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Phase Equilibria in Ternary Systems with Carbon Dioxide, Water, and Carboxylic Acids at Elevated Pressures

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Vapor–liquid and vapor–liquid–liquid equilibrium compositions have been measured for the ternary systems CO_2 + H_2O + acetic acid at 313 and 333 K, CO_2 + H_2O + propionic acid at 313 K, and CO_2 + H_2O + *n*-butyric acid at 313 K, at pressures between 2.0 and 20.0 MPa. For all systems, a three-phase equilibrium region was observed at pressures comparable to the critical pressure of pure carbon dioxide. The extent of the three-phase equilibrium region increases with the hydrocarbon chain length of the acid, while the pressure for the appearance of three phases also increases with temperature. The distribution coefficient of the acids between the supercritical fluid phase and the aqueous phase at pressures above the critical pressure of pure carbon dioxide increases with the hydrocarbon chain length of the acid: higher molecular weight acids were found to be preferentially partitioned into the supercritical fluid phase. The experimental data for the ternary systems were correlated by using a cubic equation of state and a recently proposed density-dependent mixing rule with model parameters derived from binary data only.

Introduction

Methods of using a fluid above its critical temperature and pressure as a solvent for the separation of mixtures of components have received considerable attention recently (*1*, *2*). The use of supercritical solvents for the energy-efficient recovery of low molecular weight organic compounds from aqueous solutions has been recently proposed by several investigators. Paulaitis et al. (*3*), McHugh et al. (*4*), and Gilbert and Paulaitis (*5*) investigated the recovery of ethanol with carbon dioxide, ethylene, and ethane as solvents. Kuk and Montagna (*6*) presented results for the separation of ethanol and 2-propanol from aqueous solutions using supercritical carbon dioxide. Radosz (*7*) and Paulaitis et al. (*8*, *9*) have determined phase equilibria for the system 2-propanol + water + carbon dioxide. Fleck (*10*) presented results for the extraction of *n*-propyl alcohol using a variety of supercritical fluids. Panagiotopoulos and Reid (*11*, *12*) have determined phase equilibria for ternary systems with supercritical carbon dioxide, water, and acetone or 1-butanol.

There have been relatively few experimental investigations of equilibria between aqueous solutions of low molecular weight organic acids and supercritical fluids. Previous measurements include those of Snedeker (*13*) for the system carbon dioxide + water + acetic acid and Elgin and Weinstock (*14*) for the system C_2H_4 + water + acetic acid and the corresponding system with propionic acid. Francis (*15*) measured phase equilibria for the system subcritical carbon dioxide + water + acetic acid. Shimshick (*16*) has presented data for the extraction of acetic and *n*-butyric acid from aqueous solutions using supercritical carbon dioxide. The objective of the present work was the determination of the phase equilibrium behavior for the ternary systems supercritical carbon dioxide + water + one of the first three straight-chain aliphatic acids.

Experimental Section

Equipment and Procedures. The experimental apparatus used was a high-pressure visual cell with external recirculation of all phases present. A detailed description of the equipment and operating procedures is given elsewhere (*17*). Compositions were measured by gas chromatography with on-line sampling. The chromatographic response factors for the nonvolatile components were determined by analyzing standard mixtures prepared gravimetrically. The relative response factor for carbon dioxide was determined by measuring equilibrium data for mixtures for which data are available in the literature (*18*–*20*). The stability of the relative response factors was monitored by periodic injection of reference mixtures of the liquid components. An additional check for the validity of the chromatographic analysis was provided by the agreement of the results at high pressures with the known behavior of the binary CO_2 + H_2O system at low concentrations of organic acid. The validation of the experimental procedures and comparisons with literature data is given in ref *17*.

It was determined that the composition of the less-dense supercritical fluid phase could not be reproducibly determined at lower pressures ($\leq$6.0 MPa), primarily because of the small mass of sample injected. These data were not considered reliable and were not included in the data tables.

Materials. Analytical grade acetic acid (supplied by Mallinckrodt), propionic acid (Sigma Chemical Co.), and *n*-butyric

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acid (Sigma) and glass-distilled water (Mallinckrodt) were used as received. Gas chromatographic analysis of the acids indicated a purity in the 99.5–99.7 wt % range, with water being the major contaminant. Since ternary data with water were to be measured, no effort was made to desiccate the acids. High purity CO_2 (99.99%, Matheson Gas Products) was used as received.

