

High-Pressure Phase Equilibria in Ternary Fluid Mixtures
with a Supercritical Component

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The potential of supercritical extraction (SCE), a separation process in which a gas above its critical temperature is used as a solvent, has been widely recognized in the recent years. The first proposed applications have involved mainly compounds of low volatility, and processes that utilize supercritical fluids for the separation of solids from natural matrices (such as caffeine from coffee beans) are already in industrial operation. The use of supercritical fluids for the separation of liquid mixtures, although of wider applicability, has been less well studied, as the minimum number of components for any such separation is three (the solvent, and a binary mixture of components to be separated). The experimental study of phase equilibrium in ternary mixtures at high pressures is rather complicated, and theoretical methods to correlate the observed phase behavior are lacking.

One important potential application of supercritical extraction is in the recovery of polar organic compounds from aqueous solutions. Such mixtures arise very frequently as products of biochemical syntheses. In many cases, the costs of the energy-intensive separations are quite high. It is the objective of an ongoing research project at MIT to investigate the applicability of SCE for such separations.

Previous work in the area of high-pressure phase equilibrium of aqueous solutions of organic compounds with supercritical fluids includes the pioneering work of Elgin and Weinstock (1) carried out in the 1950's. Francis (9) presented a large number of qualitative results for ternary systems of liquid CO₂ at 25 °C. In the more recent years, Paulaitis et al. (2,3), Kuk and Montagna (4), McHugh et al. (5) and Radosz (6) have reported measurements in systems with some of the first alcohols, water and supercritical fluids.

Experimental

The experimental setup that is being used is shown in Figure 1. The main element of the equipment is a visual high pressure cell (Jerguson gage model 19-TCH-40) with an internal volume of about 50 cm³, that serves as a mixing and separating vessel, as well as for the visual observation of the number and quality of the coexisting phases. Connections at the bottom, top and side of the vessel permit withdrawal of the lower, upper and middle phases, any two of which can be recirculated externally with a dual high pressure Milton-Roy Mini Pump. An on-line Mettler-Paar vibrating tube density meter (DMA 60 with a DMA 512 cell) is used to measure the density of one of the recirculating phases at a time, and can be switched between any of them.

The Jerguson gage is immersed in a constant temperature bath with silicon fluid as the heat-transfer medium, that also thermostats the density meter. The bath temperature is controlled to $\pm .01$ K with a Thermomix 1460 temperature regulator, and the temperature is measured with a calibrated mercury-in-glass thermometer to within .01 K. The lines external to the bath are maintained at the bath temperature with the help of heating tapes, and the temperature at several points is monitored with thermocouples. Pressure is measured with two calibrated Heise pressure indicators to within $\pm .16$ bar for pressures up to 160 bar, and to within $\pm .4$ bar for pressures up to 350 bar.

Sampling is done with two high pressure-switching valves of internal volume .5 μ l (for the upper phase) and .2 μ l (for the lower or middle phases). The samples are directly depressurized into a He carrier gas stream and analyzed with a Perkin Elmer Sigma 2 Gas Chromatograph, using a Porapak Q column supplied by Supelco. The response factors for the materials used were found to be close to those reported by Dietz (7). Typical reproducibility of the analysis is $\pm .003$ in mole fraction, with somewhat larger deviations for the gas-phase composition at low pressures.

After purging and evacuation of the equipment the cell is charged with a liquid mixture of known composition and with the supercritical component up to the desired pressure. The recirculation pumps are started, and the approach to equilibrium monitored by the stability of the pressure, density, and composition measurements with time. For the mixtures studied, a typical equilibration time is 15 min., but at least 30 min are allowed before the final sampling. At least two samples are taken from each phase at equilibrium. A new pressure point can then be established immediately by introducing or removing supercritical fluid and/or liquid, so that the level of the interfaces in the cell at the new desired pressure is appropriate for sampling through the available ports.

Results

Binary Systems

As a test of the validity of the equipment design and the experimental procedures, we first investigated a binary system for which results have been previously published. Knowledge of the behavior of the binary systems is in itself important, since the data provide the appropriate limits for the corresponding ternary systems.

In Figure 2 we present the experimental results and literature data for the system CO_2 - acetone at 313 and 333 K (literature results are available only at the lower temperature). As can be seen, the agreement between the two sets of results is excellent. Also shown on the same figure as continuous lines are the results of the fitting of the experimental data using a modified Peng-Robinson equation of state that is described in the Appendix. The agreement between experimental and predicted phase compositions is within the experimental uncertainty of the data, except in the critical region.

