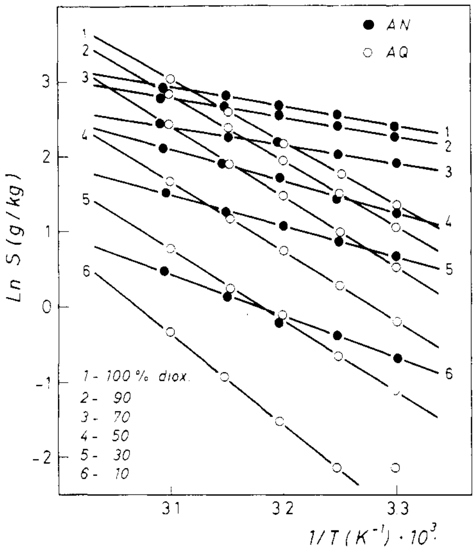

Figure 2. Solubility of AN and AQ in mixtures of 1,4-dioxane–ethylene glycol versus $1/T$.

Table IV. Entropy Variation Least-Squares Fitted Value ($-\Delta S$) Obtained from Eq 3 (J/(mol K))

	% 1,4-dioxane				
	90	70	50	30	10
AN	40.7	51.9	70.9	76.5	256.9
AQ	131.6	138.6	136.4	140.1	142.6

from eq 3) are shown in Table IV. An increasing departure from ideality at increasing concentrations of ethylene glycol is observed.

Ideal solubilities of AN and AQ in the solvent mixtures were calculated from the solubility in the pure solvents and from the molar fraction of each solvent in the mixed solvent by linear contribution. Compared with these ideal solubilities in the mixture, the experimental solubilities present positive deviations as shown in Figure 1 in pure solvents. Also good fitting of deviations to a linear relationship as in eq 2 is obtained. The constants a and b are recorded in Table III.

Glossary

ΔH	enthalpy of fusion of pure component, J/mol
ΔC_p	difference of molar specific heat between those of liquid and solid at fusion temperature, J/(mol K)
R	gas constant, J/(mol K)
S_2^M	Entropy, least-squares fitted value of eq 3, J/(mol K)
T	temperature, K
T_m	melting temperature, K
T_t	triple-point temperature, K
w	solubility on mass base, g/kg of solvent
x_2	experimental solubility in mole fraction
x_i	ideal solubility in mole fraction
γ	activity coefficient

Registry No. DMF, 68-12-2; anthracene, 120-12-7; anthraquinone, 84-65-1; dioxane, 123-91-1; ethylene glycol, 107-21-1.

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Novel Technique To Measure Equilibria of Supercritical Solvents and Liquid Mixtures

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A new flow method was developed to measure supercritical and near-critical phase equilibria. Equilibrium data for the carbon dioxide/ethanol/water system at 35 °C and 102.0 atm and the CO_2/2-propanol/water system at 25 °C and 81.6 atm and at 40 °C and 102.0 atm were determined by using this technique. The equilibria compared favorably with work reported previously.

Introduction

Since the commercialization of supercritical fluid (SCF) extraction processes in the late 1960s, interest in the separation technique has increased considerably. The sustained interest in supercritical extraction may be attributed to the unique advantages that the process offers, such as high mass-transfer rates, favorable selectivities, and low operating temperatures. These advantages can be coupled with the ready availability of nontoxic supercritical fluid solvents such as carbon dioxide. When a supercritical extraction process is designed, a key parameter to consider is the phase equilibria of the operating systems. These equilibria determine the maximum separation possible for the process, the solvent/feed ratio (and hence the size of the extraction vessels), and the selectivity for the extracted solutes.

Although much past quantitative equilibrium work with supercritical fluids dealt with solvent/solid systems, quantitative equilibrium data for supercritical fluid/liquid systems have appeared often in the recent literature. This is probably due to improvements in experimental techniques.

