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THE EFFECT OF PRESSURE ON THE SOLUBILITY OF SOLIDS IN NON-POLAR LIQUIDS*

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Solubility measurements under pressures to 10,000 atmospheres have been made in the following systems: phenanthrene in CS_2, *n*-hexane, *n*-heptane, *n*-octane; SnI_4 in CS_2, *n*-hexane, *n*-heptane, *n*-octane; C_2Cl_6 in CS_2, *n*-hexane, *n*-heptane, *n*-octane, 2-methylpentane, 3-methylpentane, 2,3-dimethylbutane, 2,2-dimethylbutane; anthracene in CS_2. The results are analyzed in terms of Scatchard-Hildebrand theory. In general, the effects of molecular structure assume greater importance at the higher pressures, especially for *n*-heptane.

While the measurement of solubility is one of the older fields of physical chemistry, there have been very few attempts to study the effect of an extended range of pressure on the solubility of simple molecular solids in non-polar organic liquids. This paper presents the results of such a study made at 25° with a maximum pressure of 10,000 atmospheres. The systems studied and the maximum pressure for each are listed in the Tables I–IV.

Experimental Procedure

A. Chemicals and Purification.—The hydrocarbons were all Phillips Petroleum Co. "Pure Grade," the carbon disulfide was J. T. Baker C.P. grade. The solvents were dried over P_2O_5 and distilled slowly in a two-foot packed column using only a center cut amounting to 50–60% of the charge. The boiling range of the product was never over 0.5°. Actually tests run with phenanthrene and SnI_4 indicated that the drying procedure had very little effect on solubility.

The SnI_4 was obtained as reagent crystals from Herstein Laboratories. Its melting range was 145.7–147.9° compared with the literature value of 143.5°. Since its atmospheric solubilities in CS_2 and heptane checked very closely the values given by Dorfman and Hildebrand,[1] it was used without further purification.

The phenanthrene, anthracene and hexachloroethane were Eastman Kodak Co. purest grade. The phenanthrene melted 100–101.1° and the anthracene melted 216.7–218.2°. These were used without further purification. A few experiments on recrystallized phenanthrene gave no significant deviation from the other results.

The C_2Cl_6 melted 187.7–188.9°. It was resublimed and recrystallized from ether and ethanol, and carefully dried. The final product melted 188.5–189.2°.

B. Analytical Procedure.—Analyses were performed either by weight or by refractive index. The weighing procedure was used for all phenanthrene systems, for anthracene–CS_2 for SnI_4–CS_2 and for C_2Cl_6–CS_2. Weighings were made on an Ainsworth type DLB chainomatic balance. For the hydrocarbons, standard weighing bottles were used, while special weighing pipets were constructed for the CS_2 systems. Considerable care was necessary, and many tests on known solutions were performed, but the methods were fairly standard except for C_2Cl_6–CS_2. In this case the relatively high vapor pressure of C_2Cl_6 made it impossible to evaporate to dryness without losing C_2Cl_6, so a special procedure was adopted.[2]

The analyses by refractive index were performed on a Bausch and Lomb Precision Refractometer. The light source was a sodium vapor lamp. The systems analyzed in this manner included all of the SnI_4 and C_2Cl_6 data, except for the CS_2 runs in both cases.

The percentage error for the highest pressure runs may be 10%, at atmospheric pressure the error was certainly less than 0.3%.

C. Measurement of Solubility.—The technique used to determine solubilities at one atmosphere was essentially that of Hildebrand, Ellefson and Beebe.[3]

The high pressure equipment consisted of an intensifier, a bomb and a solubility cell. The method of obtaining and measuring the pressure was identical to that described previously.[4] The solubility cell consisted of a stainless steel tube $1/2''$ in diameter and $1\,5/8''$ long which screwed into a cup filled with mercury. The mercury served to separate the pressure transmitting fluid from the solution. The cell was separated into two sections by a layer of filter paper supported on either side by two pieces of 200 mesh stainless steel screening. These rested on a shelf about $5/8''$ from the top. The edges were sealed by a Teflon gasket held in place by a steel sleeve. Each chamber contained an iron ring. Attached to the upper plug and surrounding the cell was a solenoid through which was sent a pulsed d.c. current. This activated the iron stirrers and caused mixing in each chamber. The top cup contained a hole for a 2-56 screw and two No. 70 holes for thermocouple wires. The wires were coated with collodion and the whole top of the cell was painted with collodion after assembling.