Several of the features of the phase behavior shown on Figure 2 are quite general. In particular, it can be seen that the solubility of CO_2 in the liquid phase is quite high, even at moderate pressures. The system critical pressure is, in general, comparable to the critical pressure of CO_2 , and increases with temperature at the temperature range studied. Although the solubility of acetone in the gas phase is low in the two-phase region, there is complete miscibility between CO_2 and acetone at pressures that are not very high. CO_2 at liquid-like densities is an excellent solvent for a wide range of organic compounds, as was first observed by Francis (9) for near critical liquid CO_2 .

One additional example of the same general type of behavior is demonstrated by the CO_2 - ethanol system. Three measured isotherms for this system are presented in Figure 3. No comparable set of experimental results appears to be available in the open literature. Again, the agreement between experimental results and model predictions is very good.

Ternary Systems

As one of a series of model systems, we studied the CO_2 - acetone - water system at 313 and 333 K. The most striking feature of the system behavior, is a very extensive three-phase region at both temperatures. The three-phase region is first observed at a pressure of only 25 bar at 313 K, and extends to approximately the critical pressure of the binary CO_2 - acetone system. Table 1 provides the experimental results for the composition of the three phases at equilibrium as a function of pressure and temperature.

The physical picture that underlies this behavior, as pointed out first by Elgin and Weinstock (1), is the 'salting out' effect by a supercritical fluid on an aqueous solution of an organic compound. As pressure is increased the tendency of the supercritical fluid to solubilize in the organic liquid results in a phase split in the aqueous phase, at what can be named a lower critical solution pressure (which varies with temperature). As pressure

is further decreased, the second liquid phase and the supercritical phase become more and more similar to each other, and merge at an upper critical solution pressure, above which only two phases can coexist.

This pattern of behavior was also observed by Elgin and Weinstock for the system ethylene - acetone - water at 15 °C. In addition, the same type of behavior, but at quite different pressures relative to the pure solvent critical pressure was reported by Paulaitis et al.(3) for the system CO₂ - isopropanol - water, by McHugh et al.(5) for the system ethane - ethanol - water and again by Paulaitis et al.(2) for the CO₂ - ethanol - water system, and therefore appears to be quite general.

A more complete picture of the phase equilibrium behavior is given in Figure 4 for the system under study at 333 K. The darker lines and squares on this figure are experimentally measured tie-lines and phase compositions. The light lines are model predictions, using values of interaction parameters determined solely from regression of binary data (see Appendix). The two sets of results are in good agreement with each other.

An interesting feature of the phase equilibrium behavior is the relative insensitivity of the phase envelope and positions of the tie-lines to variations in pressure in the two-phase region, as evidenced by comparison of the diagrams at 100 and 150 bar in Figure 4. This would seem to imply that similar separations can be achieved by operation at pressures just above the upper critical solution pressure of ~95 bar as compared to operation at higher pressures.

The phase equilibrium behavior at 313 K is quite similar to that at 333 K, with the three-phase region shifted to lower pressures, as presented in Table 1.

From an engineering point of view, the most important quantities in the evaluation of a separation scheme based on a phase behavior pattern such as the one shown, are the selectivity of the separation with respect to the desired component, as well as the loading of the desired component in the extractant phase. It is well known that those two factors usually increase in different directions. Figures 5 and 6 present experimental data and model predictions for the distribution coefficient of acetone, and for the selectivity ratio α of acetone over water (defined as the ratio of distribution coefficients of acetone and water in the liquid and fluid phases), as a function of the water concentration in the liquid phase. The distribution factor shows a sharp maximum at both temperatures, with a higher value at the higher temperature, whereas the selectivity decreases smoothly from the limiting value of ~300 at low acetone concentrations to 1 as the plait point is approached. The experimental data show the same trends, although there is some scatter that is due to the fact that small absolute errors in the low supercritical phase concentrations of acetone and water result in large relative errors for the distribution coefficient and selectivity factors. Selectivities are generally higher for the lower temperature, but loadings are lower. Based on the observed behavior for the system, the maximum CO₂-free acetone concentrations in the upper phase is 85% mole (~95% w/w) acetone for operation at 150 bar and 333 K.

Conclusions

An apparatus for the determination of high pressure phase equilibrium data for mixtures of water, polar organic liquids and supercritical fluids was constructed and successfully operated for binary and ternary systems with supercritical carbon dioxide.

