J. Chem. Eng. Data **2004,** *49,* 1635−1638

High-Pressure Vapor−Liquid Equilibria in the System Carbon Dioxide + 1-Butanol at Temperatures from (293.15 to 324.15) K

Catinca Secuianu, Viorel Feroiu, and Dan Geană*

Department of Applied Physical Chemistry and Electrochemistry, Politehnica University Bucharest,
1 Polizu Str., 78126 Bucharest, Romania

Isothermal (P, T, x, y) data have been measured for the binary system carbon dioxide + 1-butanol at temperatures from (293.15 to 324.15) K. The pressure range under investigation was between (0.52 and 10.09) MPa. The new experimental data are correlated with the Soave−Redlich−Kwong (SRK) equation of state coupled with the Huron−Vidal infinite dilution (HVID) mixing rules. A linear correlation of the HVID parameters with the inverse temperature is proposed by using only the data of this study. The values of HVID parameters from the linear correlation were used to predict VLE at all temperatures for which published data are available. The VLE data are reasonably well predicted for engineering purposes.

Introduction

Thermodynamic knowledge of the high-pressure phase behavior of carbon dioxide + alcohol mixtures is essential to the design and implementation of many processes. Particularly, supercritical fluid extraction (SFE) and supercritical fluid chromatography (SFC) processes have received much attention in recent years. Data for carbon dioxide + alcohol systems are of great importance in SFE and SFC, in the oil and natural gas industry, and in the cosmetic, pharmaceutical, surfactant, and food industries.[1−4]

Vapor−liquid equilibria (VLE) data for the carbon dioxide + 1-butanol system were reported in several papers,[5−15] and some[5] of them suggested the existence of vapor−liquid−liquid equilibria (VLLE) in the vicinity of the critical region of carbon dioxide. Therefore, in this work we made new measurements using a static analytical method in a high-pressure visual cell for the carbon dioxide + 1-butanol system at (293, 303, 313, and 324) K up to 10.09 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[16] (SRK) equation of state coupled with the HVID mixing rules.[17,18] A linear correlation of the HVID parameters with inverse temperature is proposed by using the new data from this study. The values of HVID parameters from the linear correlation were used to predict VLE at all temperatures for which published data are available. The predicted VLE data are reliable for basic design purposes.

Experimental Section

Materials. Carbon dioxide (mass fraction purity >0.997) was provided by Linde Gaz Romania, Bucharest, Romania, and 1-butanol (mass fraction purity >0.998) was bought from Redox Trading 2000 S. R. L. Bucharest, Romania. The chemicals were used as supplied.

Apparatus and Procedure. A detailed description of the experimental apparatus was presented in an earlier paper.[19] The apparatus used in this work is based on the static analytical method with liquid- and vapor-phase sampling. The procedure is the same as in our previous papers.[19,20] 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 phases were collected by depressurization and expansion into glass traps by using manually operated valves. The valves were operated in such a way as to keep the pressure in the visual cell almost constant. The total amounts of the organic substance in the glass trap were about (0.05 and 0.2) g for the vapor and liquid phases, 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 (A&D Instruments Ltd, type HM-200, Tokyo, Japan) with an accuracy of ±0.0001 g.

Results and Discussion

The equilibrium compositions for the carbon dioxide + 1-butanol binary system were measured at (293, 303, 313, and 324) K, and the results are summarized in Table 1. The values are averages of two or three measurements. For the VLE measurements, the uncertainty of the mole fraction is typically ±0.001 and always <0.003. Equilibrium $P-x-y$ data obtained at 313.15 K are used to confirm the accuracy of the measurement. This shows that the data are in good agreement with the existing data at the same temperature, as shown in Figures 1 and 2.

The vapor−liquid-phase equilibrium data obtained in this work at 324.15 K are illustrated in Figure 3. Silva-Oliver and Galicia-Luna[13] have measured the VLE data only in the near-critical region at 324.16 K, and the results are also shown in Figure 3.

---

* Corresponding author. E-mail: d_geana@chim.upb.ro.