The lower chamber contained the solid and solution, the upper chamber just solution. The solid was either placed on the mercury or separated from it by a polyethylene disk. Since the solubility dropped very rapidly with increasing pressure it was necessary to prevent supersaturation at one atmosphere. For this purpose the solid was carefully covered by a piece of tin foil amalgamated with mercury. A third small stirrer was enclosed with the solid. After loading and applying pressure the coil was started and the stirrer tore open the weakened foil.

At the end of a run the system was depressured, the top plug and pressure transmitting fluid removed, and the liquid sampled through one of the No. 70 thermocouple wire holes.

For the case of phenanthrene in CS_2 the procedure had to be modified. In the first place, phenanthrene is very soluble, and secondly it is less dense than CS_2 and floats. The solid was fused into a lump in order to get enough in, and a piece of medium porosity fritted glass one mm. thick replaced the filter paper. This was successful only because of the small pressure coefficient of viscosity of CS_2.

The bomb was immersed in a bath which was controlled to ±0.1°. With the large mass of steel it is doubtful if even these fluctuations got through to the cell. Since the stirrer coil also supplied heat, the bath was maintained at 22.4°. The thermocouple measured the temperature in the upper chamber of the cell.

In order to guarantee equilibrium, runs were made with various initial concentrations of solution, since this was more convenient than varying the time of the run. (The runs were generally 20–24 hours). Various other tests were applied to insure the validity of the method.

Results

The experimental results are shown in Table I–IV. The reproducibility is ±1–2% at atmospheric pressure, and ±10% at the highest pressures. The larger deviation at high pressure is due primarily to difficulties in analysis.

Figure 1 is a plot of relative solubility *versus* relative volume of solvent for different solutes in CS_2. On the same graph are shown the atmospheric pressure results obtained for SnI_4 in CS_2 at

(*) This work was supported in part by the A.E.C.

(1) M. E. Dorfman and J. H. Hildebrand, *J. Am. Chem. Soc.*, **49**, 729 (1927).

(2) E. P. Doane, Ph.D. Thesis, Univ. of Illinois, Urbana, Illinois.

(3) J. H. Hildebrand, E. T. Ellefson and C. W. Beebe, *J. Am. Chem. Soc.*, **39**, 2301 (1917).

(4) R. C. Koeller and H. G. Drickamer, *J. Chem. Phys.*, **21**, 267 (1953).

TABLE I

SOLUBILITY OF PHENANTHRENE, 25°

The pressure in atmospheres is followed by the solubility in mole percentage in parentheses.

n-Hexane

1 (3.26), 500 (2.72), 1000 (2.26), 2000 (1.80), 4300 (1.04), 7150 (0.50), 8750 (0.36)

n-Heptane

1 (4.01), 500 (3.21), 900 (2.92), 1000 (2.72), 2000 (1.84), 3430 (1.11), 5000 (0.84), 7000 (0.52)

n-Octane

1 (4.64), 490 (3.81), 1000 (2.84), 1960 (1.97), 3850 (1.20), 5200 (0.88)

CS_2

1 (23.5), 500 (16.2), 1000 (12.5), 2000 (7.3), 4000 (4.5), 6000 (2.9), 7000 (2.2)

TABLE II

SOLUBILITY OF SnI_4

The pressure is given in atmospheres followed by the solubility in mole percentage in parentheses.

n-Hexane

1 (0.470), 10 (0.443), 480 (0.315), 1000 (0.199), 2000 (0.099), 3100 (0.057), 5100 (0.047), 7200 (0.033), 9100 (0.019)

n-Heptane

1 (0.553), 470 (0.383), 980 (0.163), 2000 (0.048), 3000 (0.031), 4600 (0.019), 7200 (0.018)

n-Octane

1 (0.621), 500 (0.429), 1000 (0.245), 1500 (0.148), 2000 (0.115)

CS_2

1 (14.61), 1000 (7.99), 2000 (5.64), 3600 (3.45), 5000 (1.96), 7000 (0.77), 10,000 (0.11)

TABLE III

SOLUBILITY OF C_2Cl_6

The pressure in atmospheres is followed by the solubility in mole percentage in parentheses.

n-Hexane

1 (13.92), 400 (9.84), 1000 (6.36), 2000 (3.40), 3300 (1.72), 5000 (0.64), 5830 (0.29), 6750 (0.26)

n-Heptane

1 (15.18), 410 (10.48), 1000 (6.79), 2000 (2.30), 2970 (1.63), 4000 (0.83), 5000 (0.40)

n-Octane

1 (15.72), 400 (10.35), 1000 (6.33), 2000 (3.44)