Correlation

For the correlation of the experimental results we used a cubic equation of state based on the Peng-Robinson form (*21*), with a new density-dependent mixing rule. A detailed discussion of the model used is given in ref *12*. The mixing rule involves two interaction parameters per binary system, $k_{12} = k_{21}$ and $\lambda_{12} = -\lambda_{21}$. The second parameter, λ_{ij}, describes the deviation of the mixture from the quadratic mixing rule at high densities. The pure component parameters for the subcritical components (H_2O and the acids) were determined by using a technique proposed by Panagiotopoulos and Kumar (*22*). The parameters thus obtained exactly reproduce vapor pressure and liquid density for the components of interest at each temperature. For the supercritical component (CO_2), the conventional acentric factor correlation (*21*) was used with values for the critical constants taken from Reid et al. (*23*).

Results and Discussion

The primary experimental results for the equilibrium compositions measured for the three systems are given in Tables I–IV. Each line in the tables gives the concentration of the coexisting phases (two or three) for the systems measured. Data from one to three chromatographic analyses (usually two) at each point were averaged to result in the reported concentration. The average standard deviation (reproducibility) for the set of analyses was ±0.003 in mole fraction with a maximum deviation between duplicate analyses of ±0.02. The absolute accuracy of the results is more difficult to ascertain. The uncertainty in the chromatographic response factors (*17*) is the main source of possible systematic errors. If these uncertainties are taken into account, the accuracy of the reported mole fractions may be estimated to be ±0.005 or ±2% of the value reported, whichever is greater. The pressure inside the cell during the time required for the analyses (15–30 min) was normally constant to within ±1.0% of the absolute value for the pressure; the pressure reported in the table is the average value. For the lower pressures, no data are available for the composition of the carbon dioxide-rich phase because of the difficulties in sampling mentioned in the previous section. The corresponding data are indicated by an "x" in the data tables. A full listing of the raw (not averaged) experimental results is available in Panagiotopoulos (*17*) and Willson (*24*); individual points are shown in Figures 1 and 2 and may help in estimating the reproducibility of the measurements.

In Tables I–IV, the phases are listed in order of decreasing density. Generally, phase 1 is the water-rich phase, phase 3 is the CO_2-rich phase, and phase 2 has an intermediate composition. However, this designation cannot be unique because of the transformation of phases into each other as pressure is changed. In the tables, an attempt was made to be consistent and to indicate the evolution of the phase diagram with pressure.

No exactly comparable results are available from the literature for any of the ternary systems studied in this work. A few data points from ref 13 are reported at similar conditions and agree with our results within the stated accuracy. An additional check on the accuracy of the results is provided by the reported concentrations of CO_2 in the aqueous phase and water in the CO_2 phase for low mole fraction of organic acid, extrapolated to zero concentration of acid, which agree with the accepted literature values from Wiebe and Gaddy (*18*) and Wiebe (*19*).

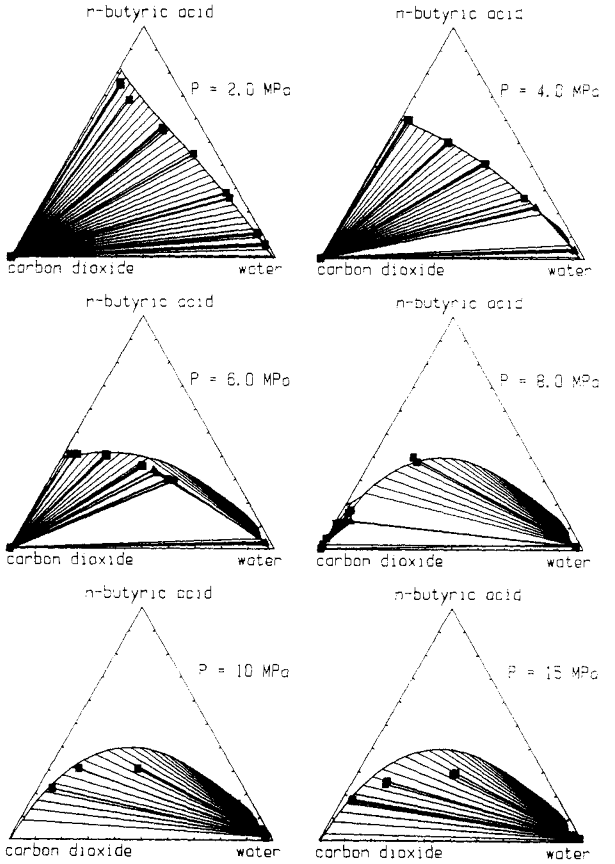

Figure 1. Phase equilibrium behavior for the system water–*n*-butyric acid–carbon dioxide at 313 K. (■) and (—) measured tie lines; (▲) measured three-phase equilibrium compositions; (—) predicted tie lines.

