x_i	liquid-phase mole fraction of component i
x_{wi}	liquid-phase mass fraction of component i
X_{wi}	liquid-phase mass fraction of component i on a solvent-free basis
y_i	vapor-phase mole fraction of component i
α_{ij}	parameter of the NRTL equation, eq 2
γ_i	activity coefficient of component i
τ_{ij}	parameter of the NRTL equation, eq 2
$\sigma(x_w)$	standard deviation, mass fraction

Subscripts

calc	calculated
exp	experimental
i,j	component indexes (1, acetonitrile; 2, water; 3, aromatic hydrocarbon)
j	phase index (1, aqueous; 2, organic)
k	tie-line index
m	running variable, eq 5
p,r	running variables, eq 2

Literature Cited

(1) Tollefson, E. L.; Decker, R. M.; Johnson, C. B. *Can. J. Chem. Eng.* **1970**, *48*, 219.
(2) Hartwig, G. M.; Hood, G. C.; Maycock, R. L. *J. Phys. Chem.* **1955**, *59*, 52.
(3) Francis, A. W. *J. Chem. Eng. Data* **1965**, *10*, 145.
(4) Rao, D. S.; Rao, K. V.; Raviprasad, A.; Chiranjivi, C. *J. Chem. Eng. Data* **1979**, *24*, 241.
(5) Rao, C. V. S. R.; Rao, K. V.; Raviprasad, A.; Chiranjivi, C. *J. Chem. Eng. Data* **1978**, *23*, 23.
(6) Renon, H.; Prausnitz, J. M. *AIChE J.* **1968**, *14*, 135.
(7) Renon, H.; Asselineau, L.; Cohen, G.; Raimbault, C. *Calcul sur ordinateur des equilibres liquide-vapeur et liquide-liquide*; Technip: Paris, 1971; p 16.
(8) Sorensen, J. M.; Arlt, W. *Liquid-Liquid Equilibrium Data Collection: Binary Systems*; DECHEMA: Frankfurt Main, FRG, 1979; Vol. 5, Part I, p 341.
(9) Di Cave, S.; Mazzarotta, B. *J. Chem. Eng. Data*, preceding paper in this issue.
(10) Volpicelli, G. *Chim. Ind.* (*Milan*) **1967**, *49*, 720.
(11) Sugi, H.; Katayama, T. *J. Chem. Eng. Jpn.* **1978**, *11*, 167.

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Vapor–Liquid Equilibria in the Carbon Dioxide + Ethanol and Carbon Dioxide + 1-Butanol Systems

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Vapor–liquid equilibrium data for CO_2 + ethanol mixtures at 314.5, 325.2, and 337.2 K and for CO_2 + 1-butanol mixtures at 314.8, 325.3, and 337.2 K have been measured by using a high pressure flow apparatus. The pressure in the experiments ranged from 4.633 to 11.776 MPa. Our results for the CO_2 + ethanol system are in good agreement with the recent results of Suzuki et al. and with the results of Panagiotopoulos. However, the results for the CO_2 + 1-butanol system are significantly different from those reported by King et al.

Introduction

CO_2 + alcohol systems are of interest because of their importance as supercritical fluid/cosolvent pairs in the separation of biomaterials (*1–4*). A knowledge of vapor–liquid equilibrium in these systems is therefore necessary for evaluating models for the extraction of biomaterials with supercritical fluid/cosolvent pairs. In spite of these interests, however, only the CO_2 + methanol (*5–8*) and CO_2 + ethanol (*8–11*) systems have been studied extensively. Surprisingly, the CO_2 + 1-propanol (*8*, *11*), CO_2 + 2-propanol (*11–12*), and CO_2 + 1-butanol (*13*) systems have received very little attention, and CO_2 + higher alcohol systems have not been studied at all.

We have constructed a flow apparatus to measure high-pressure vapor–liquid equilibria in systems containing CO_2 + alcohol and biomaterials in liquid solutions. A flow apparatus was chosen because large sample sizes could be generated for analysis, and this can be particularly valuable when dealing with components present in dilute concentrations. We are currently evaluating the CO_2 + ethanol, CO_2 + propanol, and CO_2 + 1-butanol systems for the supercritical extraction of pyrrolizidine alkaloids. We have therefore measured vapor–liquid equilibria in the CO_2 + ethanol and CO_2 + 1-butanol systems. The CO_2 + ethanol system was chosen as a test system to check the validity of the measurements from the new apparatus, since a number of investigators have reported data for this system at the conditions of interest. The only previously reported data for the CO_2 + 1-butanol system are those of King et al. (*13*) at 313.15 and 383.15 K. The CO_2 + 1-butanol system was studied in the present work because of a need for data at temperatures other than those previously reported.

