ized.[4] However, it was found possible to obtain this material directly from trifluorotrichloroethane ($CF_2ClCFCl_2$)[6] and aluminum chloride.[7]

Summary

Fluoropentachloroethane, *sym*-difluorotetrachloroethane 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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(6) "Freon 113" of Kinetic Chemicals Inc., Carney's Point, N. J.

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

[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[1] 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[2] 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.[3] 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.[4]

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[5] $\log N = -\Delta E_f\,(T_m - T)/4.575\,T_mT$, in which ΔE_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

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(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).

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

TABLE I

MOLE FRACTIONS OF POLYSUBSTITUTED BENZENES IN SATURATED SOLUTION IN BENZENE

	Solute	t, °C. = 8.77	19.92	29.93 N	41.88
A	Hexachlorobenzene	0.0077	0.0102	0.0147	0.0209
B	Hexamethylbenzene	.0277	.0382	.583	.0814
C	1,3,5-Trimethyl-2,4,6-trichlorobenzene	(.007)	.0136	.0190	.0270
D	1,2,5-Trimethyl-3,4,6-trichlorobenzene	.0111	.0147	.0217	.0319
E	Pentachlorotoluene	.0083	.0112	.0153	.0224
F	Tetrachloro-*o*-xylene	.0077	.0110	.0150	.0217
G	1,2,3,4-Tetramethyl-5,6-dichlorobenzene	.0188	.0253	.0370	.0475
H	Pentamethylchlorobenzene	.0349	.0488	.0737	.1010
I	Pentachlorobenzene	.157	.184	.242	.334
J	4,5-Dichloro-*o*-xylene	.152	.213	.305	—
K	Ethylpentachlorobenzene	—	(22.12°) .468	(32.36°) .645	(42.57°) .851
L	3,4,5-Trichloro-*o*-xylene	—	(17.46°) .483	(27.83°) .526	(37.45°) .809

TABLE II

TEMPERATURES OF ROTATION AND MELTING, HEATS AND ENTROPIES OF FUSION, AND DIPOLE MOMENTS

Solute	t_r, °C.	t_m, °C.	ΔE_f, kcal./mole	ΔS_f, e. u./mole	μ ($\times 10^{18}$)
A		226	5.4	10.8	0
B		166	5.6	12.8	0
C		205	5.7	11.9	0
D	−44	210	5.8	12.0	1.83
E	11	224	5.4	10.8	1.55
F	−26	228	5.4	10.8	2.65
G	−74	193	5.1	11.0	2.93
H	−47	154	5.5	12.9	1.85
I		86	4.2	11.7	0.88
J	—	76	5.5	15.7	3.01
K	—	56	5.4	16.3	1.50

found to lie very close to a straight line drawn through the melting point at log N = 0. Several substances are omitted from Fig. 1 because their curves are very close to those shown and the curve for 3,4,5-trichloro-*o*-xylene is omitted because of the somewhat unsatisfactory character of the three values which were determined at different temperatures from the others. The slopes of similar curves plotted on a larger scale without reference to the melting points are used to calculate approximate values of the heats of fusion ΔE_f given in Table II, which, in turn, are used to calculate the entropies of fusion, $\Delta S_f = \Delta E_f/T_m$, given in Table II. The probable errors in these two quantities calculated from the slopes of the curves would appear to be about 5% but may more safely be set at 10%. Table II also lists the melting points t_m in °C. and the temperatures t_r determined by White, Biggs and Morgan below which rotation ceases or, more correctly speaking, at which rotation is so hampered that the imaginary part ϵ'' of the dielectric constant reaches a maximum for a frequency of 100 kc. A dash in this column indicates the absence of rotation in the solid. The dielectric constant of the solid would fail to give information as to the rotation of the symmetrical molecules of the first three substances listed and is not conclusive as to pentachlorobenzene. The last column gives the dipole moments found for the substances.[3]

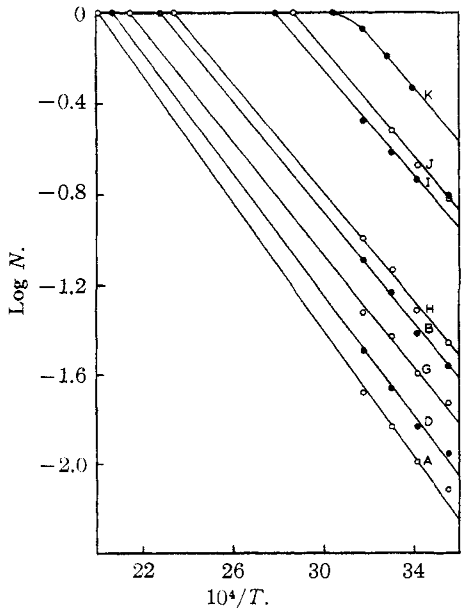

Fig. 1.—Solubilities of substituted benzenes in benzene.