CS_2

1 (19.5), 500 (12.0), 1000 (8.0), 1970 (4.1), 3400 (2.3), 5000 (1.3), 7000 (0.31)

2-Methylpentane

1 (13.02), 400 (9.15), 1000 (5.76), 1950 (3.14), 3350 (1.43), 5000 (0.52), 6900 (0.22)

3-Methylpentane

1 (13.52), 400 (9.56), 1000 (6.21), 2000 (3.15), 3500 (1.19), 5000 (0.61), 7000 (0.18)

2,3-Dimethylbutane

1 (13.15), 400 (9.19), 990 (5.74), 1970 (2.83), 3500 (1.15), 4950 (0.51), 6800 (0.14)

2,2-Dimethylbutane

1 (12.02), 400 (8.48), 990 (5.41), 2000 (2.72), 3500 (0.98), 4500 (0.45)

TABLE IV

SOLUBILITY OF ANTHRACENE

The pressure in atmospheres is followed by the solubility in mole percentage in parentheses.

CS_2

1 (0.84), 240 (0.70), 500 (0.59), 1000 (0.41), 2000 (0.27), 4000 (0.13)

various temperatures by Dorfman and Hildebrand.[1] The density coefficient of solubility varies considerably more rapidly at constant pressure than at constant temperature. A similar result was found for SnI_4 in *n*-heptane.

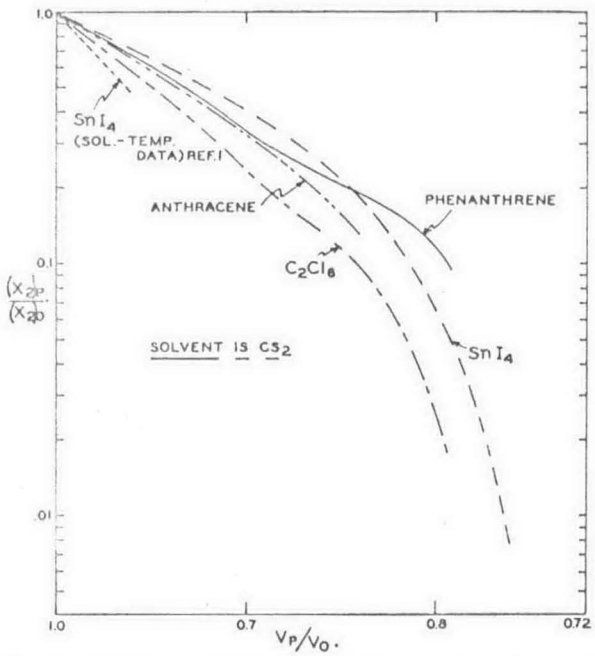

Fig. 1.—Relative solubility *vs.* relative molar volume of solvent.

It is useful to compare our atmospheric pressure data with values in the literature. In Table V

TABLE V

COMPARISON OF SOLUBILITIES OBTAINED IN THIS WORK WITH PUBLISHED SOLUBILITY VALUES OF SnI_4 (MOLE %)

Solvent	Dorfman and Hildebrand[1]	This work
Heptane	0.533	0.552
CS_2	14.64	14.61

Solubility of phenanthrene (mole %)

Solvent	Hildebrand Ellefson and Beebe[2]	This work Eastman	Recrystallized
CS_2	25.5	23.5	21.6
n-Hexane	4.2	3.26	3.09

Solubility of anthracene (mole %)

Solvent	Ref. 2	This work
CS_2	1.09	0.84

we see such a comparison. We find excellent agreement for the solubility of SnI_4 in CS_2 and in heptane, but no agreement for the solubility of

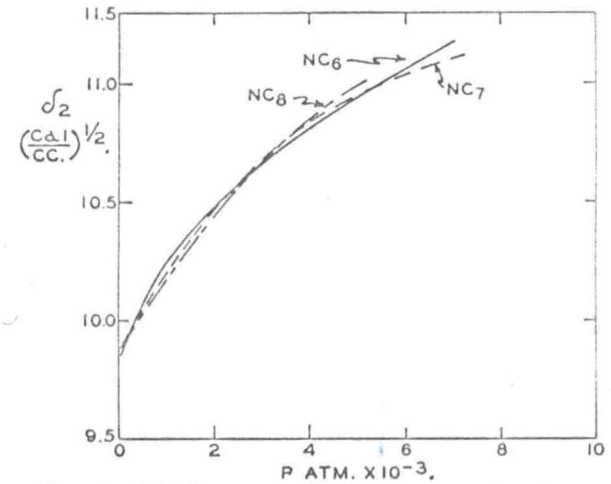

Fig. 2.—Solubility parameter *vs.* pressure for phenanthrene.