Experimental Section

Experimental Apparatus. In the flow apparatus, two or more components are mixed thoroughly and continuously at constant temperature until vapor–liquid equilibrium is achieved. The vapor and liquid phases are then separated and analyzed to obtain the concentrations of the phases in equilibrium. A schematic diagram of the apparatus used in this work is shown in Figure 1, and a more detailed description is given below. The apparatus is similar to those described by Simnick et al. (*14*), Thies and Paulaitis (*15*), Inomata et al. (*16*), and Radosz et al. (*17*).

Liquid carbon dioxide was obtained from a cylinder equipped with an eductor tube and was compressed to the desired pressure by using a Milton Roy metering pump (Model 396–89). The inlet tube and the pump head were covered with an ice bath to ensure that the carbon dioxide remained liquid during the compression process. A regulator was used instead of the pump when the desired pressure was lower than the carbon dioxide cylinder pressure. Liquid ethanol and 1-butanol were compressed to the desired pressure by using another Milton Roy metering pump (Model 396–57).

The CO_2 and alcohol were pumped through a section of 0.125-in.-o.d. × 0.069-in.-i.d. stainless steel tubing, tubing coils, and two 0.1875-in.-o.d. × 0.132-in.-i.d. × 7-in. static mixers placed inside a constant-temperature air bath. Vapor–liquid

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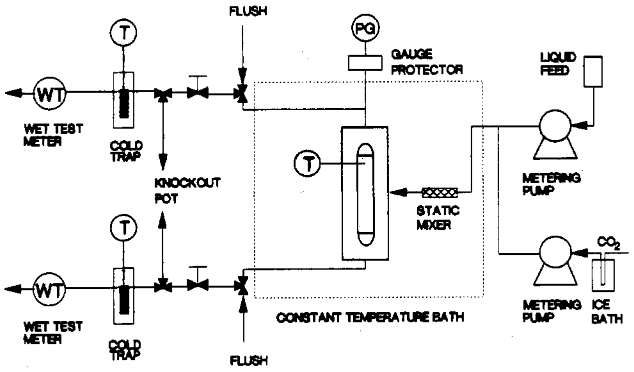

Figure 1. Schematic diagram of flow apparatus.

equilibrium was attained in this section, and the two phases were then separated in a high-pressure view cell (Jerguson liquid level gauge, Model 17-T-40). The use of the view cell offered two advantages: first, it provided visual confirmation that the experimental conditions were in the two-phase region, and, second, it allowed the liquid level to be controlled so that pressure fluctuations could be minimized.

The two phases exited from the top and bottom of the view cell. The analysis of the phases was carried out by first depressurizing each phase across a HIP micrometering valve and further through a Whitey three-way ball valve. The three-way ball valves allowed the phases to be directed to a "knockout pot" or to a sampling analysis arrangement. The valves were wrapped with heating tape to counteract Joule-Thompson cooling effects. Each depressurized equilibrium phase resulted in a liquid and vapor phase. This condensed liquid phase consisted of essentially pure alcohol, and the vapor phase consisted of essentially pure noncondensible carbon dioxide.

The equilibrium liquid phase was expanded into a sample trap placed in an ice bath, where the alcohol was condensed and collected in the trap. The noncondensible portion, carbon dioxide, passed through the trap and then through a wet-test meter. The vapor phase was treated in a similar fashion, with the exception that the sample trap was placed in an ethanol/dry ice bath and glass wool was placed near the top of the trap. Precision wet-test meters (Models 63115 and 63111) were used to measure the noncondensible gas volume from the liquid and vapor phases, respectively. Equilibrium-phase compositions were calculated from the weight of alcohol condensed and the measured volumes of the noncondensible portion.

