

## Estimation of Supercritical Fluid-Liquid Solubility Parameter Differences from Stirred Reactor Data

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### INTRODUCTION

Solubility parameters provide a means to explain and predict solubilities of both pure and mixed materials (1). Although computation of solubility parameters involves idealized approximations, it provides a valuable tool in applications as diverse as paint and polymer formulation and chromatographic analysis. Calculation of solubility parameters has been extended to supercritical fluids (2) and we are currently investigating its utility in our research concerning the extraction of oil seeds and other materials.

Attempts to measure solubility in supercritical fluids quantitatively with a Jurgeson gage (Jurgeson Gage and Valve Co., Burlington, MA) designed for pressures up to 10,000 psi were not successful because of a tendency for droplets to hang up in the apparatus. The gage however did provide an opportunity to observe when two clear phases were present. We were able to use a small, stirred reactor for mixing and for sampling from both phases after equilibration to overcome the problems of the Jurgeson gage. Solubility parameter differences between supercritical carbon dioxide and liquid solute were calculated from composition of the two phases. For the series of experiments discussed here, we selected three vegetable oils and, for contrast, four polar liquids which were expected to give relatively higher differences in solubility parameter than the oils.

### EXPERIMENTAL

The soybean oil selected was a refined, bleached and deodorized commercial oil, whereas the castor oil was a cold-pressed product obtained from a local drug store. Jojoba oil had been extracted with supercritical carbon dioxide from nuts obtained from a commercial supplier. The glycerol, ethylene glycol and n-butanol were reagent grade, whereas the triethylene glycol was listed as purified. All were obtained from Fisher Chemical Co. Carbon dioxide used in these experiments was Carbon Dioxide Liquified UN2187 (Matheson Division, Searle Medical Products Inc.) furnished in tanks without dip tubes.

Our stirred reactor was a 300 cc Bench Scale Magne-Drive Packless Autoclave (Autoclave Engineers Inc., 2930 West 22nd Street, Erie, PA 16512). The autoclave had two sampling ports, one of which was used to sample from the upper phase. The other port, equipped with a dip tube, was used for sampling from the lower phase. The reactor was equipped with a gas dispersion impeller for mixing. Temperature of the system (52° or 72°) was maintained by thermostatically controlled external heating tapes placed on the head and jacket of the reactor. Both external and internal reactor temperatures were measured with thermocouples. Pressure in the system was maintained with a 30,000 psi rated, two-stage, double-ended, electric motor-driven, diaphragm compressor (Aminco Model J46-13427, American Instrument Company, Division of Travenol Laboratories, Inc., 830 Georgia Avenue, Silver Springs, MD 20190).

Fifty ml. of liquid was placed in the stirred reactor and carbon dioxide at supercritical temperature charged into the system until the desired pressure was obtained. All charges were mixed at 1,000 rpm for at least 10 min and settled for the same length of time before sampling.

Use of longer agitation times did not appear to change results. At least 3 and frequently 4 or more samples of each phase were taken. Pressure drops during sampling were recorded, but results were not affected by differing pressure drops. Normally, all samples of a phase (usually the top one) were taken before sampling the other. Where a different order was followed, results were not changed.

Samples of 3.7 ml. were taken from both upper and lower phases. The apparatus provided for isolating the samples in a section of tubing by means of valves. The isolated sample was drawn off into a weighed container which allowed the carbon dioxide to come to a standard temperature and pressure and escape into another part of the apparatus for volume measurement. After rinsing the sample tube with a suitable solvent, the liquid was recovered by solvent evaporation and weighed with an analytical balance. Molecular volumes of each of the components as well as mole fractions and volume fractions in each of the phases were computed from weight, density and molecular weight. Solubility parameter differences were computed from Equation 1, which was published by Fujishiro and Hildebrand (3) for calculation of solubility parameter differences between immiscible liquids:

$$(\delta_1 - \delta_2)^2 = \frac{RT}{2} \left( \frac{1}{V_1} \ln \frac{X_{1B}}{X_{1A}} + \frac{1}{V_2} \ln \frac{X_{2A}}{X_{2B}} \right) / (\phi_{1B} - \phi_{1A}) \quad 1)$$

where  $\delta$  is the solubility parameter,  $x$  the mole fraction,  $\phi$  the volume fraction,  $T$  temperature and  $V$  the molecular volume. In Equation 1, subscripts 1 and 2 refer to components and A and B to phases. In our experiments, phase B was arbitrarily selected as the upper phase. This upper phase was sometimes liquid rich and sometimes carbon dioxide rich. Some systems, because of a greater change in supercritical fluid density than in liquid density, inverted within the pressure range of the experimental series.