10.1021/je0499521 CCC: $27.50

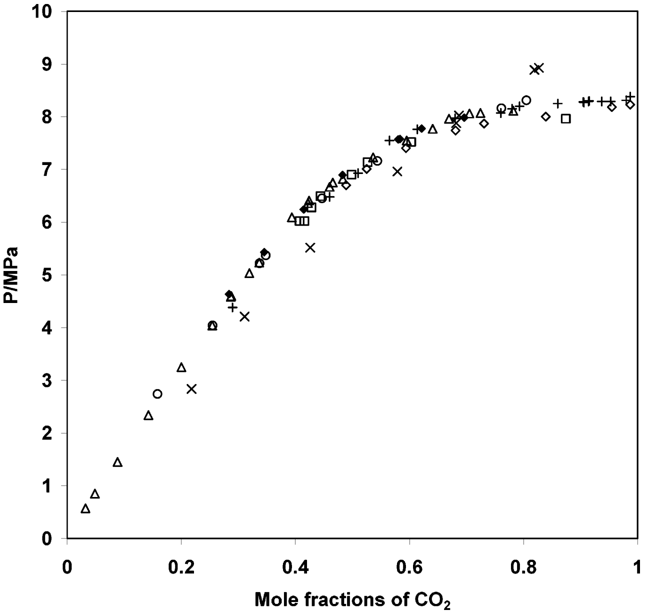

Figure 1. Pressure−composition data for the CO_2 + 1-butanol system at 313.15 K, comparing the experimental results for the liquid phase: Δ, experimental, this work; □, Hiaki et al.;[12] ◇, Ishihara et al.;[10] ○, Borch-Jensen et al.;[9] ◆, Jennings et al.;[6] ×, King et al.;[5] +, Byun and Kwak.[15]

Table 1. Mole Fractions of Component 1 in the Liquid Phase x_1 and Mole Fractions of Component 1 in the Vapor Phase y_1 at Various Pressures P and Temperatures T for the Binary System Carbon Dioxide (1) + 1-Butanol (2)

P/MPa	x_1	y_1	P/MPa	x_1	y_1
		T/K = 293.15 ± 0.1			
0.63	0.0444	0.9847	4.31	0.3867	0.9933
1.23	0.0884	0.9919	4.95	0.4927	0.9930
2.26	0.1761	0.9934	5.46	0.7414	0.9923
3.09	0.2540	0.9932			
		T/K = 303.15 ± 0.1			
0.52	0.0281	0.9926	5.51	0.4265	0.9948
0.96	0.0539	0.9941	6.12	0.5496	0.9944
1.93	0.1307	0.9948	6.48	0.6394	0.9941
2.89	0.1939	0.9949	6.65	0.7638	0.9932
3.62	0.2591	0.9951	6.68	0.7799	0.9929
4.25	0.2969	0.9952	6.70	0.8119	0.9915
4.96	0.3618	0.9949	6.74	0.8367	0.9914
		T/K = 313.15 ± 0.1			
0.57	0.0322	0.9916	6.41	0.4240	0.9982
0.85	0.0485	0.9943	6.67	0.4600	0.9978
1.45	0.0882	0.9978	6.75	0.4655	0.9978
2.34	0.1424	0.9982	6.82	0.4832	0.9975
3.25	0.2004	0.9986	7.23	0.5363	0.9972
4.04	0.2543	0.9986	7.55	0.5950	0.9969
4.58	0.2867	0.9986	7.77	0.6407	0.9961
4.60	0.2876	0.9985	7.96	0.6693	0.9958
5.03	0.3193	0.9986	8.06	0.7053	0.9954
5.23	0.3367	0.9986	8.07	0.7245	0.9952
6.09	0.3939	0.9982	8.11	0.7821	0.9921
6.36	0.4223	0.9982			
		T/K = 324.15 ± 0.1			
1.65	0.0886	0.9892	8.39	0.5411	0.9942
2.58	0.1398	0.9929	9.04	0.5785	0.9933
3.60	0.1926	0.9960	9.11	0.6000	0.9929
4.60	0.2554	0.9963	9.46	0.6585	0.9919
5.63	0.3026	0.9962	10.00	0.8183	0.9890
6.38	0.3592	0.9958	10.05	0.8231	0.9867
7.58	0.4466	0.9944	10.09	0.8815	0.9890
7.63	0.4511	0.9946			

