

Mixed Supercritical Solvents for Selective Solubility Enhancement

J. G. Van Alsten and C. A. Eckert

Department of Chemical Engineering
University of Illinois
Urbana, IL 61801

Supercritical fluids have generated a great deal of interest in the chemical engineering community for a variety of applications, including enhanced oil recovery, resid upgrading, and extraction (1). This being the case, we have been involved in an intensive program designed to understand both qualitatively and quantitatively the complex phase behavior inherent in mixtures of solutes dissolved in supercritical solvents.

This program involves measurements on thermodynamic modeling of selected supercritical systems. Our work first involved analysis of solutes dissolved in pure supercritical fluids to determine what differences, if any, solute nature had on the solubility behavior. Our data analysis requires two properties of the solute: first, its solubility in the selected supercritical fluid, second, the solute sublimation pressure at system temperature. Combining these two quantities yields the enhancement factor

$$K = \frac{y_2 P}{P_{2 \text{ sat}}} \quad 1)$$

which is simply a dimensionless solubility that scales out the saturation pressure contribution to the solubility. Comparison of enhancement factors (not solubilities!) yields the true solution behavior of the various solutes used in these studies.

We have compared enhancement factors for a variety of solid compounds of different polarities and functionalities in pure supercritical fluids and have found that the solution behavior is relatively insensitive to the chemical nature of the solute species. Thus, as Figure 1 illustrates, the solution behavior of the solutes phenanthrene and acridine is virtually identical, even though acridine has a relatively large dipole moment at 2.1 Debyes and is a heterocyclic analogue to the base pyridine. To understand why this is so, a rough order of magnitude calculation was performed to determine the relative magnitudes of the various forces involved in this system. Table 1 shows that the contribution from polar forces, e.g. those dipole/induced dipole forces between the acridine and CO₂ molecules, is only one one hundredth that of the contribution from non-specific van der Waals forces, which should be nearly identical for the acridine/CO₂ and phenanthrene/CO₂ systems. Since the forces involved in solutions of pure fluids arise almost exclusively from these van der Waals forces, one expects the solubility behavior to be the same in the class of solutes we have studied.

It is apparent that to induce some differentiability into the solution behavior, one will need to either use some associating fluid (such as ammonia) or modify the supercritical fluid by adding chemical "entrainers" to the solution. We have begun such studies in which dilute (1-5%) concentrations of polar entrainers are added to the bulk supercritical phase (CO₂). Dilute solutions are necessary for two reasons. First and foremost is the fact that dilute solutions allow us to operate over a broad range of pressures and temperatures without having to be concerned with separation into entrainer-rich and CO₂-rich phases; we can be assured that we always have a single, homogeneous phase. The second reason concerns the fact that while we would like to modify the fluid's solution behavior, we also wish to leave its useful phase behavior as intact as possible.

The two entrainers chosen were methanol and acetone. Both are small, relatively polar molecules which go into solution with CO₂ readily (2,3). Methanol, with its hydroxyl proton, is also a likely candidate for hydrogen bond formation with proton accepting species.

The entrainer effect can be quite large, as seen in Figure 2, where we show the solubility increase of the solute acridine in doped SCF's. This figure shows an over 500% increase in the solute's solubility over that in a pure supercritical solvent. Of even greater interest is the fact that this solubility increase is quite sensitive to the chemical nature of the solute species involved; Figure 3 illustrates this behavior. Here, the highly polar species acridine and fluorenone are seen to have solubilities greatly promoted by the presence of the entrainer methanol in supercritical CO₂. The much less polar species dibenzofuran is promoted to a much lesser extent, and the non-polar species phenanthrene and fluorene show virtually no solubility promotion in the entrained solvent. This behavior is in marked contrast to that of pure SCF's, where there is little if any solvent selectivity to these solute species.

As Table 1 illustrates, the relative magnitudes of the dipole-dipole and dipole-forces between a polar solute and polar entrainer molecule do not appear to be great enough to account for this solubility increase if the entrainer were randomly dispersed within the fluid. This suggests an aggregation or clustering of the entrainer species around the solute molecule in solution. Spectroscopic information is needed, however, to confirm this speculation.