Discussion of Results

Certain simple and expected relations are apparent in the data of Tables I and II and certain seeming anomalies occur. The hexamethylbenzene molecule with its hydrocarbon surface[6] is about four times as soluble in benzene as the hexachlorobenzene molecule with its less similar chlorine surface, and the melting point of the substance is correspondingly lower. Trichloromesitylene, sub-

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[6] See Langmuir, "Third Colloid Symposium Monograph," The Chemical Catalog Company, Inc., New York, N. Y., 1925, p. 3.

stance C, is not half-way between hexachlorobenzene and hexamethylbenzene in solubility but is much closer to the former in solubility and melting point. The interchange of position of a chlorine and a methyl group to give the unsymmetrical 1,2,5-trimethyl-3,4,6-trichlorobenzene molecule with a considerable dipole moment has only a very small effect upon the solubility and melting point. Increase of the number of chlorines in the hexasubstituted molecule to four and five reduces the solubilities and raises the melting points a little so that they are hardly distinguishable from those of hexachlorobenzene, although tetrachloro-*o*-xylene possesses a particularly large dipole moment. The solubility curves for this substance and pentachlorotoluene are omitted from Fig. 1 because of their practical coincidence with that for hexachlorobenzene, A. Increase in the number of methyl groups in the hexa-substituted molecule increases the solubility until pentamethylchlorobenzene has a solubility about 25% greater than that of hexamethylbenzene together with a slightly lower melting point. These eight hexa-substituted benzenes may be grouped roughly as having relatively low solubilities and high melting points. Their dipole moments vary from 0 to 2.93 without having any apparent effect upon the solubility. The last five of them, D-H, have been found[2] to possess freedom of molecular rotation in the crystal and thus possess additional entropy in the solid, which raises their melting points according to the relation observed by Baker and Smyth[1] and lowers their solubilities. The first three substances, A–C, fit so well into this group that one would certainly expect their molecules also to possess freedom of rotation in the crystal. Also, it is difficult to see how the five somewhat less symmetrical hexa-substituted benzenes can rotate if these do not. However, Lonsdale[7] has interpreted careful X-ray analyses of hexamethyl- and hexachlorobenzene at room temperature on the basis of non-rotation of the molecules and Brockway and Robertson[8] have done the same with hexamethylbenzene. The results of White, Biggs and Morgan[2] indicate that molecular rotation should occur in hexachlorobenzene, but possibly only above the temperature employed in the X-ray investigation. The rotation of hexamethylbenzene might be expected to begin at a lower temperature and it seems possible that its transition at −165°, which produces a change in the slope of the specific heat–temperature curve and involves an entropy of transition of 2.28 e. u. per mole,[9] may mark the acquisition of rotational freedom in the plane of the ring. At any instant of time, most of the molecules would be executing rotational oscillation about potential energy minima which would occur at angular intervals of 60°. As location of the molecule in any one of these six minima would be indistinguishable from that in any other, it appears possible that the results of the X-ray analysis may correspond to that given by nearly stationary molecules in spite of the existence of rotational freedom. It appears possible, therefore, tentatively to regard the eight substances, which have been grouped because of low solubilities and high melting points, as possessing freedom of molecular rotation in the plane of the ring.

The dielectric constant results for pentachlorobenzene communicated to the authors by Dr. Morgan suggest a restricted rotation of the molecule somewhat like that in isopropyl bromide,[1] which apparently raises the melting point of the latter some 20 or 30°. The solubility and melting point of pentachlorobenzene are nearer to those of the non-rotating substances, although the melting point is somewhat raised as in the case of isopropyl bromide.