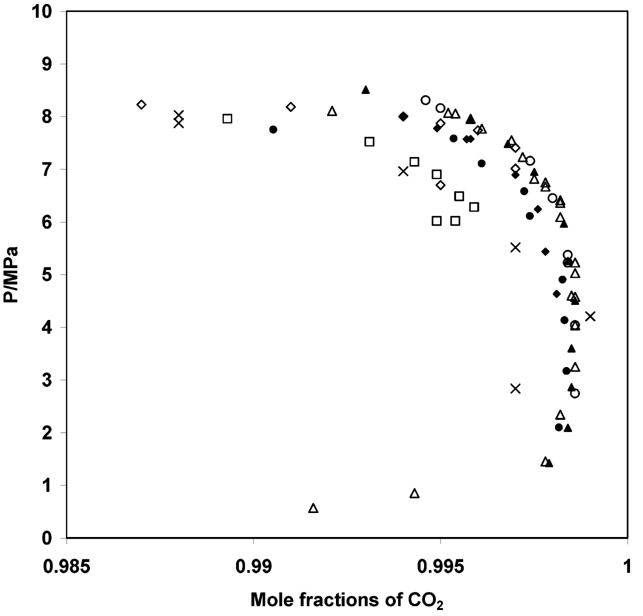

Figure 2. Pressure−composition data for the CO_2 + 1-butanol system at 313.15 K, comparing the experimental results for the vapor phase: Δ, experimental, this work; □, Hiaki et al.;[12] ◇, Ishihara et al.;[10] ○, Borch-Jensen et al.;[9] ◆, Jennings et al.;[6] ×, King et al.;[5] ●, Stevens et al.;[11] ▲, Suzuki et al.[7]

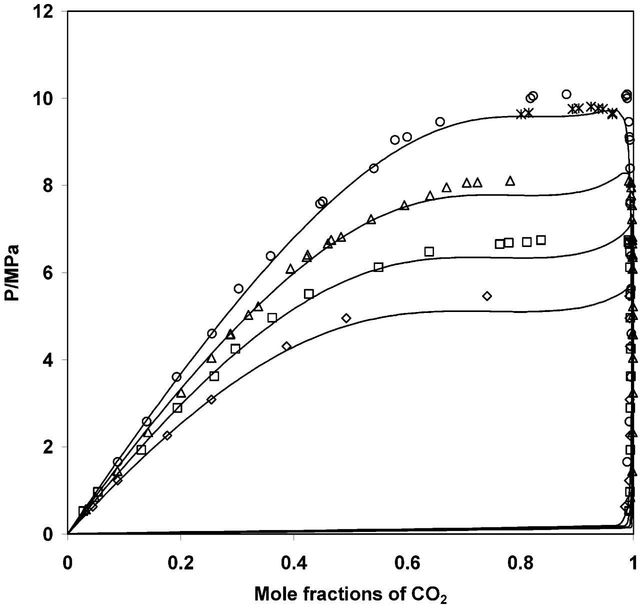

Figure 3. Pressure−composition data for CO_2 (1) + 1-butanol (2) comparing the experimental results with model results. Experimental data: ◇, 293.15 K; □, 303.15 K; Δ, 313.15 K; ○, 324.15 K; *, 324.16 K (Silva-Oliver and Galicia-Luna[13]); —, correlated with the SRK/HVID equation.

Measured VLE data for the carbon dioxide + 1-butanol system were correlated with the SRK equation of state[16] coupled with the HVID mixing rules.[17,18] At temperatures near the critical point of carbon dioxide, the calculation leads to a false liquid−liquid splitting. By restricting the interaction parameters in the optimization routine to avoid the false liquid−liquid splitting, a good fit of the data was obtained in accord with the experimentally observed behavior.