The pressure was measured by a digital Heise pressure gauge (Model 710A), which was calibrated against a Budenburg dead-weight tester. The pressure measurements were estimated to be accurate to within ±0.014 MPa. The temperature was determined by a thermistor inserted into the top side of the view cell. The thermistor was calibrated against a Leeds and Northrup platinum resistance thermometer for the CO_2 + ethanol system and against a Fluke digital thermometer equipped with a platinum probe (Model 2180 A) for the CO_2 + 1-butanol system. The temperature measurements were estimated to be accurate within ±0.1 K. Both wet-test meters were factory calibrated with a stated accuracy of 0.5%. A Sartorius balance (Model 1872) was used to measure the weight of alcohol condensate collected. The weight measurements were reproducible within ±0.0001 g, and the accuracy of the weight measurements was estimated to be within ±0.0010 g.

Experimental Procedure. The first step in the experimental procedure was to begin pumping the two components at the desired pressure. The level of the liquid in the view cell was set by adjusting the flow rate of the liquid phase. Constant pressure was maintained by adjusting the vapor-phase flow rate during the experiment. Analysis of the phases after depressurization was begun after maintaining "steady-state" conditions for approximately 20–30 min at the desired pressure. In many cases, this was adequate to purge the initial portion of the phases that had not equilibrated at the desired conditions from the apparatus. Occasionally, however, compositions of the first samples collected were slightly different from those of the remaining samples due to inadequate purging. These initial samples, therefore, were discarded. Typically, four to six liquid samples and three to five vapor samples were collected. The reported compositions represent an average of all the samples equilibrated at the desired pressure and temperature. Additionally, to verify that equilibrium conditions had been attained, some experiments were repeated at different flow rates at the same temperature and pressure.

The vapor-phase compositions at 314.5 K for the CO_2 + ethanol system are an exception and represent averages of only two samples. The 314.5 K isotherm was the first isotherm measured with the new apparatus. It was found that complete condensation of ethanol did not always occur in the sample collection tubes during these measurements. The problem was not severe and was solved simply by placing glass wool at the top of the collection tube. This helped to increase heat transfer and to eliminate any possible entrainment of the alcohol. The measurement at 314.5 K and 5.550 MPa was repeated at a later date with glass wool in place and was found to be consistent with the previous measurement. Therefore, the data at 314.5 K are included in our reported results, although they are, perhaps, slightly less precise than the other measurements.

The pressure and temperature were recorded throughout the experiment to determine how "equilibrium conditions" were being maintained. The pressure fluctuations were generally less than ±0.024 MPa during an experiment. The temperature generally increased slightly from the first to the last sample, but this change was less than 0.3 K. The reported temperature is an average of the maximum and minimum temperatures recorded during the sampling period.

The reproduciblity of the liquid-phase compositions was usually within ±0.001 mode fraction, and that of the vapor-phase compositions, within ±0.0015 mole fraction for the CO_2 + ethanol system and ±0.0003 mole fraction for the CO_2 + 1-butanol system. The difference in the reproducibility between the two systems can be attributed to the lower volatility of 1-butanol, which leads to condensation of essentially all the 1-butanol.

Although small, corrections were made for the residual alcohol present in the noncondensible portion of the sample leaving the sample collection trap and for the carbon dioxide present in the condensed alcohol. Corrections for the residual ethanol were on the order of 0.0001 and 0.005 mole fraction for the CO_2 + ethanol vapor and liquid compositions, respectively. Corrections for residual 1-butanol were even smaller. Corrections for the dissolved carbon dioxide were estimated to be 1 order of magnitude smaller than the precision of the measurements and were neglected.

The liquid-phase compositions were estimated to be accurate within ±0.003, and the vapor-phase compositions, to be within ±0.003 for the CO_2 + ethanol system and ±0.0006 for the CO_2 + 1-butanol system. These estimates are based on the accuracy and the precision of the instruments used in measuring the compositions, the reproducibility of the measurements, and on comparison of the results with measurements of other investigators.

Source and Purity of the Materials. Coleman grade carbon dioxide of minimum purity 99.99% was obtained from Matheson Gas Products. Absolute ethanol (200 proof) was obtained from Quantum Chemical Corp. 1-Butanol was obtained from Fischer Chemicals and had a stated purity of 99.8%. All substances were used without further purification.