Two approaches are used to measure supercritical fluid/liquid equilibrium: static and dynamic methods. With the static method, the components of interest are metered into a high-pressure viewing cell and agitated to establish equilibrium between the contacting phases (*1–3*). Mercury displacement is used to maintain the operating pressure while sampling. Another static technique that does not require sampling involves measuring cell loadings, determining phase volumes, and ob-

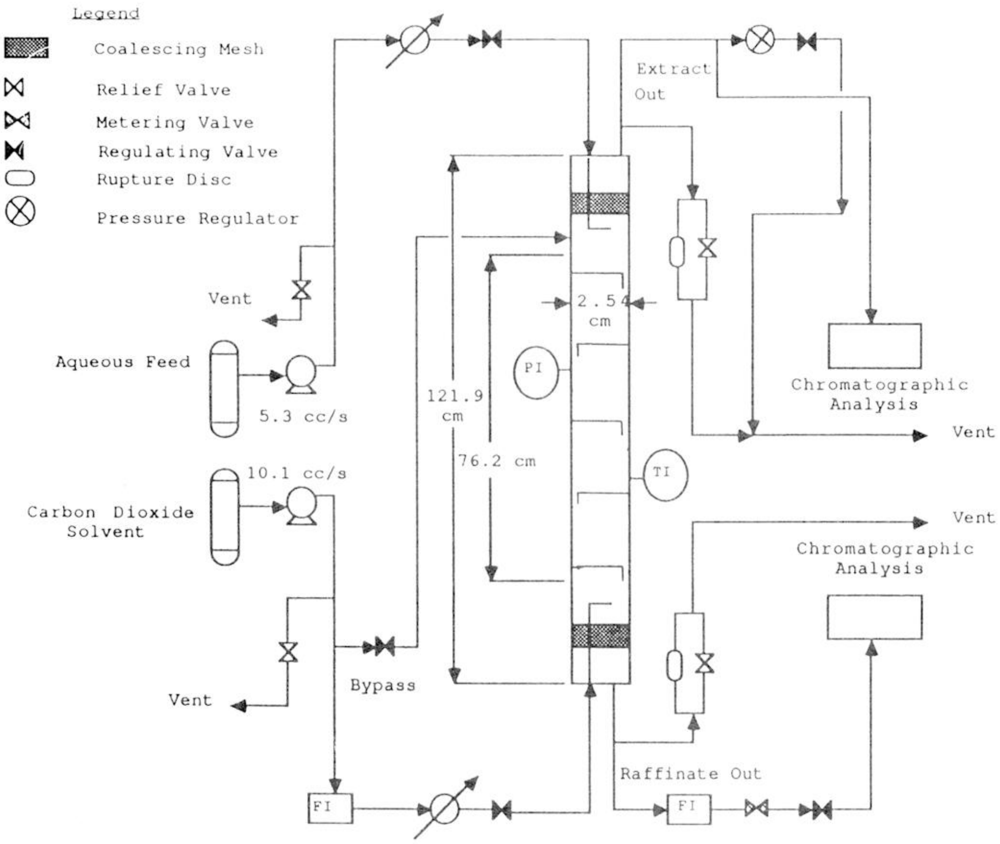

Figure 1. Supercritical extraction apparatus.

taining phase compositions from a component mass balance (*4*, *5*).

With the dynamic method, the coexisting phases are continuously recirculated through a windowed, high-pressure vessel and an external loop (*4*, *6–8*). After equilibrium is attained, the phases are sampled on-line with high-pressure switching valves that are connected directly to a gas chromatograph. In one variation of the dynamic method, two process streams are mixed in small-diameter crimped tubing (*9*) or in an in-line mixing element (*10*). The equilibrated mixture is then directed to a view cell, where the supercritical and liquid phases are separated and sampled.

Within the past decade, several studies of the phase equilibria of supercritical solvents with water/alcohol mixtures have been performed. One reason for this effort is the commercial importance of the system in the chemical and fermentation industries. Another reason is that existing separation processes for alcohol and water tend to be energy intensive and in general are limited to near-azeotrope compositions. Investigators who have studied the phase equilibria of the supercritical fluid/alcohol/water model system include McHugh et al. (*2*), Paulaitis et al. (*5*, *9*, *11*), Kuk and Montagna (*6*), and Radosz (*8*).

Experimental Section

Carbon dioxide (CO_2) was the solvent used in this work, water was the carrier, and 2-propanol and ethanol were the solutes. Operating temperatures and pressures were 25 °C and 81.6 atm (2-propanol solute), 40 °C and 102.0 atm (2-propanol solute), and 35 °C and 102.0 atm (ethanol solute). Since the critical temperature of CO_2 is 31.01 °C and the critical pressure is 72.8 atm, carbon dioxide may be considered to be near critical in the first case and supercritical in the latter two cases. For all run conditions, care was taken to operate in the two-phase region (*5*, *6*).