The optimum values of the HVID − residual UNIQUAC parameters[17] (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 average absolute deviations in bubble-point pressures (AADP%) and the average absolute deviations in the vapor-

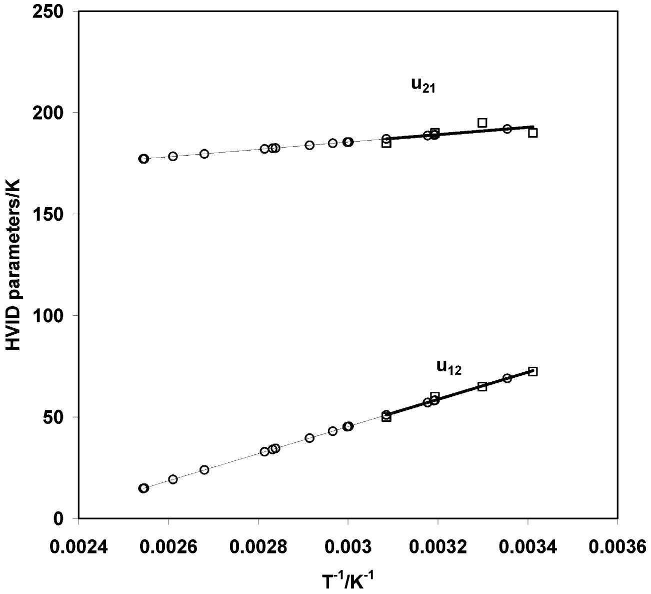

Figure 4. Correlation of HVID parameters (u_{12}, u_{21}) with temperature: □, experimental, this work; EnDash−, correlation of the experimental data of this work; ○, all available published data; −, predicted HVID parameters.

Table 2. HVID Parameters (u_{12}, u_{21}), Average Absolute Deviations in Bubble-Point Pressure (AADP), and Average Absolute Deviations in Vapor-Phase Compositions (AADY) for the Carbon Dioxide + 1-Butanol System

T/K	u_{12}/K	u_{21}/K	AADP/%	AADY/%
293.15	72.5	190.0	2.6	0.7
303.15	65.0	195.0	4.5	0.4
313.15	60.0	190.0	1.9	0.1
324.15	50.0	185.0	2.5	0.3

phase compositions (AADY%). The AADP and AADY are calculated from the following equations:

$$\mathrm{AADP\%} = \frac{1}{N_{\mathrm{exptl}}} \sum_{i=1}^{N_{\mathrm{exptl}}} \left| \frac{P_i^{\mathrm{exptl}} - P_i^{\mathrm{calcd}}}{P_i^{\mathrm{exptl}}} \right| \times 100 \qquad (1)$$

$$\mathrm{AADY\%} = \frac{1}{N_{\mathrm{exptl}}} \sum_{i=1}^{N_{\mathrm{exptl}}} |Y_i^{\mathrm{exptl}} - Y_i^{\mathrm{calcd}}| \times 100 \qquad (2)$$

The correlations by the SRK/HVID equation are compared with the experimental data for the above temperatures in Figure 3. The agreement is good, except the near critical region where the fitting is slightly less accurate.

Figure 4 presents the correlation of HVID parameters with the inverse temperature. The new data from this study were used to obtain a linear correlation. The linear equations for the temperature dependence of the HVID parameters (u_{12} and u_{21}) are

$$u_{12} = 66\,890T^{-1} - 155.32 \qquad (3)$$

$$u_{21} = 18\,183T^{-1} + 130.96 \qquad (4)$$

with u_{ij} and T in kelvin.

The linear correlation obtained with our data was used to predict the parameter values for all available published data. In Figure 4, the thick, solid lines correspond to the correlation of the experimental data of this work, and the thin lines are the predictions for other temperatures of the literature data. The calculations with the SRK equation of state coupled with the HVID parameters obtained from eqs 3 and 4 were made for all available data. The corresponding average absolute deviations in bubble pressures together with the average absolute deviations in vapor-phase compositions are summarized in Table 3. As can be seen, the parameters from eqs 3 and 4 lead to reasonable predictions of VLE at all temperature for the carbon dioxide + 1-butanol systems. The greatest deviations in bubble pressure are less than ~5%. Several higher deviations (>10%) appear at temperatures where the data have been measured in the critical range[13,15] or the data show liquid−liquid behavior[5] that was not confirmed by the experiments of this study.