Table I. Experimental Data for Liquid x_{CO_2} and Vapor y_{CO_2} Composition for the CO_2 + Ethanol System

P/MPa	T/K	x_{CO_2}	y_{CO_2}
5.550	314.7	0.343	0.991
6.191	314.6	0.402	0.992
6.571	314.5	0.446	0.991
6.881	314.5	0.486	0.991
7.453	314.4	0.611	0.989
7.894	314.2	0.845	0.984
	av: 314.5		
6.274	325.1	0.333	0.987
6.902	325.2	0.379	0.986
7.260	325.2	0.411	0.985
7.632	325.2	0.446	0.984
8.356	325.1	0.527	0.982
8.591	325.2	0.568	0.980
8.825	325.2	0.605	0.976
9.204	325.2	0.702	0.967
9.349	325.0	0.775	0.964
	av: 325.2		
6.219	337.2	0.272	0.978
6.853	337.2	0.311	0.978
7.605	337.2	0.357	0.978
8.287	337.2	0.404	0.977
9.011	337.1	0.459	0.972
9.604	337.2	0.511	0.966
10.363	337.2	0.601	0.955
10.845	337.1	0.704	0.935
	av: 337.2		

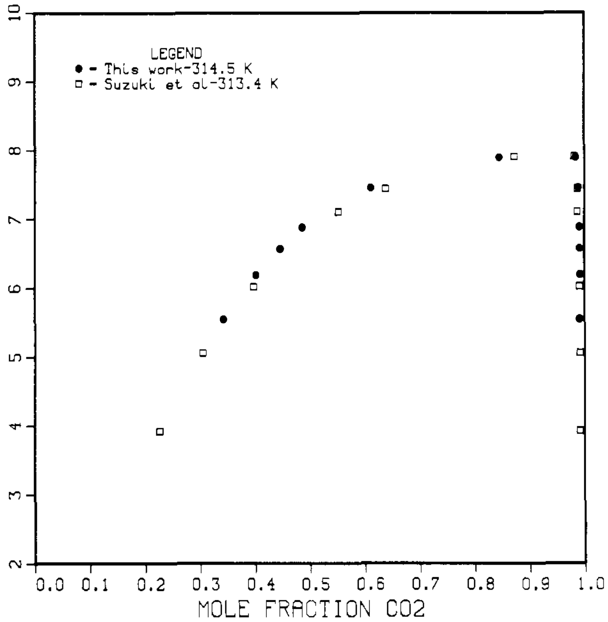

Figure 2. Vapor-liquid equilibria for CO_2 + ethanol at 314.5 K.

Results and Discussion

Vapor-liquid equilibrium data for CO_2 + ethanol at 314.5, 325.2, and 337.2 K are presented in Table I. The results at 314.5 K are compared with the recent measurements at 313.4 K by Suzuki et al. (*8*) in Figure 2, and the results at 325.2 K are compared with the measurements of Panagiotopoulos (*10*) at 323.2 K in Figure 3. Note that, although the temperatures are not identical in these comparisons, both isotherms show good agreement with the data of the other investigators. The K values for the three isotherms are presented in Figure 4. The results of Yao et al. (*11*) at 313.1 and 323.1 K are not in agreement with our measurements or with the measurements of Suzuki et al. and Pangiotopoulos.

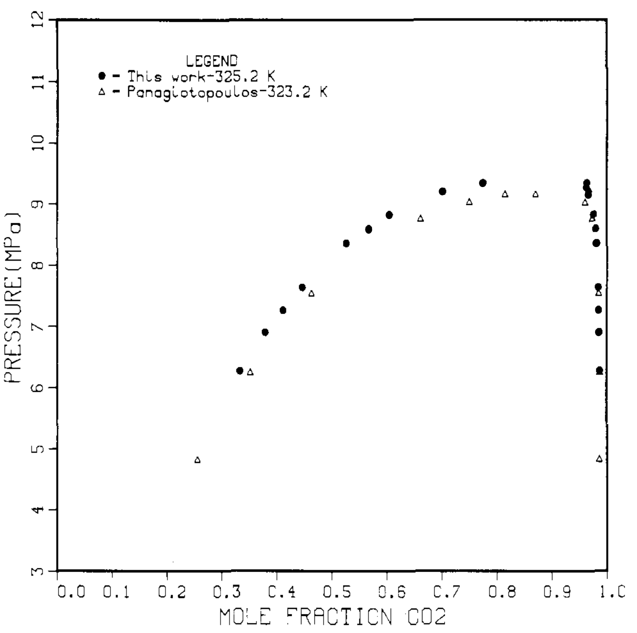

Figure 3. Vapor-liquid equilibria for CO_2 + ethanol at 325.2 K.