The apparatus used in the present work was the same one utilized in a study to measure mass transfer and hydraulic data for an SCF process (*12*). The principal component of the experimental system (shown in Figure 1) is a windowed, column-type, multistage contactor which is capable of separating liquid mixtures with high-pressure solvents. The solvent and feed were contacted countercurrently in the vessel, which could be operated as a packed, spray, or sieve tray extraction column. The sieve-tray configuration was used in this investigation.

The inside diameter of the extraction column was 2.54 cm. It was 121.9 cm high and was fabricated from 7.62 cm × 7.62 cm stainless steel bar stock. Twelve pairs of 1.75-cm-diameter borosilicate windows, spaced 5.08 cm apart (center to center), were located on opposite faces of the column: five pairs at the top of the vessel, four in the middle, and three at the bottom.

The extraction vessel was insulated with fiberglass and wrapped in heating tape. The heating tape output was regulated with an Omega controller which maintained the temperature within 0.2 °C of the operating point.

Five brass sieve trays, 0.32 cm thick and spaced 10.16 cm apart, were assembled on a threaded rod which was passed through the smooth, circular bore of the column to place the trays in their correct position. Polypropylene mesh coalescing pads in each end of the column aided in phase disengagement. The dimensions of the column and the trays are summarized in Table I; further details are given in the Lahiere dissertation (*13*).

The distributor tubes consisted of 0.64-cm stainless steel tubing with a 1.91-cm-diameter hollow, circular ring brazed onto the end. Twelve 0.16-cm holes were tapped into the ring to allow adequate dispersion of the feed and solvent.

High-pressure, controlled-volume liquid pumps by Milton Roy (Milroy A, maximum capacity of 5.3 cm^3/s for the alcohol/water feed and 10.1 cm^3/s for the CO_2 solvent) were used to pump the process streams. To prevent cavitation of the solvent pump, the CO_2 stream was precooled by coiling a 610-cm length of the 0.635-cm-diameter solvent line in an ice–water bath upstream of the pump suction. To reduce further heat

Table I. Extraction Column and Sieve-Tray Geometries

column	
diameter, cm	2.58
height, cm	121.9
cross-sectional area, cm^2	5.22
sieve tray	
number of trays	5
tray spacing, cm	10.16, 15.24
number of holes	5
sieve hole diameter, cm	0.318
hole area, cm^2	0.396
hole area/column area	0.0758
pitch/hole diameter ratio	2.85
downcomer diameter, cm	0.472
downcomer area, cm^2	0.175
downcomer area/column area	0.0335
downcomer length, cm	8.57

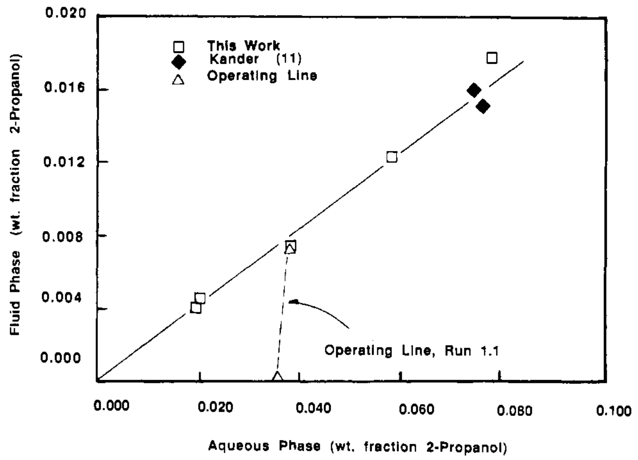

Figure 2. Equilibrium measurements: supercritical carbon dioxide/2-propanol/water at 40 °C and 102.0 atm.

transfer to the carbon dioxide, the pump was equipped with a ceramic plunger and the pump head was cooled with an ice–water jacket. Heat exchangers consisting of coiled lengths of 0.635-cm-diameter tubing immersed in a controlled temperature bath located upstream of the extraction vessel equilibrated the temperature of the process streams to that of the operating conditions.

A Tescom back-pressure regulator (Model 54-2124) controlled the pressure in the system, while a micrometering valve regulated the interface level in the column. An Ashcroft pressure gauge (0–204 atm) confirmed that the operating pressure was held within 1.0 atm of the process value. Mass flowmeters by Micro Motion (0–0.28 g/s), capable of instantaneous and total flow readings, measured the flow rates of the high-pressure streams. A Tracor 540 gas chromatograph equipped with dual thermal conductivity detectors and columns packed with Porapak Q was used to analyze the solvent and aqueous streams as they exited the column.

