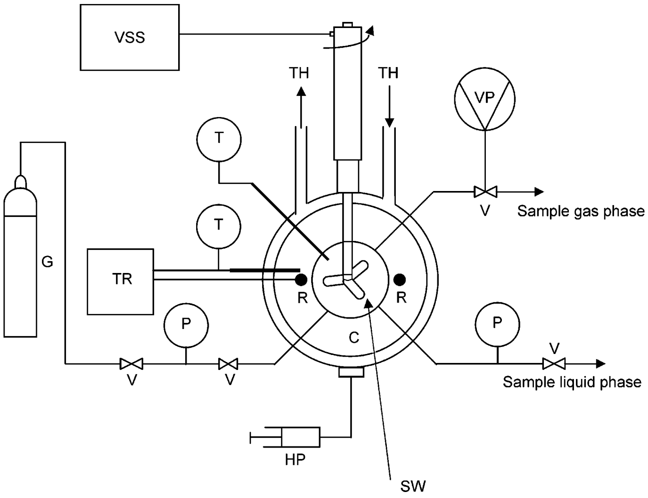

Figure 1. Schematic diagram of the experimental apparatus: C, variable volume cell; G, carbon dioxide reservoir; HP, hand pump; P, pressure gauge; R, electric resistance; SW, sapphire window; T, thermocouple; TH, thermostat; TR, temperature regulator; V, valve; VP, vacuum pump; VSS, variable speed stirring assembly.

Experiments were carried out as follows. The entire internal loop of the apparatus including the equilibrium cell was rinsed several times with carbon dioxide. Then, the equilibrium cell was evacuated with a vacuum pump. The cell was charged with alcohol; then, it was slightly pressurized with carbon dioxide to the experimental pressure and was heated to the experimental temperature. To facilitate the approach to an equilibrium state, the mixture in the cell was stirred for a few hours. Then the stirrer was switched off and about 1 h was allowed to pass until the coexisting phases were completely separated. Samples of the liquid and vapor phase were collected by depressurization and expansion into glass traps, by using manu-

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Table 1. Mole Fraction of Component 1 in the Liquid Phase, x_1, and Mole Fraction of Component 1 in the Vapor Phase, y_1, at Various Pressure, P, and Temperature, T, for the Binary System Carbon Dioxide (1) + 2-Propanol (2)

P/MPa	x_1	y_1	P/MPa	x_1	y_1
		T/K = 293.25 ± 0.1			
0.68	0.0494	0.9911	4.21	0.4191	0.9968
1.16	0.0844	0.9954	4.75	0.5623	0.9973
1.61	0.1208	0.9966	5.11	0.7892	0.9970
2.18	0.1672	0.9966	5.12	0.7907	0.9974
2.76	0.2239	0.9969	5.27	0.8884	0.9975
3.16	0.2692	0.9969	5.56	0.9562	0.9981
3.71	0.3363	0.9973			
		T/K = 298.15 ± 0.1			
1.05	0.0718	0.9930	5.39	0.6407	0.9955
2.13	0.1576	0.9952	5.68	0.7702	0.9961
2.97	0.2269	0.9965	5.81	0.7905	0.9960
4.46	0.4092	0.9960	6.07	0.8863	0.9970
4.9	0.4577	0.9958			
5.2	0.5404	0.9962			
		T/K = 308.15 ± 0.1			
1.59	0.0963	0.9910	6.72	0.7227	0.9923
3.85	0.2592	0.9940	7.15	0.8935	0.9939
5.49	0.4562	0.9932			
		T/K = 316.65 ± 0.1			
1.33	0.0701	0.9842	6.68	0.5203	0.9884
2.51	0.1434	0.9893	6.8	0.5270	0.9878
3.48	0.1981	0.9900	7.51	0.6931	0.9857
4.02	0.2434	0.9902	7.76	0.7729	0.9859
5.15	0.3321	0.9912	8.38	0.8742	0.9819
5.77	0.3912	0.9896			
		T/K = 323.15 ± 0.1			
1.52	0.0742	0.9801	5.82	0.3643	0.9869
3.01	0.1621	0.9872	7.7	0.5642	0.9843
4.47	0.2449	0.9879	8.6	0.7277	0.9782

ally operated valves. The valves were operated in such a way as to keep almost constant the pressure in the visual cell. The total amount of the organic substance in the glass trap was about (0.05 and 0.2) g for the vapor phase and liquid phase, respectively. The amount of carbon dioxide in each phase was obtained by expansion in a glass bottle of calibrated volume. In a typical experiment the measured volumes of carbon dioxide were about 100 cm^3 from the vapor phase and 50 cm^3 from the liquid phase. The liquid samples of both phases were weighed with a precision balance (type HM 200, AND, Tokyo, Japan) with an accuracy of 0.0001 g.