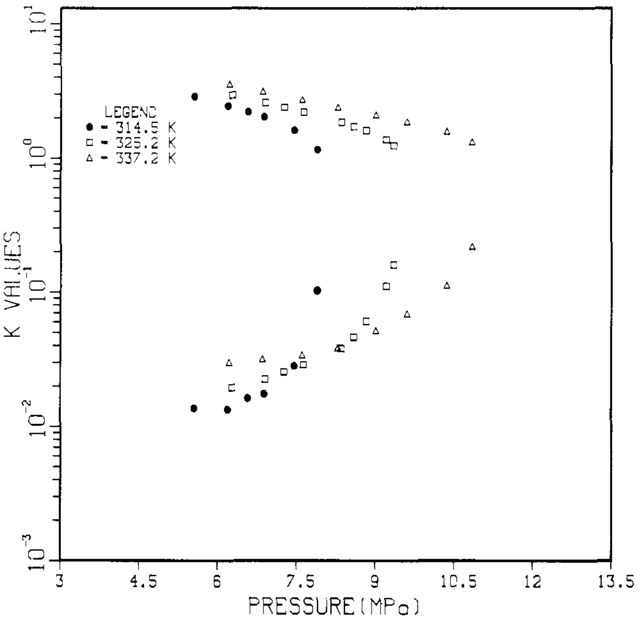

Figure 4. K values in the CO_2 + ethanol system.

Vapor-liquid equilibrium data for CO_2 + 1-butanol at 314.8, 325.3, and 337.2 K are presented in Table II. Our measurements at 314.8 K are compared with the measurements of King et al. (*13*) at 313.15 K in Figure 5. Our results are in considerable disagreement with those of King et al. even after allowance is made for the temperature differences of the two sets of measurements. Measurements of King et al. (*18*) for the system CO_2 + n-hexadecane at 60 °C also showed a higher CO_2 composition in the liquid phase than measurements of Charoensombut-amon et al. (*19*) and D'Souza et al. (*20*) at the same temperature. Additionally, the measurements of King et al. were made with a blind cell, and, because of the odd shape of the isotherm in the critical region, they speculated that the two highest pressure measurements represent two liquid phases. Our results, however, show that liquid-liquid-phase separation is unlikely since at these conditions the isotherms show the rapid change in liquid-phase compositions in the

Table II. Experimental Data for Liquid x_{CO_2} and Vapor y_{CO_2} Composition for the CO_2 + 1-Butanol System

P/MPa	T/K	x_{CO_2}	y_{CO_2}
4.633	314.8	0.2837	0.9981
5.433	314.8	0.3454	0.9978
6.240	314.8	0.4147	0.9976
6.895	314.8	0.4828	0.9970
7.570	314.8	0.5803	0.9957
7.577	314.8	0.5836	0.9958
7.777	314.8	0.6213	0.9949
7.984	314.6	0.6959	0.9940
	av: 314.8		
5.226	325.3	0.2857	0.9966
6.226	325.3	0.3497	0.9964
6.895	325.4	0.3978	0.9957
7.605	325.2	0.4542	0.9948
8.274	325.4	0.5164	0.9934
8.977	325.3	0.5988	0.9908
9.466	325.3	0.6778	0.9869
9.653	325.2	0.7307	0.9838
9.873	325.0	0.8057	0.9754
	av: 325.3		
6.178	337.1	0.3017	0.9941
6.902	337.2	0.3436	0.9942
7.605	337.2	0.3842	0.9931
8.094	337.1	0.4149	0.9924
8.708	337.2	0.4548	0.9915
9.184	337.3	0.4890	0.9901
9.722	337.4	0.5287	0.9877
10.342	337.3	0.5860	0.9848
11.025	337.4	0.6596	0.9773
11.507	337.4	0.7264	0.9666
11.776	337.4	0.7815	0.9519
	av: 337.2		