To reach equilibrium, solvent/feed (S/F) ratios were kept below an experimentally determined minimum. Under these conditions, the feed stream entering the top of the column and the CO_2-rich stream exiting the vessel reached equilibrium or "pinched" in about 30 min.

Chemicals used in the experiments were Linde industrial grade CO_2 (99.8% purity), Aldrich HPLC grade 2-propanol and ethanol (99.8%), and distilled water (99.99%).

Results and Discussion

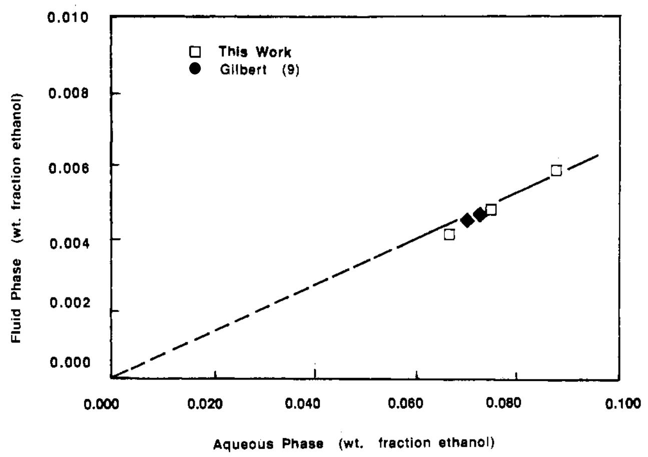

Figure 3. Equilibrium measurements: supercritical carbon dioxide/ethanol/water at 35 °C and 102.0 atm.

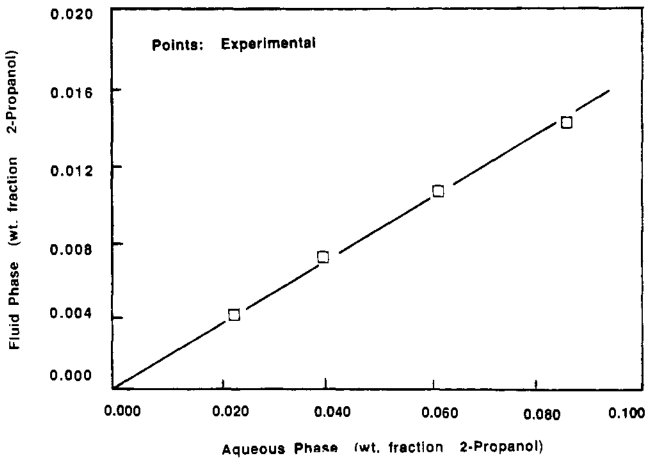

Figure 4. Equilibrium measurements: near-critical carbon dioxide/2-propanol/water at 25 °C and 81.6 atm.

Table II. Equilibrium Measurements

run	system[a]	S/F	10^2X_f	10^2Y_e	m	min S/F[b]
1.1	SC/I/W	0.35	3.83	0.73	0.190	4.7
1.2	SC/I/W	0.35	2.03	0.46	0.229	
1.3	SC/I/W	0.54	1.96	0.41	0.209	
1.4	SC/I/W	0.67	5.83	1.24	0.213	
1.5	SC/I/W	0.62	7.85	1.80	0.229	
2.1	SC/E/W	0.59	6.75	0.41	0.060	14.7
2.2	SC/E/W	0.76	7.55	0.48	0.064	
2.3	SC/E/W	10.06	8.86	0.59	0.066	
2.4	SC/E/W	12.02	8.86	0.59	0.006	
3.1	NC/I/W	0.39	2.29	0.39	0.170	5.3
3.2	NC/I/W	0.73	2.29	0.40	0.174	
3.3	NC/I/W	0.71	3.98	0.70	0.175	
3.4	NC/I/W	0.70	6.19	1.05	0.170	
3.5	NC/I/W	0.71	8.65	1.41	0.163	

[a] SC/E/W = supercritical carbon dioxide/ethanol/water, 35 °C, 102.0 atm. SC/I/W = supercritical carbon dioxide/2-propanol/water, 40 °C, 102.0 atm. NC/I/W = near-critical carbon dioxide/2-propanol/water, 25 °C, 81.6 atm. [b] Minimum S/F ratio for efficiency runs. Equilibrium will be attained at S/F ratios below the minimum.

