Solubility Phenomena in Dense Carbon Dioxide Gas in

the Range 270–1900 Atmospheres

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A high-pressure gas chromatographic instrument has been used to measure the density dependent solubility of Carbowax 4000, Carbowax 1000, 1-octadecanol, and stearic acid in compressed CO_2 at 40°. It is shown that maxima exist in all these solubility curves at between 300 and 2500 atm, depending on the solute. This result is consistent with a form of regular solution theory developed for dense gaseous solvents. A comparison of theory and experiment relative to a number of parameters shows generally excellent qualitative agreement and in some instances a quantitative predictability.

Introduction

The enhancement of volatility caused by the presence of a dense gaseous atmosphere has been noted on many occasions.[1-13] Compression appears to give to the gas a positive solvent power not possessed in its normal, low-pressure state. This solvent power increases substantially with increasing compression. Studies of the phenomenon, which extend back to the last century,[1] are mainly limited to solute molecules of small and medium size and to pressures under 200 atm. Recently we have reported data on the solubility of biochemicals and polymers (molecular weight to 4×10^5) in dense NH_3 gas at 200 atm and dense CO_2 gas at pressures to 1560 atm.[12,13] Here we extend this work by obtaining solubilities as a function of CO_2 density for Carbowax 4000, Carbowax 1000, 1-octadecanol, and stearic acid in CO_2 in the pressure range 270–1900 atm at 135-atm intervals. We show that there are maxima in the solubility curves not seen before and indeed not present in the low-pressure range. In our cases, the maxima for different solutes occur anywhere from 300 to 2040 atm. The existence of the maxima is predicted, and their locations well approximated, by the application of a form of regular solution–solubility parameter theory.

The impetus for recent studies in dense gas solubility comes from the realization that these gaseous "solvents" may be of unique value in enhancing the volatility of complex molecules so that they can be gas chromatographed.[10-14] The sensitivity of solubility to pressure provides a rapid mechanical means for manipulating solubility both in chromatographic and in other systems. Experiments have borne out the fruitfulness of this approach.

Efforts to describe the solvent power of nonideal gases in quantitative, mathematical form have almost entirely used the virial approach. This direction has been followed for both chromatographic[11,15-22] and nonchromatographic[23-27] work. The virial treatment is rigorous, but is inapplicable at pressures much beyond 100 atm because of difficulties in evaluating higher virial coefficients and series convergence problems.[9] Hence

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