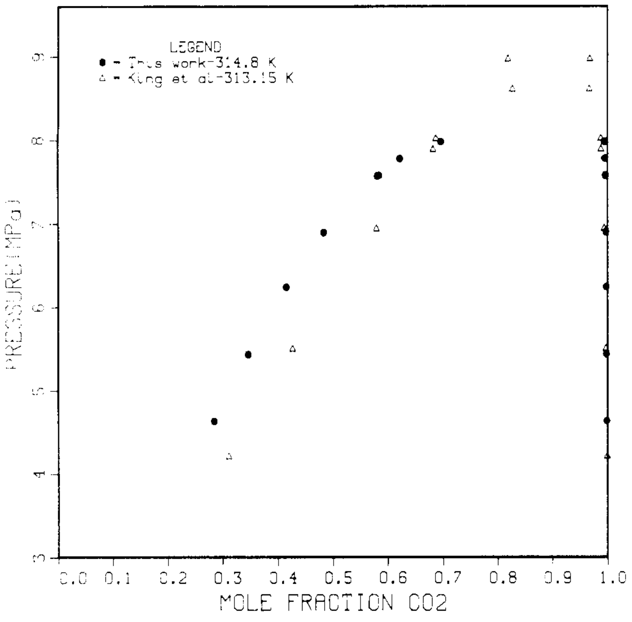

Figure 5. Vapor-liquid equilibria for CO_2 + 1-butanol at 314.8 K.

critical region, which is characteristic of vapor-liquid equilibrium behavior. This is supported by the recent work of Lam et al. (*21*), who report that the liquid-liquid-vapor locus in the CO_2 + 1-butanol system terminates at an upper critical end point at 22.99 bar and 259.25 K. Liquid-liquid phase separation is therefore unlikely at the condition studied by King et al. (*13*). Similarly, Suzuki et al. reported that all of the CO_2 + alcohol systems they studied (CO_2 + methanol, CO_2 + ethanol, and CO_2 + 1-propanol) "showed a similar $P-T-x-y$ envelope shape". Our results for the CO_2 + 1-butanol system follow this trend.

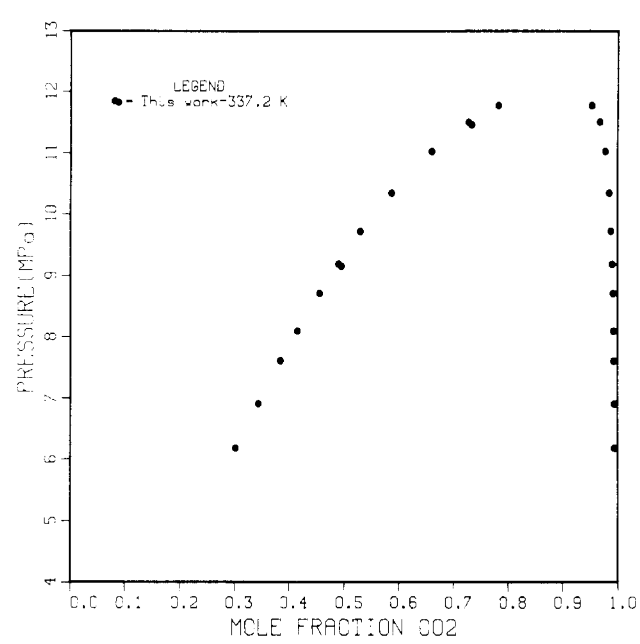

Figure 6. Vapor-liquid equilibria for CO_2 + 1-butanol at 337.2 K.

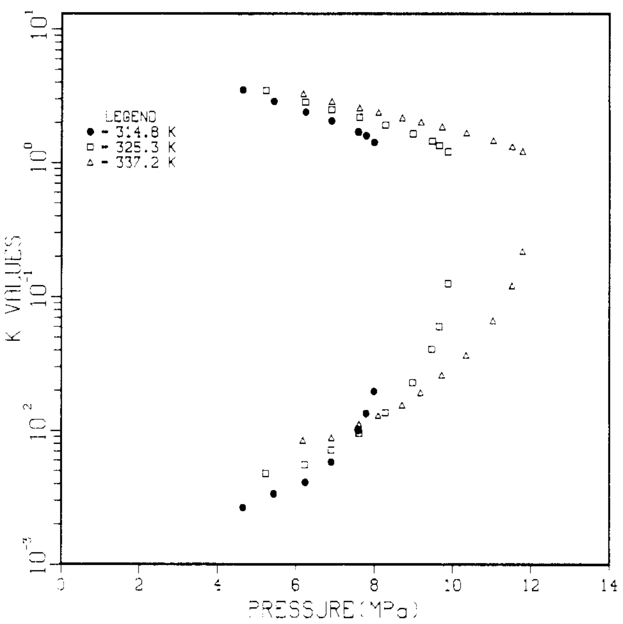

Figure 7. *K* values in the CO_2 + 1-butanol system.