A typical evolution of the phase equilibrium behavior with pressure is given in Figure 1 for the system $CO_2 + H_2O +$ *n*-butyric acid at 313 K. At low pressures ($P = 2.0$ MPa) the diagram represents equilibrium between a low-density gas phase and a completely miscible liquid mixture. As pressure is increased, the dissolution of carbon dioxide in the liquid phase results in a split of the liquid into two phases, one richer in water and the other higher in acid concentration. The three-phase region is represented in Figure 1 as a triangular open area in the diagram for 4.0, 6.0, and 8.0 MPa.

The physical picture that underlies this behavior, as first described by Elgin and Weinstock (*14*), is the "salting out" effect of a supercritical fluid on an aqueous solution of an organic compound. As pressure is increased, dissolution of the supercritical fluid in the aqueous phase results in a phase split at a lower critical solution pressure (which varies with temperature). As pressure is further increased, the second liquid phase and the supercritical phase increasingly similar and merge at an upper critical solution pressure, above which only two phases coexist at equilibrium.

A three-phase equilibrium region was observed for all systems studied, as indicated in the data tables. The extent of the three-phase region (defined by the difference between the upper and lower critical solution pressure) becomes larger as the hydrocarbon chain length of the acid is increased. It is of the order of 0.1 MPa for acetic acid at both 313 and 333 K, 0.5 MPa for propionic acid, and greater than 4 MPa for *n*-butyric acid. The three-phase equilibrium region moves to higher pressures as temperature is increased for the acetic acid system.

The shape and extent of the two-phase coexistence region for all the systems studied were relatively insensitive to changes

Table I. Experimental Results for the System Water–Acetic Acid–Carbon Dioxide at 313 K

	mole fractions								
	phase 1			phase 2			phase 3		
P, MPa	H_2O	acid	CO_2	H_2O	acid	CO_2	H_2O	acid	CO_2
2.09	0.011	0.826	0.163				x	x	x
1.94	0.026	0.829	0.145				x	x	x
2.09	0.078	0.787	0.135				x	x	x
2.11	0.158	0.731	0.111				x	x	x
2.08	0.359	0.573	0.069				x	x	x
2.01	0.565	0.399	0.037				x	x	x
1.97	0.778	0.205	0.017				x	x	x
1.93	0.891	0.099	0.010				x	x	x
2.01	0.944	0.047	0.009				x	x	x
3.96	0.008	0.661	0.331				x	x	x
3.99	0.068	0.643	0.289				x	x	x
4.01	0.139	0.620	0.241				x	x	x
4.01	0.318	0.528	0.154				x	x	x
3.97	0.537	0.387	0.076				x	x	x
3.88	0.765	0.204	0.032				x	x	x
3.99	0.877	0.104	0.019				x	x	x
3.99	0.933	0.052	0.015				x	x	x
5.90	0.004	0.425	0.571				x	x	x
5.91	0.043	0.452	0.506				x	x	x
5.88	0.098	0.474	0.427				x	x	x
5.88	0.276	0.469	0.255				x	x	x
5.94	0.511	0.367	0.122				x	x	x
5.99	0.877	0.096	0.027				x	x	x
5.88	0.927	0.053	0.020				x	x	x
6.95	0.003	0.263	0.734				0.000	0.021	0.979
7.01	0.024	0.282	0.694				x	x	x
6.98	0.062	0.324	0.613				0.000	0.017	0.983
7.00	0.230	0.401	0.369				x	x	x
6.88	0.494	0.361	0.145				x	x	x
6.88	0.702	0.231	0.066				0.001	0.017	0.983
6.93	0.748	0.200	0.052				x	x	x
7.49	0.001	0.163	0.836				0.000	0.015	0.985
7.78	0.024	0.116	0.860				0.001	0.009	0.990
7.79	0.030	0.108	0.862				0.002	0.012	0.987
7.92				0.001	0.080	0.919	0.000	0.008	0.992
7.86				0.007	0.103	0.891	0.001	0.015	0.984
3-phase 7.80	0.571	0.308	0.121	0.032	0.132	0.835	0.001	0.014	0.985
3-phase 8.08	0.749	0.192	0.060	x	x	x	x	x	x
8.00	0.868	0.098	0.034				0.004	0.006	0.990
8.01	0.925	0.051	0.024				0.001	0.001	0.998
8.02	0.960	0.020	0.020				0.000	0.003	0.998
9.97	0.472	0.351	0.177				0.063	0.347	0.590
10.13	0.575	0.296	0.130				0.022	0.162	0.817
10.27	0.683	0.232	0.085				0.019	0.157	0.825
9.98	0.785	0.159	0.056				x	x	x
9.90	0.874	0.093	0.033				x	x	x
10.00	0.931	0.043	0.027				0.012	0.006	0.982
10.00	0.962	0.016	0.023				0.003	0.001	0.997
15.18	0.402	0.368	0.231				0.067	0.266	0.667
14.80	0.550	0.309	0.140				0.026	0.186	0.788
14.44	0.693	0.225	0.082				0.012	0.103	0.885
14.77	0.772	0.170	0.058				0.025	0.074	0.901
14.68	0.879	0.088	0.033				0.005	0.030	0.965
14.70	0.926	0.045	0.029				0.005	0.008	0.987
15.14	0.963	0.014	0.023				0.002	0.001	0.997
19.55	0.408	0.360	0.232				0.069	0.270	0.661
17.60	0.540	0.312	0.148				0.034	0.193	0.772
20.10	0.709	0.212	0.079				0.014	0.108	0.878
19.65	0.783	0.159	0.058				0.015	0.071	0.913
20.35	0.881	0.085	0.034				0.006	0.029	0.965
20.00	0.927	0.046	0.027				0.004	0.012	0.984
19.73	0.958	0.017	0.024				0.003	0.001	0.997