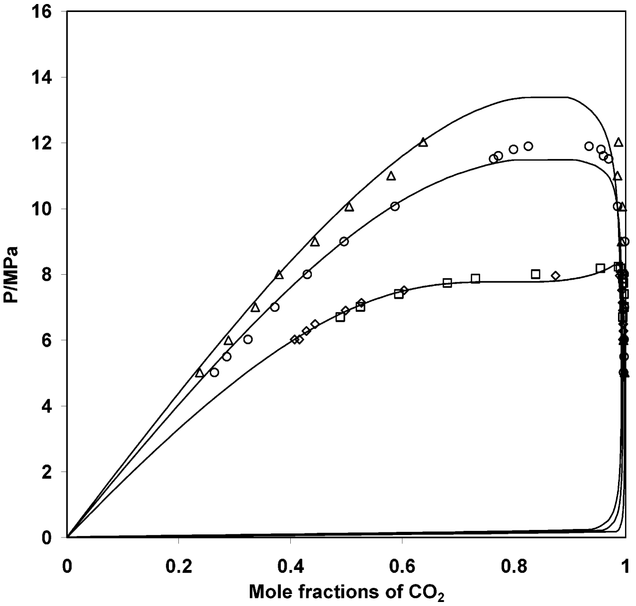

Figure 5. Comparison of literature vapor−liquid equilibrium data for the CO_2 + 1-butanol system and HVID model predictions. Experimental data: ◇, 313.2 K, Hiaki et al.;[12] □, 313.15 K, Ishihara et al.;[10] ○, 333.15 K, Chen et al.;[14] Δ, 343.15 K, Chen et al.;[14] —, predicted with the SRK/HVID equation with parameters from eqs 3 and 4.

Table 3. Average Absolute Deviations in Bubble-Point Pressure (AADP) and Vapor-Phase Compositions (AADY) Calculated with the Parameters Predicted from Equations 3 and 4 for the Carbon Dioxide + 1-Butanol System (Literature Data)

T/K	AADP/%	AADY/%	ref
298.15	7.0		8
313.15	3.5		15
313.15	1.3	0.1	10
313.15	11.1	0.3	5
313.20	0.9	0.2	12
313.40	2.1	0.1	9
314.80	0.3	0.1	6
324.16	2.0	0.1	13
325.30	4.1	0.2	6
333.15	2.3	1.3	14
333.15	1.6		15
333.58	3.4	1.2	13
337.20	1.9	0.4	6
343.15	2.1	0.8	14
353.15	2.4	1.0	14
353.15	5.9		15
355.38	7.4	1.8	13
373.15	9.5		15
383.13	12.8	2.8	5
392.72	13.7	1.7	13
393.15	11.0		15

Figure 5 presents the comparison of some literature data with the model predicted results.

Conclusions

New VLE experimental data (P, T, x, y) for the binary system carbon dioxide + 1-butanol were measured at (293.15, 303.15, 313.15, and 324.15) K and pressures up to 10.09 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 inverse temperature is proposed on the basis of the data of this study. The values of HVID parameters from the linear correlation were used to predict VLE at all temperatures for which published data are available. The predicted VLE data are reasonably good for engineering purposes.

Literature Cited

(1) Staby, A.; Mollerup, J. Mutual solubilities of mono-alcohols and carbon dioxide: A review of experimental data. *Fluid Phase Equilib.* **1993**, *89*, 351−381.

(2) Dohrn, R.; Brunner, G. High-pressure fluid-phase equilibria: Experimental methods and systems investigated (1988−1993). *Fluid Phase Equilib.* **1995**, *106*, 213−282.

(3) Christov, M.; Dohrn, R. High-pressure fluid phase equilibria experimental methods and systems investigated (1994−1999). *Fluid Phase Equilib.* **2002**, *202*, 153-218.

(4) Radcliffe, C.; Maguire, K.; Lockwood, B. Applications of supercritical fluid extraction and chromatography in forensic science. *J. Biochem. Biophys. Methods* **2000**, *43*, 261−272.

(5) King, M. B.; Alderson, D. A.; Fallah, F. H.; Kassim, D. M.; Kassim, K. M.; Sheldon, J. R.; Mahmud, R. S. Some Vapor/Liquid and Vapor/Solid Equilibrium Measurements of Relevance for Supercritical Extraction Operations, and Their Correlations. In *Chemical Engineering at Supercritical Fluid Conditions*; Paulitis, M. E., Penninger, J. M. L., Gray, R. D., Davidson, P., Eds.; Ann Arbor Science: Ann Arbor, MI, 1983; Vols. 31−80.