Figure 6 shows the results for the 337.2 K isotherm and Figure 7 shows the *K* values for all three isotherms for the CO_2 + 1-butanol system. Once again, there is no evidence of liquid-liquid type behavior in the critical region in this system.

Registry No. CO_2, 124-38-9; ethanol, 64-17-5; 1-butanol, 71-36-3.

Literature Cited

(1) Schaeffer, S. T.; Zalkow, L. H.; Teja, A. S. *Fluid Phase Equilib.* **1988**, *43*, 45.
(2) Schaeffer, S. T.; Zalkow, L. H.; Teja, A. S. *Biotechnol. Bioeng.* **1989**, *34*, 1357.
(3) Wong, J. M.; Johnston, K. P. *Biotechnol. Prog.* **1986**, *2*, 29.
(4) Larson, K. A.; King, M. L. *Biotechnol. Prog.* **1986**, *2*, 73.
(5) Ohgaki, K.; Katayama, T. *J. Chem. Eng. Data* **1976**, *21*, 53.
(6) Semenova, A. I.; Emel'yanova, E. A.; Tsimmerman, S. S.; Tsiklis, D. S. *Russ. J. Phys. Chem.* (*Engl. Transl.*) **1979**, *53*, 1428.
(7) Hong, J. H.; Kobayashi, R. *Fluid Phase Equilib.* **1988**, *41*, 269.
(8) Suzuki, K.; Sue, H.; Itou, M.; Smith, R. L.; Inomata, H.; Arai, K.; Saito, S. *J. Chem. Eng. Data* **1990**, *35*, 63.
(9) Takishima, S.; Saiki, K.; Arai, K.; Saito, S. *J. Chem. Eng. Jpn.* **1986**, *19*, 48.
(10) Panagiotopoulos, A. Z. Ph.D. Dissertation, Massachusetts Institute of Technology, 1986.
(11) Yao, S.; Liu, F.; Han, Z.; Zhu, Z. *Proc. Int. Symp. Thermodyn. Chem. Eng. Ind.* **1988**, *1*, 688.
(12) Radosz, M. *J. Chem. Eng. Data* **1986**, *31*, 43.

J. Chem. Eng. Data **1991**, *36*, 307-311

(13) King, M. B.; Alderson, D. A.; Fallah, F. H.; Kassim, D. M.; Kassim, K. M.; Sheldon, J. R.; Mahmud, R. S. In *Chemical Engineering at Supercritical Fluid Conditions*; Paulaitis, M. E., Penninger, J. M. L., Gray, R. D., Davidson, P., Eds.; Ann Arbor Science: Ann Arbor, MI, 1983; Chapter 2.
(14) Simnick, J. J.; Lawson, C. C.; Lin, H. M.; Chao, K. C. *AIChE J.* **1977**, *23*, 469.
(15) Thies, M. C.; Paulaitis, M. E. *J. Chem. Eng. Data* **1984**, *29*, 438.
(16) Inomata, H.; Tuchiya, K.; Arai, K.; Saito, S. *J. Chem. Eng. Jpn.* **1986**, *19*, 386.
(17) Radosz, M.; Cotterman, R. L.; Prausnitz, J. M. *Ind. Eng. Chem. Res.* **1987**, *26*, 731.
(18) King, M. B.; Kassim, K.; Bott, T. R.; Sheldon, J. R.; Mahmud, R. S. *Ber. Bunsen-Ges. Phys. Chem.* **1984**, *88*, 820.
(19) Charoensombut-amon, T.; Martin, R. J.; Kobayashi, R. *Fluid Phase Equilib.* **1986**, *31*, 89.
(20) D'Souza, R.; Patrick, J. R.; Teja, A. S. *Can. J. Chem. Eng.* **1988**, *66*, 319.
(21) Lam, D. H.; Jangkamolkulchai, A.; Luks, K. D. *Fluid Phase Equilib.* **1990**, *60*, 131.