in pressure and temperature above the critical pressure of the pure supercritical fluid, for the range of pressures between 10 and 20 MPa for the two temperatures studied. This is in agreement with the results of previous investigators for the ethanol + water + carbon dioxide system (*5*); it may not be correct when the system behavior at the high-pressure range is complicated by the presence of three-phase equilibrium regions. An example of this latter case is provided by the 2-propanol + water + carbon dioxide system, which has been studied by Paulaitis et al. (*8*, *9*) and Radosz (*7*).

From the point of view of practical applications of the phase equilibrium behavior demonstrated here, the crucial parameters are the selectivity of the supercritical fluid phase for the organic compound over water, and the ratio of acid mole fraction in the supercritical fluid phase to that in the aqueous phase, or distribution coefficient. A pronounced effect of the hydrocarbon chain length in a homologous series of organic compounds on the distribution coefficient and the selectivity of the supercritical solvent for the organic compound over water was observed. This can be best described by comparing the results for the

Table II. Experimental Results for the System Water–Acetic Acid–Carbon Dioxide at 333 K

	mole fractions								
	phase 1			phase 2			phase 3		
P, MPa	H_2O	acid	CO_2	H_2O	acid	CO_2	H_2O	acid	CO_2
2.07	0.012	0.888	0.099				x	x	x
2.04	0.139	0.776	0.085				x	x	x
2.02	0.415	0.539	0.046				x	x	x
2.03	0.467	0.498	0.035				x	x	x
2.02	0.564	0.408	0.028				x	x	x
2.03	0.680	0.299	0.021				x	x	x
2.06	0.860	0.132	0.008				x	x	x
2.09	0.949	0.045	0.006				x	x	x
1.97	0.978	0.017	0.005				x	x	x
3.98	0.009	0.794	0.197				x	x	x
4.02	0.124	0.696	0.180				x	x	x
3.96	0.389	0.516	0.096				x	x	x
3.81	0.457	0.470	0.073				x	x	x
4.11	0.554	0.393	0.052				x	x	x
3.84	0.662	0.300	0.038				x	x	x
4.04	0.865	0.118	0.018				x	x	x
3.95	0.940	0.049	0.011				x	x	x
3.89	0.972	0.019	0.010				x	x	x
5.98	0.009	0.625	0.366				x	x	x
6.16	0.106	0.591	0.303				x	x	x
5.86	0.356	0.496	0.149				x	x	x
5.92	0.433	0.447	0.120				x	x	x
6.01	0.435	0.446	0.120				x	x	x
6.07	0.529	0.383	0.089				x	x	x
6.05	0.649	0.292	0.059				x	x	x
6.06	0.859	0.116	0.025				x	x	x