(6) Jennings, D. W.; Lee, R.-J.; Teja, A. S. Vapor−Liquid Equilibria in the Carbon Dioxide + Ethanol and Carbon Dioxide + 1-Butanol Systems. *J. Chem. Eng. Data* **1991**, *36*, 303−307.

(7) Suzuki, T.; Tsuge, N.; Nagahama, K. Solubilities of ethanol, 1-propanol, 2-propanol, and 1-butanol in supercritical carbon dioxide at 313 K and 333 K. *Fluid Phase Equilib.* **1991**, *67*, 213−226.

(8) Chang, C. J. The solubility of carbon dioxide in organic solvents at elevated pressures. *Fluid Phase Equilib.* **1992**, *74*, 235−242.

(9) Borch-Jensen, C.; Staby, A.; Mollerup, J. Mutual solubility of 1-butanol and carbon dioxide, ethene, ethan, or propane at a reduced supercritical solvent temperature of 1.03. *J. Supercrit. Fluids* **1994**, *7*, 231−244.

(10) Ishihara, K.; Tsukajima, A.; Tanaka, H.; Kato, M.; Sako, T.; Sato, M.; Hakuta, T. Vapor−Liquid Equilibrium for Carbon Dioxide + 1-Butanol at High Pressure. *J. Chem. Eng. Data* **1996**, *41*, 324−325.

(11) Stevens, R. M. M.; Shen, X. M.; De Loos, Th. W.; De Swaan Arons, J. A new apparatus to measure the vapour-liquid equilibria of low-volatility compounds with near-critical carbon dioxide. Experimental and modeling results for carbon dioxide + n-butanol, + 2-butanol, + 2-butyl acetate and + vinyl acetate systems. *J. Supercrit. Fluids* **1997**, *11*, 1−14.

(12) Hiaki, T.; Miyagi, H.; Tsuji, T.; Hongo, M. Vapor-liquid equilibria for supercritical carbon dioxide + butanol systems at 313.2 K. *J. Supercrit. Fluids* **1998**, *13*, 23−27.

(13) Silva-Oliver, G.; Galicia-Luna, L. A. Vapor-liquid equilibria near critical point and critical points for the CO_2 + 1-butanol and CO_2 + 2-butanol systems at temperatures from 324 to 432 K. *Fluid Phase Equilib.* **2001**, *182*, 145−156.

(14) Chen, H.-I.; Chang, H.-Y.; Chen, P.-H. High-Pressure Phase Equilibria of Carbon Dioxide + 1-Butanol, and Carbon Dioxide + Water + 1-Butanol Systems. *J. Chem. Eng. Data* **2002**, *47*, 776−780.

(15) Byun, H.-S.; Kwak, C. High-Pressure Phase Behavior for Carbon Dioxide−1-Butanol and Carbon Dioxide-1-Octanol Systems. *Korean J. Chem. Eng.* **2002**, *19*, 1007−1013.

(16) Soave, G. Equilibrium constants from a modified Redlich-Kwong equation of state. *Chem. Eng. Sci.* **1972**, *27*, 1197−1203.

(17) Feroiu, V.; Geană, D. Prediction of vapor-liquid equilibria at high pressures using activity coefficients at infinite dilution. *Fluid Phase Equilib.* **1996**, *120*, 1−10.

(18) Geană, D.; Feroiu, V. Prediction of vapor-liquid equilibria at low and high pressures from UNIFAC activity coefficients at infinite dilution**.** *Ind. Eng. Chem. Res.* **1998**, *37*, 1173−1180.

(19) Secuianu, C.; Feroiu, V.; Geană, D. High-Pressure Vapor−Liquid Equilibria in the System Carbon Dioxide and 2-Propanol at Temperatures from 293.25 K to 323.15 K. *J. Chem. Eng. Data* **2003**, *48*, 1384−1386.

(20) Secuianu, C.; Feroiu, V.; Geană, D. High-Pressure Phase Equilibria for the Carbon Dioxide + Methanol and Carbon Dioxide + 2-Propanol Systems. *Rev. Chim. (Bucharest)* **2003**, *54*, 874−879.

Received for review January 29, 2004. Accepted September 8, 2004. We are grateful to the National Council for Scientific Research of Romania for financial support.

JE0499521