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Multiphase Equilibrium Behavior of the Mixture Ethane + Methanol + 1-Decanol

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The liquid-liquid-vapor (LLV) phase equilibria of the ternary mixture ethane + methanol + 1-decanol were experimentally studied by using a visual cell (stoichiometric) technique with pressure discrimination of ±0.01 bar, achieved by coupling a dead-weight gauge to the cell pressure transducer. The pressure, phase compositions, and molar volumes of the two liquid phases of the ternary LLV system are reported at 295.15 K. Also presented are LLV phase equilibrium data for the binary mixture ethane + methanol. The ternary system has two constituent binary mixtures that exhibit LLV partial miscibility. The portion of the three-phase region of the ternary system examined is bounded by these binary LLV loci and from above by an upper critical end point (L-L=V) locus and from below by a lower critical end point (L=L-V) locus.

Introduction

During the past several years, our group has been engaged in the study of liquid-liquid-vapor (LLV) phase equilibria in well-defined systems such as carbon dioxide + hydrocarbon, ethane + hydrocarbon, and nitrous oxide + hydrocarbon binary mixtures, where the hydrocarbon has frequently been one of the members of the homologous series of *n*-paraffins or *n*-alkylbenzenes. The goals of these studies were to map out the patterns of the multiphase equilibria of these prototype mixtures in thermodynamic phase space and to generate phase equilibrium data that would support the prediction of phase equilibria within and near regions of LLV immiscibility. With the studies of these essentially nonpolar systems as a point of reference, we have undertaken a series of studies of the multiphase equilibria of binary mixtures composed of both polar and nonpolar species. Recent studies have reported the LLV immiscibility behavior of certain members of the homologous series of ethane + 1-alkanol (*1*), carbon dioxide + 1-alkanol (*2*), and nitrous oxide + 1-alkanol (*3*) binary mixtures. Of these binary mixture homologous series, only the ethane-containing system does not have a lower 1-alkanol limit on LLV immiscibility. The LLV behavior of this series at the higher carbon numbers is similar to those of the other homologous series of nitrous oxide + 1-alkanol and carbon dioxide + 1-alkanol mixtures, as well as for the several *n*-paraffin solute series that have been studied. (Teja et al. (*4*) have recently pointed out that the properties of the 1-alkanols converge to those of the corresponding alkanes as their chain lengths increase.) However, following a decrease in the extent of the LLV immiscibility loci down to 1-butanol in the ethane + 1-alkanol homologous series of binary mixtures, there is an increase in LLV immiscibility with lower carbon number down to methanol (*1*). Apparently, at the lower 1-alkanol carbon numbers in these ethane-rich mixtures, the solvent-free concentration of the hydroxyl groups increases to the point that it offsets the decreasing size of the hydrocarbon solutes, in turn promoting LLV immiscibility.

Of particular interest here, on the basis of this observation, is the LLV behavior of the ternary mixture ethane + methanol + 1-decanol. The binary constituent subsystems ethane + methanol and ethane + 1-decanol both exhibit sizable LLV extent. We examine herein whether ternary mixtures with methanol + 1-decanol solute ratios having proportions of carbon number-to-hydroxyl groups in the solute-rich L_1 phase characteristic of 1-propanol or 1-butanol will correspondingly display significantly reduced LLV extent (i.e., a maximum in the lower critical end point, or L=L-V, temperature function) as does the binary mixture ethane + 1-butanol in the homologous series. Ternary systems containing a gas solvent and two relatively nonvolatile solutes of differing molecular nature with each being immiscible with the solvent gas have been studied by Miller and Luks (*5*) and Kohn's group (*6*-*10*). Their LLV regions were generally found to be narrow surfaces located close to and just below the solvent gas vapor pressure curve when projected onto pressure-temperature coordinates.

Stoichiometric techniques are capable of measuring the molar volumes and compositions of all the fluid phases if very precise pressure measurements are made. This precision is required due to the rapid change of the phase properties over the narrow LLV pressure range at a fixed temperature. An earlier ternary study (*5*) coupled a differential pressure transducer with a dead-weight gauge to permit pressure measurements to a precision of ±0.007 bar. In this present study we found that it was adequate to calibrate the pressure transducer at the end of each run over the narrow pressure range of interest for that run (typically, 0.15 bar) to achieve a precision of no worse than ±0.01 bar, a magnitude more precise than we normally achieve in our phase equilibrium studies using a transducer alone. In this present study, this added precision was sufficient to give reproducible results.

The LLV phase equilibria of the ternary mixture ethane + methanol + 1-decanol was studied by using a visual cell

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