4,5-Dichloro-*o*-xylene and ethylpentachlorobenzene, which are definitely shown by their low dielectric constants[2] to possess practically no rotational freedom, have low melting points and high solubilities. The solubilities of pentachlorobenzene and 4,5-dichloro-*o*-xylene differ but slightly from each other, while the dipole moments are very different. Ethylpentachlorobenzene has a solubility more than twice as large as those of the other two and a dipole moment intermediate between theirs. 3,4,5-Trichloro-*o*-xylene has a solubility close to that of ethylpentachlorobenzene and a higher moment, 2.46. Its high solubility and fairly low melting point would lead one to expect non-rotation in the solid, but the dielectric constant determinations[2] show a rotational transition at 15–20°. This constitutes the only definitely established exception among these substances to the rule that molecular rotation in a solid tends to give the solid lower solubility than it would have in the absence of rotation, but the answer to the question of molecu-

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(7) Lonsdale, *Proc. Roy. Soc.* (London), **A123**, 494 (1929); **A133**, 536 (1931).

(8) Brockway and Robertson, *J. Chem. Soc.*, 1324 (1939).

(9) Huffman, Parks and Daniels, THIS JOURNAL, **52**, 1547 (1930).

lar rotation is only tentatively indicated and not positively settled in the cases of three of the twelve substances.

It must be remembered that, at the temperature of a rotational transition, the solubility of the low-temperature form of a solid in equilibrium with the high-temperature form must be the same as that of the latter. The difference in slope of the solubility curves above and below the transition depends primarily upon the heat of transition. Although the substances under consideration here do not show sharp, reversible transitions, it is not unreasonable to suppose that solubilities measured not far from the temperatures at which molecular rotation ceases may well be either high or low as determined by factors other than molecular rotation, but, in a great majority of the cases here investigated, molecular rotation reduces the solubility.

The curves in Fig. 1 and those omitted from it show that the solubilities of these highly-substituted benzenes in benzene are close to the ideal. The curve for ethylpentachlorobenzene is the only one which does not pass through the melting point, partly, at least, because its points are so near the melting point that a slight adjustment in its slope cannot make it reach the melting point. A melting point only 10° lower, but still 10° higher than the apparently incorrect[2] value given in Beilstein, would fall on the line.

The entropies of fusion of all but the last two substances, J and K, in Table II lie between 10.8 and 12.9 units, differing from a mean value by no more than their possible errors. The last two substances, 4,5-dichloro-*o*-xylene and ethylpentachlorobenzene, which are the only two definitely proved to have no molecular rotation in the solid, have entropies of fusion four or five units higher, as they acquire degrees of rotational freedom on melting which most, at least, of the other substances have already acquired in the solid. The entropies of fusion of the rotating substances are higher than those found previously for substances with smaller molecules rotating in the solid, but are much lower than the value 22.1 found for the long molecule of cetyl alcohol,[10] which, because of molecular rotation around the long axis, is little more than half of that found for non-rotating hydrocarbons of about the same length. The values for the hexa-substituted benzenes with rotating molecules are close to those for the lighter molecules of the xylenes and dichlorobenzenes, which do not have freedom of molecular rotation in the solid. The value for hexamethylbenzene is lower than that calculated empirically by Huffman, Parks and Daniels[9] without allowance for rotation by about the amount which rotation might cause. In other words, the two substances, which have been definitely shown not to rotate, have reasonable values for their entropies of fusion, and the other substances in Table II have values lower by an amount which can arise from their possession of rotational freedom in the solid.

In conclusion, it may be said that, in the case of these similarly shaped molecules, the dipole moment of the molecule as a whole has no detectable effect upon the solubility of the substance in the non-polar solvent, benzene. The solubilities of these substituted benzenes are almost ideal and tend to be lower when the molecules possess freedom of rotation in the solid, although other factors occasionally predominate over this tendency. In view of the relations between molecular rotation and melting point and between melting point and solubility, an at least approximate relation between molecular rotation and solubility follows almost inevitably and from the same fundamental cause.

The writers wish to express their gratitude to Dr. S. O. Morgan of the Bell Telephone Laboratories for the loan of the substances upon which these measurements have been made as well as for information concerning them.

Summary

The solubilities in benzene of twelve tetra-, penta-, and hexa-chlorine and methyl substituted benzenes have been measured at four temperatures. The solubilities are approximately ideal and are independent of the dipole moments of the molecules. The heats and entropies of fusion have been calculated from the slopes of the solubility curves. In accordance with the relation previously observed between molecular rotation in the solid and melting point, the solubilities and entropies of fusion tend to be low and the melting points high when the molecules possess freedom of rotation in the solid.

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[10] Baker and Smyth, THIS JOURNAL, **60**, 1229 (1938).