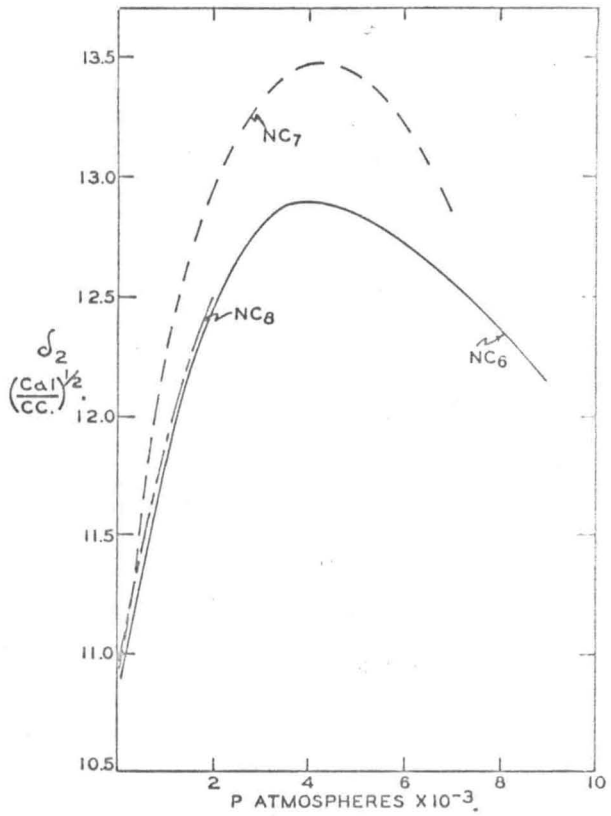

Fig. 3.—Solubility parameters *vs.* pressure for SnI_4.

phenanthrene and anthracene in heptane. We have no good explanation of this. We tried two different batches of Eastman phenanthrene, and recrystallized one batch several times. We never obtained any variation from batch to batch greater than 10%, and the more highly purified batches deviated most widely from Hildebrand's values.

Comparison of Theory and Results.—By far the most widely used theory of solutions is that developed by Scatchard and Hildebrand. Recently theories with a sounder basis in statistical mechanics have been developed by Guggenheim,[5] Kirkwood[6] and Prigogine and co-workers.[7] These, however, are not readily applied to a discussion of solubility under pressure.

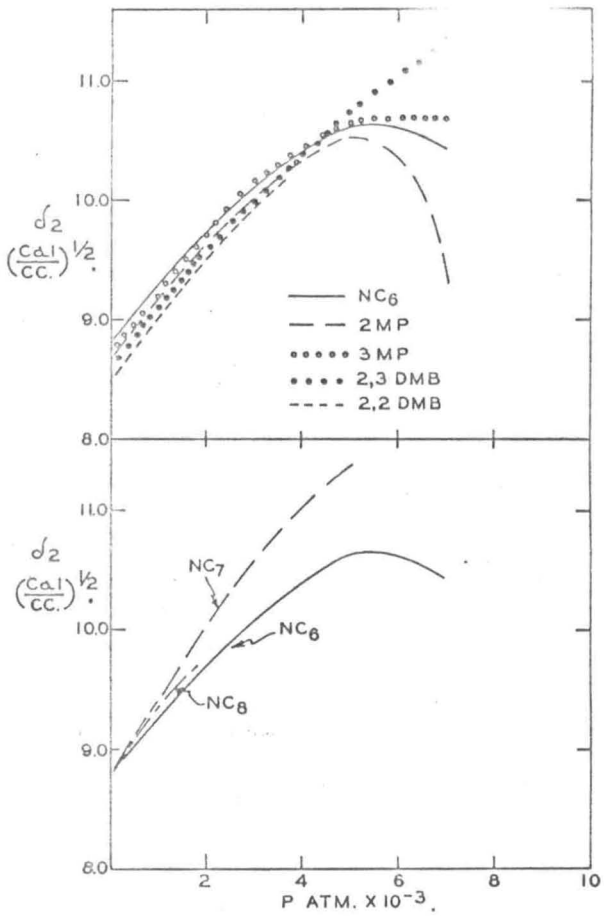

Fig. 4.—Solubility parameter *vs.* pressure for C_2Cl_6.