The system CO₂ - acetone - water was extensively investigated at 313 and 333 K. The system demonstrates several of the general characteristics of phase equilibrium behavior observed earlier for similar systems, including an extensive LLV region that appears at relatively low pressures.

A model based on a modified form of the Peng-Robinson equation of state was able to reproduce quantitatively all features of the observed phase equilibrium behavior, with model parameters determined from only binary data. The use of such models may facilitate substantially the task of process design and optimization for separations that utilize supercritical fluids.

A substantial sensitivity of the separation efficiency, as determined by the ability of the solvent to selectively extract the organic compound with high loadings was observed when the operating conditions were varied.

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References

1. Elgin, J.C. and Weinstock, J.J., J. Chem. Eng. Data (1959), 4(1) 3-12.
2. Paulaitis, M.E., Gilbert, M.L. and Nash, C.A., 'Separation of Ethanol - Water Mixtures with Supercritical Fluids', paper presented at the 2nd World Congress of Chemical Engineering, Montreal, Canada, Oct. 5, 1981.
3. Paulaitis, M.E., Kander, R.G. and DiAndreth, J.R., Ber. Bunsenges. Phys. Chem. (1984), 88, 869-875.
4. Kuk, M.S. and Montagna, J.C., 'Solubility of Oxygenated Hydrocarbons in Supercritical Carbon Dioxide', Ch. 4 in Paulaitis, M.E. et al. (ed), 'Chemical Engineering at Supercritical Fluid Conditions', Ann Arbor Science Publishers, Ann Arbor, Mich., 1983 p. 101-111.
5. McHugh, M.A., Mallett, M.W. and Kohn, J.P., 'High Pressure Fluid Phase Equilibria of Alcohol - Water - Supercritical Solvent Mixtures, paper presented at the 1981 annual AIChE meeting, New Orleans, Louisiana, Nov. 9, 1981.
6. Radosz, M., Ber. Bunsenges. Phys. Chem. (1984), 88, 859-862.
7. Dietz, W.A., J. Gas Chrom. (1967), 5(2) 68-71.
8. Panagiotopoulos, A.Z. and Reid, R.C., 'A New Mixing Rule for Cubic Equations of State for Highly Polar, Asymmetric Systems', paper presented at the national American Chemical Society meeting in Miami,

- Florida, May 1, 1985
9. Francis, A.W., J. Phys. Chem. (1954), 58, 1099-1114
 10. Katayama, T., Oghaki, K., Maekawa, G., Goto, M. and Nagano, T., J. Chem. Eng. Jpn. (1975), 8(2), 89-92.
 11. Panagiotopoulos, A.Z. and Kumar, S. 'A generalized technique to obtain pure component parameters for two-parameter equations of state', Fluid Phase Equil. (1985), in print.

APPENDIX

Equation of State used

For the correlation of the experimental results, we used a modification of the Peng-Robinson equation of state developed by the authors. The essence of the method, which is presented in detail in (8), is the use of a non-quadratic mixing rule for the attractive parameter a , that involves two binary interaction parameters. The equations for the pressure, the mixing rule used and the resulting expression for the chemical potential of a component in a mixture are shown below.

$$P = \frac{RT}{V - b_m} - \frac{a_m}{V^2 + uVb_m + wb_m^2} \quad 1)$$

$$a_m = \sum_i \sum_j x_i x_j a_{ij} \quad 2)$$

$$b_m = \sum_i x_i b_i \quad 3)$$

$$a_{ij} = \sqrt{a_i a_j} [1 - k_{ij} + (k_{ij} - k_{ji})x_i] \quad 4)$$

$$\ln \phi_k = \ln \frac{\hat{f}_k}{x_k P} = \frac{b_k}{b_m} \left(\frac{PV}{RT} - 1 \right) - \ln \frac{P(V-b)}{RT} +$$

$$+ \left[\frac{\sum_i x_i (a_{ik} + a_{ki}) - \sum_i \sum_j x_i^2 x_j (k_{ij} - k_{ji}) \sqrt{a_i a_j} + x_k \sum_i x_i (k_{ki} - k_{ik}) \sqrt{a_k a_i}}{a_m} - \frac{b_k}{b_m} \right] \times$$

$$\times \frac{a_m}{\sqrt{u^2 - 4w} b_m RT} \ln \frac{2V + b_m (u - \sqrt{u^2 - 4w})}{2V + b_m (u + \sqrt{u^2 - 4w})} \quad 5)$$

For the estimation of the subcritical pure component parameters, we used the technique of Panagiotopoulos and Kumar (11), that provides results that exactly reproduce the vapor pressure and liquid density of a subcritical component. Table 2 presents the pure component parameters that were used. For the supercritical components, the usual acentric factor correlation was utilized.

