

purified by two different methods and certain of its physical constants were determined.

The diffusion constant calculated to the water basis at 25° was found to be  $4.78 \times 10^{-7}$  cm.<sup>2</sup> per sec. (At 20°,  $D = 4.3 \times 10^{-7}$  cm.<sup>2</sup>/sec.)

A calculation by means of sedimentation methods, using this value of "D" and an estimated value of the sedimentation constant, gave a

molecular weight for secalin of approximately 40,000. Thus the predominant constituent of secalin seems to belong in the egg albumin molecular weight class of molecules.

The ordinary isoelectric point for secalin as determined by electrophoretic mobilities was found to be at pH 6.67.

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RECEIVED JANUARY 6, 1940

[CONTRIBUTION FROM THE BAKER CHEMISTRY LABORATORY OF CORNELL UNIVERSITY]

## Fluorochloroethanes as Solvents for the Cryoscopic Determination of Molecular Weights

BY JACK BERNSTEIN AND WILLIAM T. MILLER

The purpose of this paper is to call attention to the suitability of fluoropentachloroethane, *sym*-difluorotetrachloroethane and *unsym*-difluorotetrachloroethane for use as solvents for the determination of molecular weights. These substances have large molecular freezing point depressions, are chemically inert and melt within convenient working ranges. Their solvent action is in general very good for non-associated substances. A representative list of qualitative solubilities of organic compounds in *sym*-difluorotetrachloroethane has been reported by Booth.<sup>1</sup>

**Fluoropentachloroethane.**—Fluoropentachloroethane was found to work particularly well as a molecular weight solvent using a semimicro procedure modeled after the Rast procedure as modified by Munster.<sup>2</sup> A sealed tube is necessary for the melting point determinations because of the high vapor pressure of this substance near its melting point. Small thin-walled "micro boiling point tubes" were used ( $4.5 \times 60$  mm.), and the fluoropentachloroethane was added by rolling it into small pellets which were dropped into the tube. In each case the ratio of the weight of the solute to the weight of the solvent was such as to give a depression of the freezing point between 9 and 15°.

From the observed values of the depression of the freezing point values of the freezing point constant  $k$  as calculated by the usual formula  $k = \Delta TSM/s1000$  were obtained. The concentrations varied from 3–10%, and the values listed are the mean values of at least two determinations with an average deviation from the mean of about 0.1, except where otherwise indicated: benzyl bromide, 41.5; benzyl ether, 42.1; decachlorobutane, 42.6; *p*-dichlorobenzene, 42.1; 4,4'-difluorodiphenyl, 42.8; isoamyl acetate, 41.3; methyl benzoate, 41.1; naphthalene, 42.1; acetone,  $s/S = 0.0201, 0.0221, k = 31.5, 32.3$ ; benzoic acid,  $s/S = 0.0230, 0.0483, 0.0682, k = 24.5, 22.0, 21.3$ ;

benzyl alcohol,  $s/S = 0.0485, 0.0691, k = 26.7, 23.6$ ; *n*-butyl alcohol,  $s/S = 0.0304, 0.0512, k = 23.7, 23.5$ ; butyraldehyde,  $s/S = 0.0149, 0.0220, 0.0226, 0.0379, k = 31.3, 33.5, 33.2, 27.7$ ;  $\alpha$ -naphthol,  $s/S = 0.0241, 0.0482, k = 38.3, 32.9$ ; nitrobenzene,  $s/S = 0.0392, 0.0429, k = 35.8, 36.7$ , respectively.

Acetanilide, aniline and dimethylaniline were sparingly soluble in fluoropentachloroethane and hexachloroethane formed a crystalline solid phase of higher melting point. For the measurements in which there was complete solubility and no apparent association or compound formation, the average value of  $k$  was 42.0.

The fluoropentachloroethane used in this work was prepared by fluorinating pentachloroethane<sup>3</sup> and melted at 99.9° after purification by distillation. This substance also may be prepared readily from hexachloroethane and antimony trifluoride.<sup>1,4</sup>

***sym*- and *unsym*-Difluorotetrachloroethane.**—These compounds do not work well with the semimicro procedure because of the difficulty of observing crystallization in the small tubes. However, their large freezing point depressions and convenient melting temperatures may be utilized in the usual macro procedure,<sup>5</sup> and their use for precise cryoscopic measurements is indicated. The constant  $k$  for *sym*-difluorotetrachloroethane was determined as 37.7 and for *unsym*-difluorotetrachloroethane as 38.6, using naphthalene and *p*-dichlorobenzene.

Naphthalene,  $s/S = 0.00140, 0.00140, 0.00127, k = 37.1, 36.7, 37.4$ ; *p*-dichlorobenzene,  $s/S = 0.00129, 0.00121, 0.00134, k = 38.1, 38.0, 38.8$ ; naphthalene,  $s/S = 0.000660, 0.00113, k = 38.2, 37.9$ ; *p*-dichlorobenzene,  $s/S = 0.000794, 0.000863, 0.000919, k = 38.2, 39.4, 39.3$ , respectively.