5.99	0.935	0.050	0.016				x	x	x
6.07	0.968	0.019	0.014				x	x	x
8.16	0.007	0.441	0.552				0.001	0.064	0.936
7.97	0.084	0.477	0.440				0.009	0.083	0.908
8.01	0.331	0.448	0.221				0.103	0.049	0.849
7.91	0.413	0.425	0.162				0.087	0.030	0.883
7.92	0.502	0.378	0.120				0.100	0.027	0.874
7.97	0.636	0.287	0.077				0.003	0.026	0.971
7.95	0.850	0.120	0.030				x	x	x
7.90	0.930	0.050	0.019				x	x	x
7.88	0.964	0.019	0.017				0.006	0.000	0.994
8.97	0.007	0.342	0.652				0.001	0.056	0.944
9.92				0.004	0.217	0.780	0.001	0.070	0.929
9.93				0.048	0.274	0.678	0.007	0.067	0.926
3-phase 10.24	0.212	0.389	0.399	0.090	0.311	0.599	0.009	0.073	0.918
9.98	0.295	0.398	0.307				0.001	0.026	0.973
9.91	0.389	0.393	0.218				0.001	0.024	0.974
10.17	0.488	0.360	0.152				0.001	0.019	0.980
10.20	0.630	0.277	0.093				0.004	0.016	0.980
10.30	0.843	0.122	0.035				x	x	x
10.25	0.930	0.048	0.022				x	x	x
10.20	0.963	0.019	0.018				0.004	0.004	0.993
13.21	0.341	0.375	0.284				0.065	0.242	0.693
10.91	0.366	0.377	0.257				0.047	0.176	0.778
10.88	0.419	0.375	0.206				0.022	0.100	0.878
12.08	0.472	0.352	0.176				0.028	0.135	0.837
11.02	0.510	0.340	0.150				0.020	0.060	0.920
12.07	0.544	0.317	0.140				0.031	0.094	0.875
12.18	0.573	0.300	0.127				0.023	0.094	0.882
11.04	0.634	0.271	0.095				0.034	0.057	0.909
12.04	0.644	0.264	0.092				0.034	0.073	0.894
11.06	0.857	0.108	0.035				0.052	0.010	0.938
12.04	0.929	0.047	0.024				x	x	x
11.95	0.960	0.020	0.020				0.004	0.000	0.996
14.83	0.315	0.381	0.304				0.069	0.247	0.683
15.04	0.530	0.322	0.148				0.027	0.139	0.834
14.94	0.580	0.295	0.125				0.022	0.117	0.861
15.05	0.673	0.240	0.087				0.012	0.079	0.909
14.90	0.859	0.105	0.036				x	x	x
14.79	0.932	0.043	0.025				0.010	0.003	0.988
14.79	0.934	0.042	0.025				0.006	0.003	0.991
15.05	0.962	0.017	0.021				0.006	0.001	0.993
18.40	0.381	0.367	0.252				0.073	0.248	0.679
19.96	0.456	0.348	0.196				0.050	0.205	0.745
20.00	0.525	0.314	0.160				0.042	0.167	0.791
19.63	0.595	0.283	0.122				0.024	0.132	0.843
19.85	0.661	0.247	0.092				0.017	0.102	0.881
19.30	0.858	0.099	0.043				x	x	x
19.75	0.933	0.041	0.025				0.007	0.007	0.986
19.64	0.962	0.017	0.022				0.006	0.001	0.994

Table III. Experimental Results for the System Water-Propionic Acid-Carbon Dioxide at 313 K