REFERENCES:

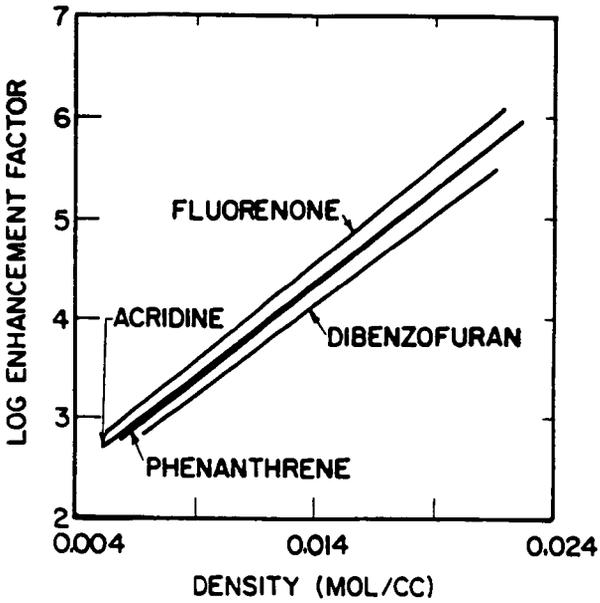
- (1) Paulaitis, M. P.; Krukonis, V.; Reid, R.; Kurnik, R.; Reviews in Chemical Engineering, 1 (2), 1983, 179.
- (2) Semenova, A.; Emel yanova, E.; Tsimmerms, S.; Tsiklis, D.; Russ. J. Phys. Chem., 53 (10), 1979, 1428.
- (3) Katayama, K.; Ohgaki, K.; Maekawa, G.; Goto, M.; Nagano, T.; J. ChE Japan, 8 (2), 1975, 89.
- (4) Prausnitz, J. M.; "Molecular Thermodynamics of Fluid Phase Equilibria", copyright 1969 Prentice-Hall, Englewood Cliffs, NJ.

TABLE 1

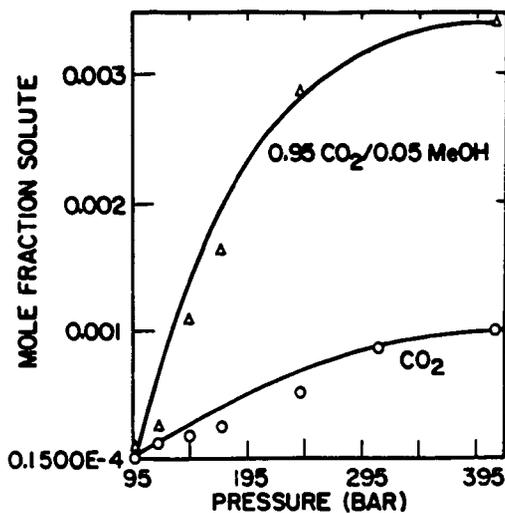
RELATIVE MAGNITUDES OF INTERMOLECULAR FORCES (4)

System: acridine/CO₂/acetone

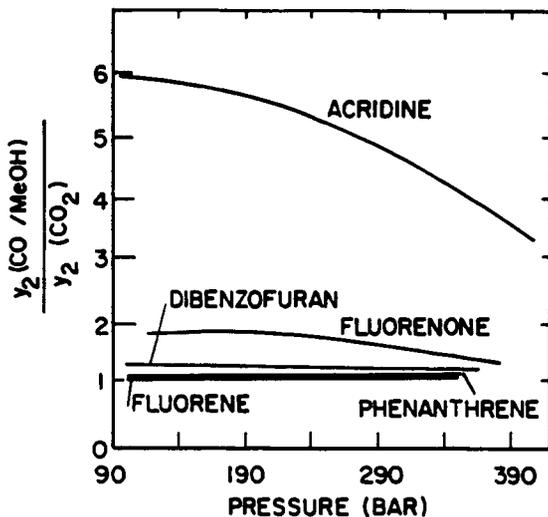
CO ₂ disp	CO ₂ ind dip	acetone disp	acetone ind dip	acetone dip/dip
1	.01	.89	.30	.27



ENHANCEMENT FACTOR FOR SEVERAL SOLUTES IN CO₂ AT 323 K



**INCREASE IN SOLUBILITY WITH ENTRAINER-DOPED
SOLVENT SYSTEM : ACRIDINE @ 323 K**



**ENTRAINER EFFECT WITH VARIOUS SOLUTES
5 mole % MeOH/CO₂ @ 323 K**