It is important to note, that the interaction parameters between the components (two per binary) were estimated solely from binary phase equilibrium data (including low-pressure VLE data for the binary acetone - water); no ternary data were used in the fitting. The values of the interaction parameters obtained are shown in Table 3.

TABLE 1 : Three phase equilibrium compositions for the system Water (1) - Acetone (2) - CO₂ (3)

P (bar)	lower phase		upper phase		middle phase	
	x ₁	x ₂	y ₁	y ₂	z ₁	z ₂
T = 313 K						
29.3	0.810	0.153	0.005	0.025	0.294	0.454
35.9	0.864	0.106	0.006	0.019	0.197	0.427
43.2	0.904	0.075	0.003	0.017	0.153	0.360
55.9	0.920	0.052	0.002	0.015	0.119	0.230
61.1	0.942	0.037	0.004	0.015	0.114	0.191
65.8	0.944	0.032	0.002	0.015	0.130	0.148
75.2	0.959	0.017	0.002	0.014	0.020	0.069
79.6	0.966	0.011	0.002	0.015	0.049	0.035
T = 333 K						
39.4	0.795	0.163	¹	¹	0.400	0.398
51.1	0.880	0.091	¹	¹	0.182	0.418
59.4	0.906	0.068	0.006	0.030	0.173	0.359
70.3	0.925	0.049	0.008	0.035	0.117	0.300
79.2	0.939	0.039	0.006	0.032	0.089	0.234
92.6	0.946	0.029	0.010	0.046	0.084	0.127

¹ not available

TABLE 2 : Pure component parameters

Component	T(K)	a ($J \times m^3/mol$)	10^6 b (m^3/mol)
Acetone	313.15	2.1772	62.35
	333.15	2.1165	62.65
Ethanol	308.15	2.0292	48.23
	323.15	1.9679	48.44
	338.15	1.9069	48.61
Water	313.15	.81614	16.07
	333.15	.79123	15.99

TABLE 3 : Interaction parameters

System	T (K)	k_{12}	k_{21}
CO ₂ (1) - acetone(2)	313.15	-0.02	0.00
	333.15	-0.02	0.00
CO ₂ (1) - ethanol(2)	308.15	0.072	0.069
	323.15	0.093	0.077
	338.15	0.089	0.061
CO ₂ (1) - water(2)	313.15	-0.205	0.162
	333.15	-0.185	0.160
acetone(1) - water(2)	313.15	-0.310	-0.150
	333.15	-0.293	-0.132

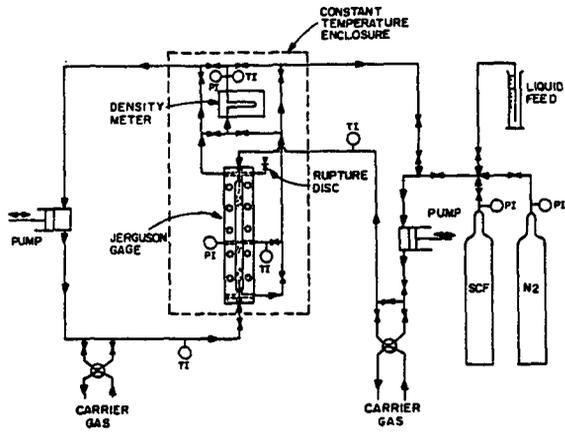


Figure 1 Schematic drawing of the equipment

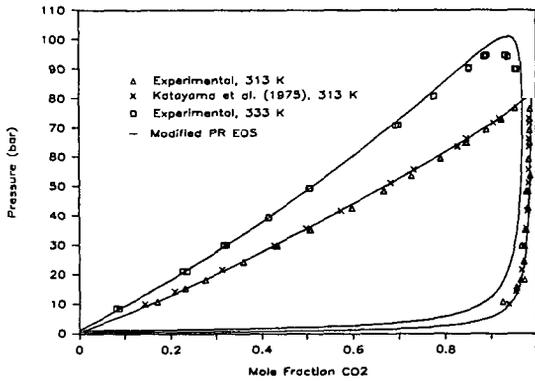


Figure 2 Experimental (crosses), literature (squares) and predicted (lines) phase equilibrium behavior for the system $\text{CO}_2(1) - \text{Acetone}(2)$ at 313 and 333 K. Experimental data are from reference (10).