Results and Discussion

The equilibrium compositions for the carbon dioxide + 2-propanol binary system were measured at (293, 298, 308, 316, and 323) K, and the results are given in Table 1. The values are typically averages of two or three measurements. For the VLE measurements, the uncertainty of the mole fraction is typically 0.001 and always <0.003. As usually in the literature,[5] we calculated the mole fractions with four decimal places.

Figure 2 shows a detailed comparison of our data at 293.25 K with the existing data of Bamberger and Maurer[5] for the same temperature. The results of this reference agree with our experimental data to nearly within the experimental uncertainty (0.001 in mole fraction).

Measured VLE data for the carbon dioxide + 2-propanol system were correlated with the Soave−Redlich−Kwong (SRK) equation of state[6] coupled with the HVID mixing rules.[7,8] Other mixing rules (classical van der Waals and G^E mixing rules) were tried, but the correlation with the HVID mixing rules was the most accurate. Moreover, in this work, VLLE phase separation was not observed in the critical region of the mixtures, and this fact was correctly described only by the HVID model.

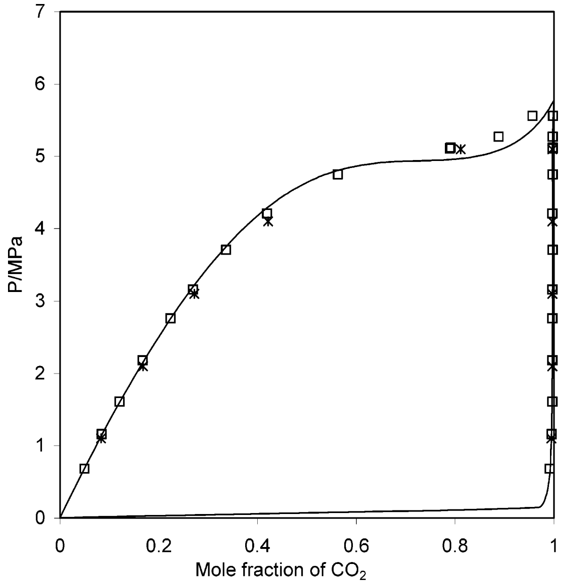

Figure 2. Comparison of measured and literature vapor−liquid equilibrium data for the CO$_2$ + 2-propanol system at 293.25 K: □, experimental, this work; ∗, Bamberger et Maurer;[5] —, calculated with the SRK/HVID equation.

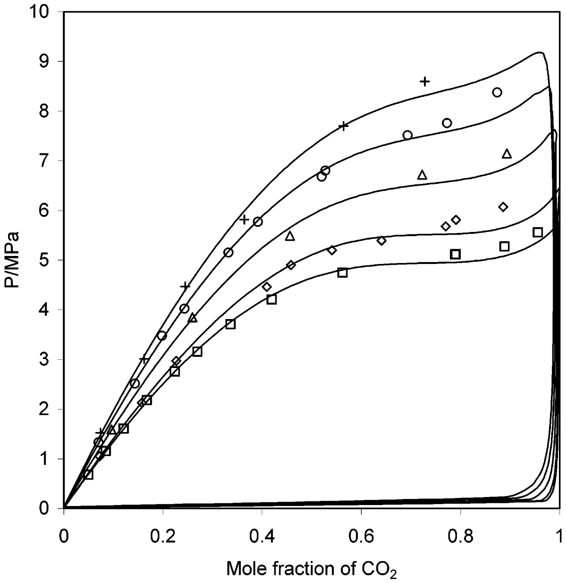

Figure 3. Pressure−composition data for carbon dioxide (1) + 2-propanol (2), comparing the experimental results with model results for the liquid phase. Experimental data (liquid phase): □, 293.15 K; ◇, 298.25 K; △, 308.15 K; ○, 316.65 K; +, 323.15 K. —, calculated with the SRK/HVID equation.

The correlations by the SRK/HVID equation are compared with the experimental data for the above temperatures in Figures 3 and 4. The optimum values of the HVID-residual UNIQUAC parameters[7] (u_{12} and u_{21}) are given in Table 2. The calculation model is in good agreement with the experimental data, as can be seen in Table 2 from the values of the average absolute deviations in bubble point pressures (AADP < 2.3%). The AADP is calculated by the equation

$$\text{AADP (\%)} = \frac{1}{N_{\text{exp}}} \sum_{i=1}^{N_{\text{exp}}} \left| \frac{P_i^{\text{exp}} - P_i^{\text{calc}}}{P_i^{\text{exp}}} \right| \times 100 \qquad (1)$$

Figure 5 presents the correlation of HVID parameters with temperature. All reliable published data and those of