Equilibrium data for the supercritical CO_2/2-propanol/water (SC/I/W) system are shown in Figure 2. The pinching of the feed stream and the CO_2-rich phase at the top of the extraction vessel is shown in Figure 2 by the intersection of the equilibrium curve with the operating line (run 1.1 in Table II). At the pinch point, the mass-transfer driving force in the extraction column equals zero.

Alcohol loadings for the supercritical carbon dioxide/ethanol/water (SC/E/W) and the near-critical carbon dioxide/2-propanol/water (NC/I/W) systems are plotted in Figures 3 and 4, respectively. The graphs demonstrate that the equilibrium curves were linear for dilute solute concentrations. The equilibrium solute loadings are given in Table II. For several pairs of runs, identical CO_2-phase alcohol loadings were obtained with the same feed composition but at different solvent flow rates, confirming that equilibrium was attained in the column.

Feed/solvent pinching would not occur at S/F ratios above a minimum value. The minimum S/F ratio for each system was determined experimentally and is given in Table II. The minimum ratio is approximately equal to the inverse of the distribution coefficient *m*, defined as

$$m = Y_e/X_f$$

where Y_e = alcohol loading in the exiting solvent phase and X_f = alcohol loading in the feed.

The measured distribution coefficients compared quite well with previously published values. Average percent differences from the literature of 5.5% and 8.4% were obtained for the SC/E/W (*9*) and SC/I/W (*11*) systems, respectively. The experimental uncertainty in the distribution coefficient values was ±2%.

Finally, it is interesting to compare the distribution coefficients for the SC/I/W system at 40 °C and 102.0 atm to those for the NC/I/W system at 25 °C and 81.6 atm. Values in Table II indicate that the alcohol loadings in the supercritical CO_2 phase are only 20% more than in near-critical CO_2.

Conclusions

A novel technique was developed to measure equilibrium information for liquid mixtures and high-pressure solvents. The phase equilibria for near-critical and supercritical CO_2/alcohol/water systems were measured by using this method, and the data compared favorably with previously reported values. For experiments with 2-propanol solute, it was observed that the solute loading in supercritical CO_2 was only slightly larger than its loading in near critical carbon dioxide. This implies that a commercial alcohol/water separation unit could be run as efficiently with near-critical carbon dioxide as with supercritical carbon dioxide, but for less cost due to the lower pressures involved.

Registry No. CO_2, 124-38-9; ethanol, 64-17-5; 2-propanol, 67-63-0.

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Excess Volumes of the System Benzene + 1,1,2-Trichloroethylene at 283.15 and 313.15 K

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Excess volumes were measured for the benzene + 1,1,2-trichloroethylene system at 283.15 and 313.15 K and atmospheric pressure. The excess volumes were positive, decreasing with temperature, and exhibited maxima at approximately 59.1 mol % benzene. Data have been correlated by generalized equations.

This article reports the excess volume measurements for (*x*)benzene + (1 − x)1,1,2-trichloroethylene at 283.15 and 313.15 K. Also reported are the empirical equations fitted to the results obtained at each temperature.

Experimental Methods

The excess volumes were measured directly by means of a Kumaran and McGlashan type continuous dilution dilatometer with a back-pressure device (*1*). The temperature of the water bath containing the dilatometer was kept constant to within ±0.001 K with a Tamson Model TCV 70 bath and associated cooler. Values of temperature were measured with an NBS calibrated thermometer to ±0.05 K. The operational technique has been described elsewhere) (*2*).

Table I. Experimental Densities at Various Temperatures and Refractive Indices at 293.15 K and Comparison with Literature Values

	density, kg/m^3		refract. index
	283.15 K	313.15 K	293.15 K
	Experimental		
benzene	890.23	858.37	1.50067
trichloroethylene	1483.44	1431.78	1.44705
	Literature		
benzene	889.5[b]	857.7[b]	1.5011[c]
trichloroethylene	1482[a]	1430[a]	1.4773[c]

[a] Reference *3*. [b] Reference *4*. [c] Reference *5*.

An attempt was made to further purify the benzene (Aldrich purity >99.9%) and trichloroethylene (Aldrich purity >99%) by means of simple distillation with the first and last 20% of the distillate being discarded. Precision refractometry indicated that the purity of each product was not enhanced by this process, and hence, they were used as received. The reagents were

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