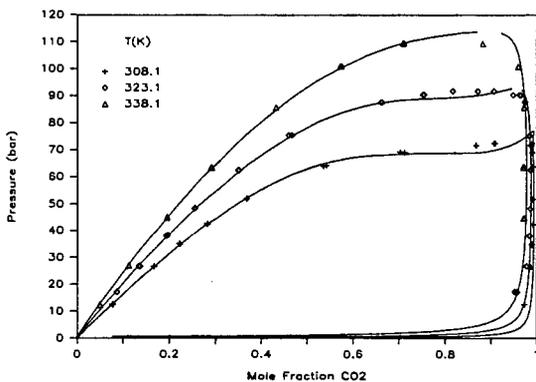


Figure 3 Experimental (symbols) and predicted (lines) phase equilibrium behavior for the system $\text{CO}_2(1)$ - water(2) at 308, 323 and 338 K

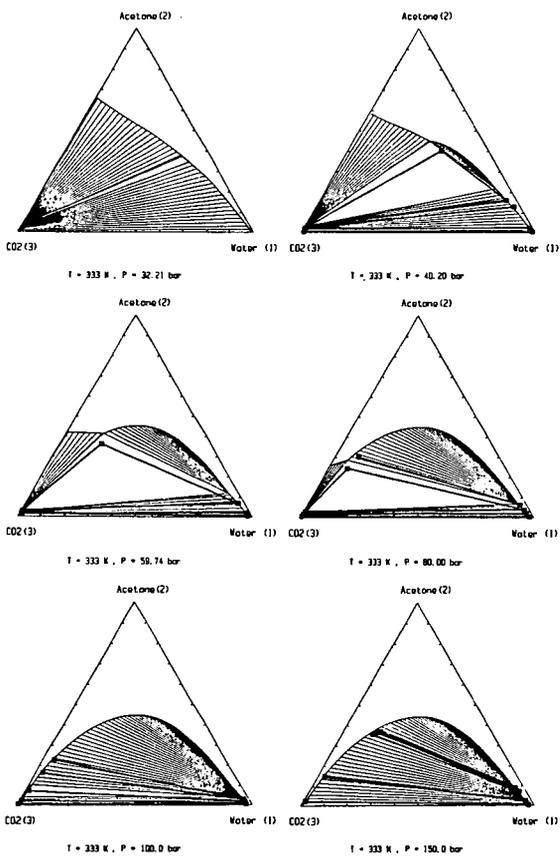


Figure 4 Experimental (dark lines and squares) and predicted (light lines) phase equilibrium behavior for the water(1) - acetone(2) - $\text{CO}_2(3)$ system at 333 K.

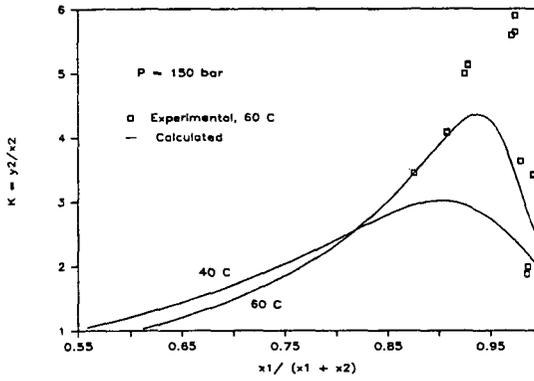


Figure 5 Distribution coefficient for acetone from experimental data (points) and model predictions (lines) for the water(1) - acetone(2) - CO_2 (3) system at 150 bar, as a function of the water concentration in the lower phase (on a CO_2 -free basis).

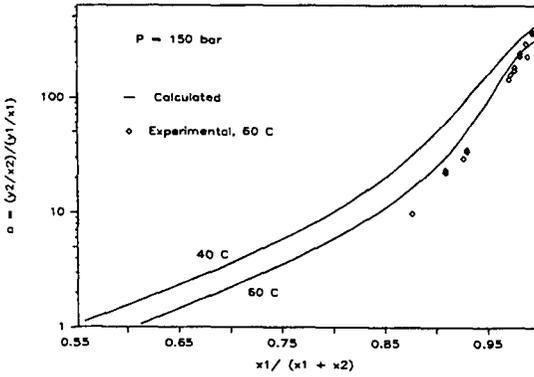


Figure 6 Selectivity factor for acetone over water for the water(1) - acetone(2) - CO_2 (3) system at 150 bar, as a function of the water concentration in the lower phase (on a CO_2 -free basis).