The *sym*-difluorotetrachloroethane was prepared by adding fluorine to tetrachloroethylene<sup>3</sup> and melted at 24.7°. It also may be prepared from hexachloroethane and antimony trifluoride.<sup>1,4</sup> No direct methods for the preparation of *unsym*-difluorotetrachloroethane have appeared in the literature although it has been character-

(3) Miller, *THIS JOURNAL*, **62**, 341 (1940).

(4) Locke, Brode and Henne, *ibid.*, **56**, 1726 (1934).

(1) Booth, Mong and Burchfield, *Ind. Eng. Chem.*, **24**, 328 (1932).  
(2) Gattermann and Wieland, "Laboratory Methods of Organic Chemistry," The Macmillan Co., New York, N. Y., 1937, p. 86.

(5) Reilly and Rae, "Physico-Chemical Methods," Methuen and Co., Ltd., London, 1933, p. 439.

ized.<sup>4</sup> However, it was found possible to obtain this material directly from trifluorotrchloroethane (CF<sub>2</sub>ClCFCl<sub>2</sub>)<sup>6</sup> and aluminum chloride.<sup>7</sup>

### Summary

Fluoropentachloroethane, *sym*-difluorotetra-

(6) "Freon 113" of Kinetic Chemicals Inc., Carney's Point, N. J.

(7) Miller, *THIS JOURNAL*, **62**, 993 (1940).

chloroethane and *unsym*-difluorotetrachloroethane were shown to be good cryoscopic solvents for non-associated substances. Their large molecular freezing point depressions, chemical inertness and convenient melting temperatures recommend their use.

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RECEIVED DECEMBER 28, 1939

[CONTRIBUTION FROM THE FRICK CHEMICAL LABORATORY, PRINCETON UNIVERSITY]

## Solubility and Molecular Rotation of Certain Tetra-, Penta- and Hexa-Substituted Benzenes

BY CHARLES P. SMYTH AND GEORGE L. LEWIS

In a discussion by Baker and Smyth<sup>1</sup> of the process of fusion, it has been pointed out that the gain of entropy by a solid through the setting in of molecular rotation in the crystal tends to raise the melting of the solid to a temperature much higher than that at which it presumably would have melted in the absence of such rotation. In view of the close relation between the processes of solution and fusion, it has seemed desirable to investigate the influence of molecular rotation in a solid upon its solubility. Recent dielectric constant measurements by White, Biggs and Morgan<sup>2</sup> have shown that the molecules of many penta- and hexa-substituted benzenes have rotational freedom in the plane of the benzene ring. Dr. Morgan has very kindly made a number of pure samples of these substances available to us for solubility and dipole moment measurements, the latter of which are discussed elsewhere.<sup>3</sup> In addition, the solubilities of hexamethylbenzene and hexachlorobenzene obtained from the Eastman Kodak Company have been measured. Benzene was used as a solvent which would dissolve adequate quantities of the least soluble of the substances investigated. It was purified in the usual manner.<sup>4</sup>

### Experimental Method

The solubility measurements were carried out at four different temperatures in a thermostat. An excess of the substance, the solubility of which was to be measured, was added to the benzene in a test-tube mounted on a mechanical shaker in a water-bath and shaken at a temperature of about 48° until the solution was thought to be saturated, some of the solid still remaining undissolved.

The temperature of the bath was then lowered to 41.88° where it was held fixed for at least forty-five minutes. The formation of new crystals was used as the criterion of saturation. Part of the saturated solution was withdrawn by means of a completely water-jacketed pipet, in which the temperature of the water was higher than that of the solution, and run into a weighing bottle. After this sample of solution had been weighed, the solvent was evaporated at about 40° in a current of warm, dry air, and the solute remaining as a residue in the bottle was weighed. The concentrations of the saturated solutions at three lower temperatures were successively determined in the same way, an ordinary pipet being used for temperatures below that of the room. The probable error in the solubilities thus determined was 2%.

### Experimental Results

The solubilities expressed as the mole fraction  $N$  of solute in the saturated solution are listed in Table I for the four different temperatures at which they were determined. The substances are designated by letters in the first column, which are used in place of the long names of the substances in Table II and in Fig. 1. The solubilities may be examined with the aid of a slightly modified equation given by Hildebrand<sup>5</sup>  $\log N = -\Delta E_f (T_m - T)/4.575 T_m T$ , in which  $\Delta E_f$  is the latent heat of fusion of the solute and  $T_m$  its melting point on the absolute scale. According to this equation which represents the ideal solubility, the plotting of  $\log N$  against  $1/T$  should give a nearly straight line with slope  $-\Delta E_f/4.575$  and upper limit with  $N = 1$  at the melting point of the solute. As the latent heats of fusion of the substances under consideration here have not been determined, the ideal solubility curves cannot be drawn, but, in Fig. 1, the values of  $\log N$  plotted against  $1/T$  for each substance are

(5) Hildebrand, "Solubility," Reinhold Publishing Corporation, New York, N. Y., 1936, p. 34.

(1) Baker and Smyth, *THIS JOURNAL*, **61**, 1695 (1939).

(2) White, Biggs and Morgan, *ibid.*, **62**, 16 (1940).

(3) Smyth and Lewis, *ibid.*, **62**, 721 (1940).

(4) Smyth and Walls, *ibid.*, **54**, 1854 (1932).