	mole fractions								
	phase 1			phase 2			phase 3		
P, MPa	H_2O	acid	CO_2	H_2O	acid	CO_2	H_2O	acid	CO_2
1.96	0.033	0.786	0.181				x	x	x
2.00	0.196	0.651	0.153				x	x	x
2.04	0.361	0.563	0.076				x	x	x
1.99	0.636	0.322	0.042				x	x	x
2.00	0.741	0.243	0.016				x	x	x
2.03	0.817	0.168	0.015				x	x	x
2.16	0.903	0.087	0.010				x	x	x
1.99	0.950	0.045	0.005				x	x	x
2.05	0.981	0.011	0.008				x	x	x
4.00	0.016	0.619	0.365				x	x	x
3.89	0.136	0.592	0.271				x	x	x
3.98	0.339	0.466	0.195				x	x	x
4.04	0.600	0.295	0.105				x	x	x
4.10	0.715	0.233	0.052				x	x	x
4.17	0.804	0.166	0.030				x	x	x
4.15	0.897	0.083	0.020				x	x	x
4.06	0.944	0.039	0.017				x	x	x
4.00	0.974	0.013	0.012				x	x	x
5.96	0.015	0.393	0.592				x	x	x
6.06	0.102	0.403	0.495				x	x	x
5.99	0.257	0.370	0.374				x	x	x
6.04	0.538	0.282	0.179				x	x	x
6.02	0.690	0.227	0.083				x	x	x
6.03	0.779	0.167	0.055				x	x	x
6.04	0.883	0.087	0.031				x	x	x
6.03	0.938	0.039	0.023				x	x	x
5.92	0.964	0.014	0.022				x	x	x
7.99	0.006	0.058	0.936				x	x	x
8.02	0.009	0.062	0.929				0.004	0.012	0.983
7.79	0.667	0.201	0.132				0.087	0.207	0.706
3-phase 7.81	x	x	x	0.081	0.122	0.798	0.008	0.001	0.991
3-phase 7.98	0.914	0.054	0.032	0.078	0.080	0.842	0.016	0.008	0.976
8.22	0.938	0.036	0.027				0.023	0.038	0.939
8.26	0.952	0.018	0.031				0.009	0.007	0.984
10.12	0.788	0.142	0.070				0.058	0.256	0.686
10.44	0.890	0.070	0.040				0.027	0.156	0.817
10.33	0.928	0.040	0.032				0.018	0.115	0.867
10.17	0.953	0.023	0.025				0.016	0.053	0.931
10.30	0.957	0.012	0.031				0.000	0.011	0.989
15.01	0.529	0.257	0.214				0.164	0.287	0.550
15.36	0.676	0.199	0.125				0.093	0.255	0.653
14.97	0.801	0.129	0.069				0.051	0.210	0.739
15.01	0.896	0.065	0.039				0.024	0.135	0.841
15.49	0.920	0.048	0.031				0.015	0.101	0.884
14.70	0.949	0.025	0.026				0.010	0.041	0.950
15.19	0.960	0.016	0.025				0.007	0.019	0.974
14.73	0.968	0.007	0.025				0.006	0.004	0.991

ternary diagrams at a constant temperature and pressure for a series of organic acids, as shown in Figure 2, comparing the results for the phase equilibrium behavior at 313 K and 15 MPa for acetic, propionic, and *n*-butyric acid. As can be seen in Figure 2, the change in hydrocarbon chain length for this series of straight-chain organic acids has the following effects on the phase equilibrium behavior.

1. The distribution coefficient of the organic acid between the supercritical fluid and aqueous phases changes gradually: it is less than 1 (the acid prefers the aqueous phase) for acetic acid, approximately equal to 1 (tie lines parallel to the CO_2–water side of the triangular diagram) for *n*-propionic acid, and greater than 1 (the acid preferentially distributes itself to the supercritical phase) for *n*-butyric acid.

2. The extent of the two-phase envelope (on a mole fraction basis) is less the higher the chain length of the acid.

A striking similarity in the qualitative behavior of the three acid systems is observed when the ternary diagrams shown in Figure 2 are compared with ternary diagrams for the systems acid–water–toluene at atmospheric pressure and 333 K from Alessi et al. (*25*). It thus appears that, at high pressures, the solvent behavior of carbon dioxide is similar to that of a nonpolar liquid

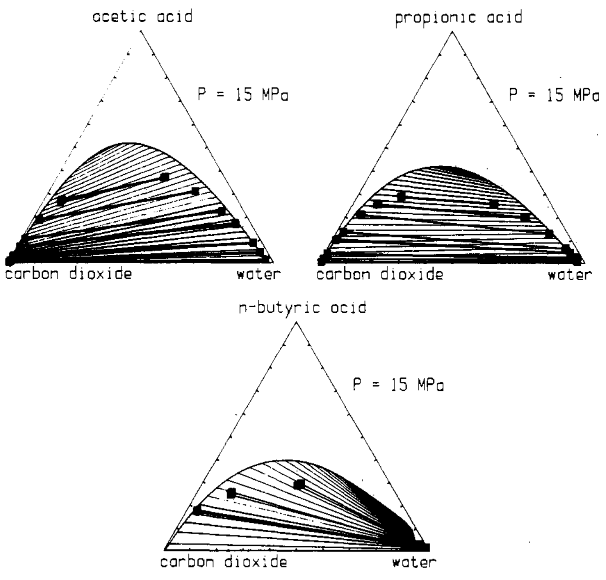

Figure 2. Comparison of the ternary phase equilibrium behavior at 313 K and 15.0 MPa for acetic, propionic, and *n*-butyric acids.

