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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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this method, which approaches dense gases from the ideal gas side, is not valid for the high densities studied here.

More likely to succeed, under the circumstances, would be an approach based on liquid solubility phenomena. Densities of practical interest are usually in the range 0.3–0.9 times the equivalent liquid density, while gases at 1 atm pressure, already showing measurable nonideal effects, are removed in density by several hundredfold from this range.

The principal difficulty with following the general path of liquid solution is that the latter are themselves imperfectly understood.[28] However, it is clearly more suitable to use approximate methods where the approximations are in accord with the physical situation than to stretch an exact theory (virial) far beyond its reasonable limit of application.

For the above reasons, we previously suggested and developed approximate methods for applying solubility parameter concepts to dense gaseous solutions.[13] Some aspects of this approach will be tested here.

The key results of the theory are given in the following two equations. First the solubility parameter is a function only of density ρ, approximated by the linear relationship

$$\delta_g = \delta_{liq}[\rho/\rho_{liq}] \quad (1)$$

and therefore reaches the value, δ_{liq}, characteristic of the parent liquid when the gas is compressed to the liquid density, ρ_{liq}. Solubility enhancement is related to this by

$$\ln I = (V_0\delta_0^2/RT)\Delta(2 - \Delta) \quad (2)$$

where I is the solubility enhancement, the solute concentration at saturation relative to its ideal gas value, V_0 and δ_0 are solute molar volume and solubility parameter, respectively, and Δ is the reduced solubility parameter of the compressed gas, δ_g/δ_0.

The direct measurement of I is impractical for large solute molecules since ideal vapor pressures are immeasurably low (estimates of I will be given later). Instead, solubility relative to the maximum value is more appropriate here. From eq 2 this is

$$\ln (I/I_{max}) = -(V_0\delta_0^2/RT)(\Delta - 1)^2 \quad (3)$$

The above equations are approximations which do not adequately allow for density-dependent entropy effects, pressure–volume effects, and the various molecular subtleties which render regular solution theory itself inexact. They are looked to more as a guide to qualitative effects and to rough quantitative estimates, both presently needed in this field.

Experimental Section

The high-pressure apparatus used in this study was basically like that described elsewhere.[12,29] A schematic diagram which helps illustrate the procedure is given in Figure 1. Modifications to the previous apparatus are as follows.

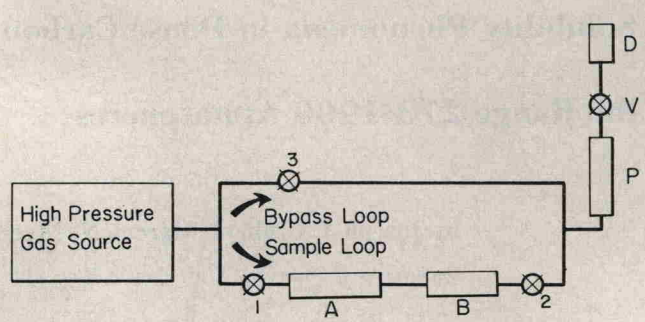

Figure 1. Schematic of high-pressure unit: 1, 2, 3, on–off valves; A, B, sample chambers; P, pyrolysis unit; V, pressure reducing valve; D, detector.

Pyrolysis Unit. It has been pointed out often that the dissolved molecules become thermodynamically unstable upon decompression and tend to condense out.[7,8,12,30] This leads to line clogging and consequently to alteration or stoppage of flow to the detector. It was suggested that pyrolysis at the downstream end of the column prior to decompression may eliminate this difficulty.[12] For this reason a pyrolysis unit was incorporated into the system.

The structure of the pyrolysis unit is shown in Figure 2. It consists of approximately 20 cm of 0.015-cm i.d. stainless steel tubing which is heated to about 650°. The outer tubing acts both as a form on which the heating wire is wound and also as a guard in the event of rupture of the inner tubing. From our experience, such a unit can withstand pressures up to 30,000 psi without failure. This, however, is not true for ammonia, where a few leaks have been encountered.

Pressure Reducing Valve. A new type of valve has been constructed which maintains very stable flow for long periods of time. A detailed description of this valve will appear elsewhere.

Splitter. The splitter and the back pressure regulator have been eliminated because of the availability of controlled flow. Under these conditions the entire sample is swept into the detector.

Detection System. The detector was a Beckman GC-4 flame ionization detector. Provisions were made to ensure constant air and hydrogen supply to the detector. The detector signal was fed into a Cary Model 31 electrometer which was coupled to a Speedomax Type G

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