

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 CS₂, *n*-hexane, *n*-heptane, *n*-octane; SnI₄ in CS₂, *n*-hexane, *n*-heptane, *n*-octane; C₂Cl₆ in CS₂, *n*-hexane, *n*-heptane, *n*-octane, 2-methylpentane, 3-methylpentane, 2,3-dimethylbutane, 2,2-dimethylbutane; anthracene in CS₂. 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 P₂O₅ 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 SnI₄ indicated that the drying procedure had very little effect on solubility.

The SnI₄ 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 CS₂ 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 C₂Cl₆ 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-CS₂ for SnI₄-CS₂ and for C₂Cl₆-CS₂. 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 CS₂ systems. Considerable care was necessary, and many tests on known solutions were performed, but the methods were fairly standard except for C₂Cl₆-CS₂. In this case the relatively high vapor pressure of C₂Cl₆ made it impossible to evaporate to dryness without losing C₂Cl₆, 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 SnI₄ and C₂Cl₆ data, except for the CS₂ 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

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(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).

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 CS₂ the procedure had to be modified. In the first place, phenanthrene is very soluble, and secondly it is less dense than CS₂ 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 CS₂.

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 CS₂. On the same graph are shown the atmospheric pressure results obtained for SnI₄ in CS₂ at

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