Table IV. Experimental Results for the System Water-*n*-Butyric Acid–Carbon Dioxide at 313.1 K

	mole fractions								
	phase 1			phase 2			phase 3		
P, MPa	H_2O	acid	CO_2	H_2O	acid	CO_2	H_2O	acid	CO_2
2.06	0.039	0.756	0.205				x	x	x
2.04	0.106	0.683	0.211				x	x	x
2.06	0.297	0.554	0.148				x	x	x
1.96	0.467	0.446	0.089				x	x	x
1.99	0.685	0.268	0.047				x	x	x
2.03	0.877	0.105	0.018				x	x	x
2.03	0.932	0.056	0.012				x	x	x
3.96				0.030	0.603	0.367	x	x	x
3.96				0.072	0.572	0.356	x	x	x
3.97				0.231	0.502	0.267	x	x	x
3.98				0.418	0.409	0.173	x	x	x
4.05				0.638	0.261	0.100	x	x	x
3-phase 3.96	0.942	0.040	0.018	0.703	0.223	0.074	x	x	x
6.05				0.022	0.406	0.571	x	x	x
6.05				0.050	0.409	0.541	x	x	x
5.93				0.162	0.403	0.435	x	x	x
5.97				0.320	0.356	0.324	x	x	x
3-phase 5.89	0.952	0.028	0.020	0.382	0.332	0.286	x	x	x
6.95				0.036	0.311	0.654	0.001	0.013	0.986
7.10				0.017	0.273	0.711	x	x	x
6.99				0.106	0.314	0.580	x	x	x
3-phase 6.94	0.963	0.018	0.020	0.130	0.321	0.549	0.002	0.010	0.989
7.90				0.019	0.114	0.868	0.002	0.005	0.993
3-phase 7.93	0.961	0.018	0.021	0.048	0.123	0.829	x	x	x
7.88	0.960	0.020	0.020	0.164	0.389	0.447			
9.90	0.934	0.046	0.020				0.760	0.169	0.071
9.74	0.958	0.022	0.020				0.335	0.306	0.359
10.12	0.961	0.018	0.020				0.123	0.285	0.592
9.97	0.966	0.013	0.021				0.052	0.220	0.728
15.10	0.948	0.031	0.021				0.371	0.294	0.336
15.01	0.954	0.025	0.021				0.129	0.252	0.620
15.10	0.960	0.019	0.022				0.040	0.175	0.785
19.73	0.952	0.024	0.024				0.418	0.279	0.302
19.40	0.954	0.024	0.022				0.130	0.251	0.619
19.60	0.963	0.015	0.022				0.050	0.179	0.772

Table V. Pure Component Parameters and Physical Property Data Used

component	*T*, K	ρ, kg m^{-3}	P_{VP}, kPa	*a*, J m^3 mol^{-2}	$10^6 b$, m^3 mol^{-1}
water	313.2	992.1	7.38	0.8162	16.07
	333.2	983.3	19.92	0.7912	15.98
acetic acid	313.2	1028.4	4.69	2.431	51.13
	333.2	1006.0	12.09	2.376	51.45
propionic acid	313.2	967.8	1.34	3.534	67.95
n-butyric acid	313.2	938.0	0.39	4.778	84.36
carbon dioxide	313.2			0.3876	26.65
	333.2			0.3696	26.65

Table VI. Interaction Parameters

binary system	*T*, K	$k_{12} = k_{21}$	$\lambda_{12} = -\lambda_{21}$, J^2 m^3 mol^{-3}
CO_2 (1)–water (2)	313.2	0.024	-1740
	333.2	0.028	-1710
CO_2 (1)–acetic acid (2)	all	0.005	530
CO_2 (1)–propionic acid (2)	313.1	0.011	381
CO_2 (1)–*n*-butyric acid (2)	313.2	0.023	527
water (1)–acetic acid (2)	313.2	–0.147	410
	333.2	–0.142	580
water (1)–propionic acid (2)	313.1	–0.127	1221
water (1)–*n*-butyric acid (2)	313.2	–0.135	1686

hydrocarbon solvent.