To discuss our results we shall use the S–H theory. This theory gives[8] for the partial molal free energy of the solute

$$\Delta\bar{F}_2 = V_2\varphi_1^2(\delta_2 - \delta_1)^2 + RT \ln X_2 \qquad (1)$$

if the entropy of mixing is ideal, or

$$\left[\Delta\bar{F}_2 = V_2\varphi_1^2(\delta_2 - \delta_1)^2 + RT \ln \varphi_2 + \varphi_1\left(1 - \frac{V_2}{V_1}\right)\right] \qquad (2)$$

if the Flory–Huggins entropy is used. Here

V_i = molal vol. of i (of the supercooled liquid for the solute)
X_2 = mole fraction of solute (measured)
φ_i = vol. fraction of i
δ_i = solubility parameter of i
$= \left(\frac{-E}{V}\right)^{1/2}$

where $-E$ = cohesive energy, at one atmosphere, the energy of vaporization into a perfect gas.

It is not hard to show[8] that

$$\overline{\Delta F_2} = RT \ln X_2^i \qquad (3)$$

(5) E. A. Guggenheim, "Mixtures," Oxford Univ. Press, New York, N. Y., 1952.

(6) Z. Salzberg and J. H. Kirkwood, *J. Chem. Phys.*, **20**, 1538 (1952); **21**, 2169 (1953).

(7) I. Prigogine and V. Mathot, *ibid.*, **20**, 49 (1952); I. Prigogine and A. Bellemans, *Disc. Faraday Soc.*, No. 15, 80 (1953); I. Prigogine, N. Trappeniers and V. Mathot, *ibid.*, No. 15, 93 (1953). See also other articles referred to in these papers.

(8) J. H. Hildebrand and R. L. Scott, "The Solubility on Nonelectrolytes," 3rd Ed., Reinhold Publ. Corp., New York, N. Y., 1950.

where X_{2i} is the "ideal solubility" of the solid.

To evaluate solubility parameters under pressure the relationship

$$\left(\frac{\partial E}{\partial p}\right)_T = -T\left(\frac{\partial V}{\partial T}\right)_p - P\left(\frac{\partial V}{\partial p}\right)_T \qquad (4)$$

is used. Then

$$E_P = E^\circ + \int_1^P \left(\frac{\partial E}{\partial p}\right)_T \partial P \qquad (5)$$

The p–v–t data of Bridgman[9] were used. The volumes of the supercooled liquids were estimated from Bridgman's data on compressibility of organic solids and volume changes or melting under pressure. It can be shown that no reasonable change in these values would change our calculations materially.

In these equations X_{2i} and δ_2 are not known under pressure. The solutions were considered in pairs; one solvent in each pair was CS_2. It was then possible to solve for δ_2, the solubility parameter of the solute, using either the Flory–Huggins entropy (eq. 2) or the ideal entropy (eq. 7). Both calculations were made. In Figs. 2–4 are shown the calculated values of δ_2 using the Flory–Huggins entropy. There were no significant differences in the trends obtained using eq. 1 or 2.

(9) P. W. Bridgman, *Proc. Amer. Acad.*, **49**, 1 (1913); **66**, 1 (1931); **76**, 9 (1945).

The measure of the applicability of the S–H theory is the consistency of the solubility parameter of the solute δ_2 calculated from different solvent pairs. From Fig. 2, it can be seen that the theory describes phenanthrene solutions quite well. From Fig. 3 and 4 we note that the theory gives consistent results for SnI_4 and C_2Cl_6, in hexane and octane, but that solubility parameters for these almost spherical solutes in heptane are high, particularly at the higher pressures. It is known that the odd-numbered normal paraffin chains pack differently than those with an even number of links. Their freezing points are displaced to a lower temperature indicating there are fewer ways of packing them in a lattice. It would seem that the deviation of heptane is due to an entropy effect not accounted for in eq. 2.

In Fig. 4 are shown the solubility parameters for C_2Cl_6 calculated for solutions in the isomers of hexane. The agreement is good to 5000 atmospheres, but beyond this point there is a spread in solubility parameters far outside experimental error. Apparently there are different packing effects for different isomers, and these become important at high densities.

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