## RESULTS

Absolute values for solubility parameter differences,  $|\delta_{CO_2} - \delta_{liq}|$  are given in Table I. Values were computed for system pressures of 5000, 8000 and 10,000 psi for all liquids and also at 16,000 and 20,300 psi for soybean oil. When compared to the oils a greater parameter difference between polar liquids and supercritical carbon dioxide correlates with experience indicating that the latter fluid acts as a relatively non polar solvent. For the series of polar liquids solubility parameter differences were estimated at 52°C which was a convenient temperature for operation of the stirred reactor. Because we wanted to compare data for the oils with results from other experiments, measurements were taken at 71 to 72°C, although control of temperature at this level was more difficult. Standard deviation for calculated values of  $|\delta_{CO_2} - \delta_{liq}|$  from the same charge was  $.23 \text{ cal}^{1/2} \text{ cm}^{-3/2}$ .

## DISCUSSION

Our method requires incomplete miscibility and relatively rapid attainment of equilibrium. Miscibility can be checked with the Jurgeson Gage. Equilibrium is more rapidly attained in super critical fluid-liquid than in liquid-liquid systems due to greater fluidity. Phase inversion, where it occurred, was apparently at pressures far enough removed from those where solubility was measured that any increased time required to reach equilibrium did not change computed parameter differences. For most of the liquids shown in Table I parameter differences were calculated by assuming the liquids incompressible, but

where information was available, theoretical (4) or actual (5) compressibilities were also used. Comparison of results indicated that errors arising from neglect of liquid compressibility were less than experimental ones. Trial calculations assuming reasonable errors (10% or less) in determined quantities of carbon dioxide and liquid in each phase also failed to produce large errors. The small change in parameter difference resulting from large changes in pressure is also in accord with theoretical calculations (4). Larger differences between parameters of polar liquids and supercritical carbon dioxide than between oils and the same supercritical fluid also agrees with the experience that supercritical carbon dioxide acts much like a nonpolar solvent, such as hexane, in vegetable oil extractions.

Employment of solubility parameters involves too many approximations to provide an exact method for predicting miscibility. Results, however, are valid often enough to be useful. In liquid-liquid systems composed of hydrocarbons and fluorocarbons, parameter difference estimates from Equation 1 were shown to more nearly reflect actual differences than calculated "theoretical" parameters based on the geometric mean assumption and regular solution theory (1). Since the final result of our estimate is an absolute value of the difference, we cannot tell from this calculation which parameter has the higher value. Judgment concerning actual magnitudes of the two solubility parameters can frequently be made from values for liquids under conventional conditions. For example, the solubility parameter of supercritical carbon dioxide can be computed from Equation 2 which was proposed by Giddings et al (2) for dense gases:

$$\delta_{\text{gas}} = 1.25 P_c^{1/2} (P_r/2.66) \quad 2)$$

where  $\delta_{\text{gas}}$  is the solubility parameter of the supercritical fluid,  $P_c$  is its critical pressure,  $P_r$  is the reduced density of the gas and 2.66 is a constant which is equivalent to an average reduced density for the corresponding liquid. Computed from Equation 2 the solubility parameter of carbon dioxide at 52°C and 8000 psi pressure is about 8.5 cal<sup>1/2</sup> cm<sup>-3/2</sup>. Values taken from literature (6) are 17.7, 17.1, 14.2 and 14.0 cal<sup>1/2</sup> cm<sup>-3/2</sup> for solubility parameters of glycerol, ethylene glycol, triethylene glycol and n-butanol, respectively. Values for liquids are usually presented for 25°C and one atmosphere pressure, but for most liquids they exhibit only little variation with increase in pressure and increase in temperature to 52°C.

While most data in Table I appear reasonable, we have no explanation for the relatively high values for ethylene glycol at 8000 psi. Our parameter differences also do not explain the increased solubility of soy oil in supercritical carbon dioxide that occurs at 11000 to 12000 psi pressure (7).

#### CONCLUSION

Calculated absolute values of solubility parameter difference for the series of polar liquids used in our experiment agree well enough with values taken or computed from literature to indicate that data from a stirred autoclave can provide a useful estimate. With sufficient attention to temperature, pressure and attainment of equilibrium, results are reproducible and the calculation does not seem unduly sensitive to small environmental variations. Results appear to correlate well with extraction experience.

The mention of firm names or trade products does not imply that they are endorsed or recommended by the U.S. Department of Agriculture over other firms or similar products not mentioned.

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TABLE I

Absolute Values† for Solubility Parameter Differences,  $|\delta_{CO_2} - \delta_{liq}|$ ,  
Between Supercritical Carbon Dioxide and Liquid

Liquid	Pressures (Psi)				
	5000	8000	10000	16000	20300
Soy Oil	1.9	1.7	1.6	1.6	1.6
Jojoba Oil	2.1	1.9	1.9		
Castor Oil <sup>a</sup>	2.0	1.8	1.8		
Glycerol <sup>b</sup>	6.0	6.2	6.1		
Ethylene glycol <sup>b</sup>	5.7	7.9	6.7		
Triethylene glycol <sup>b</sup>	5.4	5.5	5.1		
n Butanol <sup>b</sup>	4.5	4.5	4.6		

†Solubility parameter differences in  $\text{cal}^{1/2} \text{cm}^{-3/2}$

<sup>a</sup>Oil solubilities were measured at 71-72°C

<sup>b</sup>Polar liquid solubilities were measured at 52°C