The experimental data were correlated as described in the previous section. In Table V, we present the pure component properties used for the correlation and the resulting equation-of-state parameters. In Table VI, the binary interaction parameters used in the model are given. These parameters were obtained by regressing binary phase equilibrium data. For the organic acid–carbon dioxide systems, no suitable binary data were available in the literature. For these systems, we used our own ternary data, extrapolated to zero water concentration, to regress the binary interaction parameters.

The model was successful in predicting the qualitative characteristics of the experimentally observed behavior for all the cases studied, including the presence and approximate location of the three-phase equilibrium regions. The quantitative agreement between model predictions and experimental data is good in most cases, especially for the low-pressure region. For the high-pressure region, the model usually overpredicts the extent of the two-phase region and does not accurately reproduce the location of the plait points. However, since only binary parameters regressed from binary data that contain no information about the ternary system behavior were used, the overall performance of the model may be considered satisfactory.

Registry No. CO_2, 124-38-9; acetic acid, 64-19-7; propionic acid, 79-09-4; *n*-butyric acid, 107-92-6.

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Measurement and Model Prediction of Solubilities of Pure Fatty Acids, Pure Triglycerides, and Mixtures of Triglycerides in Supercritical Carbon Dioxide

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The solubilities in CO_2 of three pure triglycerides (trilaurin, trimyristin, and tripalmitin) and their corresponding fatty acids (lauric acid, myristic acid, and palmitic acid) were measured at 313 K and at pressures between 8 and 30 MPa. The data were correlated by using a lattice model equation of state. Solubilities of members of a homologous series (fatty acid or triglyceride) decreased with increasing molecular weight in accordance with previous findings. Solubilities of triglyceride mixtures in CO_2 were also measured. The solubility of the most soluble compound in the mixture was the same as the pure component solubility of that compound, but the solubilities of the less soluble species in mixtures were enhanced by the presence of more soluble triglycerides.

Introduction

Edible oils are normally produced by extracting lipids from biological materials (such as soybeans) using *n*-hexane as a solvent. The high flammability and adverse health affects of residual solvent in food products make hexane a poor choice from an industrial standpoint. Because of these issues, supercritical fluids (SCF), especially supercritical carbon dioxide which is both nontoxic and nonflammable, are now being considered as replacements for hexane (*1*, *2*). SCF extraction of lipids has been studied extensively in recent years (*2*-*15*) and a more comprehensive review has been prepared by McHugh and Krukonis (*1*).

The first reported commercial process using SCF for the fractionation of lipids was the Solexol process developed by the M. W. Kellogg Co. in 1947 (*16*, *17*). Supercritical propane was used to extract and fractionate edible oils in this process. Six plants were built to refine fish oil, animal fat, and vegetable oils (*17*).

More recently, Eisenbach (*7*) has described the separation of eicosapentenoic acid ethyl ester ($C_{20:5}$) from a mixture of fatty acid ethyl esters derived from codfish oil using CO_2 at a constant temperature (323 K) and pressure (15 MPa). All of the fatty acid ethyl esters present in the mixture are soluble in CO_2 to some extent, but at the beginning of the extraction, the lower molecular weight esters are extracted preferentially. After most of the light esters have been stripped away, the desired product is then extracted in fairly high purity. Using a two-step process, Eisenbach achieved a product purity of approximately 92% with a yield of about 80%.

While processes for the fractionation of oils have been tested, not much is known about the physical chemistry of lipid solubility in supercritical fluids. Most of the available information deals with bulk solubilities of complex oils in SCF, with little data on the solubilities of the individual components of these mixtures. The only published quantitative data on the solubilities of pure fatty acids and triglycerides were measured by Chrastil (*5*) who reported the individual CO_2 solubilities of the following lipids: stearic acid, oleic acid, behenic acid, tributyrin, tripalmitin, tristearin, triolein, and trilinolein in the temperature range of 313-353 K and at pressures between 8 and 25 MPa.

In the present work, the solubilities of pure fatty acids and pure triglycerides were measured. The fatty acids used were lauric, myristic, and palmitic acids. The triglycerides were trilaurin (LLL), trimyristin (MMM), and tripalmitin (PPP). A recently developed lattice equation of state (EOS) (*18*) was used successfully to correlate the experimental data by using a single adjustable parameter per binary. The following triglyceride mixtures were also studied: LLL-MMM-CO_2, LLL-PPP-CO_2, MMM-PPP-CO_2, and LLL-MMM-PPP-CO_2. All measurements were made at 313 K and at pressures between 8 and 30 MPa.

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