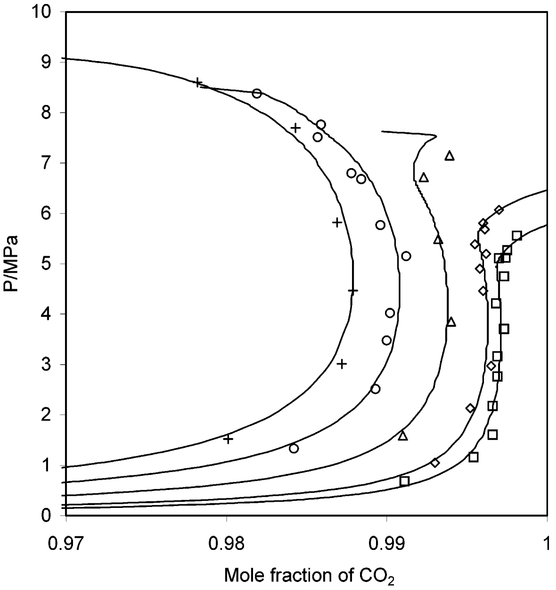

Figure 4. Pressure−composition data for carbon dioxide (1) + 2-propanol (2), comparing the experimental results with model results for the vapor phase. Experimental data (vapor phase): □, 293.15 K; ◇, 298.25 K; △, 308.15 K; ○, 316.65 K; +, 323.15 K; —, calculated with the SRK/HVID equation.

Table 2. HVID Parameters (u_{12}, u_{21}) and Average Absolute Deviations in Bubble Point Pressure (AADP) for the Carbon Dioxide + 2-Propanol System

T/K	u_{12}/K	u_{21}/K	AADP/%	u_{12}^{a}/K	u_{21}^{a}/K	AADP[b]/%
293.25	152.2	142.0	1.8	152.9	135.7	2.1
298.25	166.2	124.1	2.2	138.6	145.0	2.4
308.15	116.2	162.8	2.3	111.0	163.2	2.6
316.65	90.8	183.8	1.7	87.3	178.8	2.3
323.15	80.6	191.7	2.0	69.1	190.7	3.1
293.20[c]	130.1	149.9	1.2	152.7	135.8	1.6
313.20[c]	80.4	178.9	0.7	96.9	172.5	2.4
333.10[c]	33.8	211.5	0.2	41.3	208.9	1.4
354.45[d]	−18.7	219.9	0.2	−18.3	248.1	3.4
394.55[d]	−130.2	336.0	0.4	−130.3	321.6	1.2

[a] u_{12} and u_{21} calculated from eqs 2 and 3. [b] AADP calculated with the parameters from eqs 2 and 3. [c] Literature data.[5] [d] Literature data.[2]

this study were used. As can be seen, the data are fitted with a linear correlation. The linear equations for the temperature dependence of the HVID parameters (u_{12} and u_{21}) are

$$u_{12} = -2.7929T + 971.65 \qquad (2)$$

$$u_{21} = 1.8334T - 401.79 \qquad (3)$$

with u_{ij} and T in kelvin.

It must be mentioned that the equations are linear in a wide temperature range, (293 to 390) K. The HVID-residual UNIQUAC parameter values calculated from eqs 2 and 3 are given in Table 2, together with the corresponding average absolute deviations in pressure. As can be seen, the parameters from eqs 2 and 3 correlate well all experimental data for the carbon dioxide + 2-propanol systems.

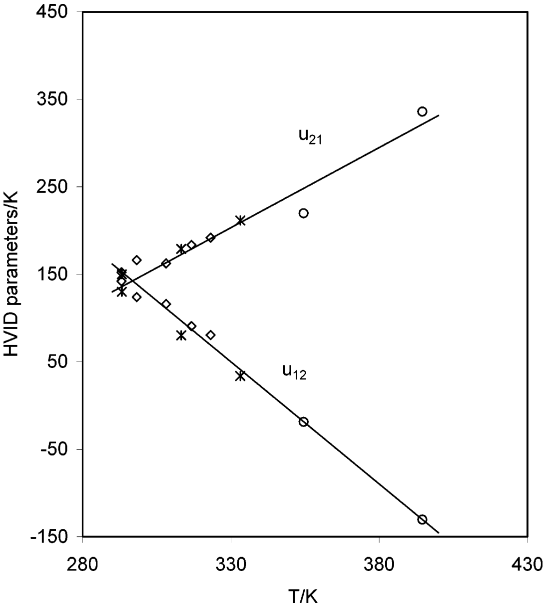

Figure 5. Correlation of HVID parameters (u_{12}, u_{21}) with temperature. Experimental data: ◇, this work; ∗, Bamberger and Maurer;[5] ○, Radosz.[2]

Conclusions

New VLE experimental data (P, T, x, y) for the binary system carbon dioxide + 2-propanol were measured at (293.15, 298.25, 308.15, 316.65, and 323.15) K and pressures up to 8.6 MPa, with a high-pressure static apparatus. The obtained experimental data were correlated by the SRK equation of state coupled with the HVID mixing rules. A linear correlation of the HVID parameters with the temperature is proposed on the basis of all reliable published data and those of this study.

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