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Solubility of Iodine in Ethyl Alcohol, Ethyl Ether, Mesitylene, *p*-Xylene, 2,2-Dimethylbutane, Cyclohexane and Perfluoro-*n*-heptane

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In a recent paper[1] quantitative spectrophotometric evidence was presented for the solvation of iodine dissolved in benzene, toluene, xylene and mesitylene to form 1–1 complexes with stabilities increasing in that order. It was pointed out that the solubility of iodine in benzene is greater than the theory of regular solutions would lead one to expect, and that the enhancement of solubility agrees well with the strength of the interaction as measured by aid of the ultraviolet absorption. This investigation was undertaken primarily to learn whether *p*-xylene and mesitylene would show a still stronger enhancement in solvent power for iodine in accord with the spectrophotometric evidence. While we were engaged in measuring solubilities of iodine it seemed worthwhile to obtain for the first time its solubility in cyclohexane, to redetermine its solubility in ether and anhydrous alcohol, which form highly solvated solutions of iodine, to complete the work on perfluoro-*n*-heptane for which Benesi and Hildebrand had reported only a single value,[2] and to add a hydrocarbon of lower internal pressure than any used heretofore, 2,2-dimethylbutane.

Experimental

Resublimed iodine by Baker Chemical Company was used after drying over phosphorus pentoxide. A sample of pure perfluoro-*n*-heptane was distilled and boiled at 82.1–82.2° (755 mm.). Merck reagent grade carbon disulfide was distilled and found to have a constant boiling fraction at 46.28° (761.2 mm.). Eastman Kodak Co. mesitylene was distilled and the fraction boiling between 163 and 165° at 750.7 mm. was collected and stored in a glass stoppered bottle. Eastman Kodak Co. *p*-xylene was purified by the following procedure. The liquid was shaken with three portions of concentrated sulfuric acid, rinsed with distilled water, shaken with three portions of 10% sodium hydroxide, rinsed with distilled water, and finally shaken with mercury. The product was then dried over calcium chloride and distilled. From freezing point data the purity was estimated at 96.4 mole per cent. The ethyl ether was kindly donated to us by Professor William G. Dauben. The ether had been distilled and stored over sodium for a period of two weeks. Commercial absolute alcohol was purified according to the procedure of Lund and Bjerrum.[3] A spectroscopic study of the alcohol prior to purification indicated about 10^{-2} mole per cent. of benzene plus some unsaturated compounds. After purification the alcohol contained no trace of benzene or unsaturated compound. Its density at 25.00° was 0.78767 g./ml. From tables in the "Handbook of Chemistry and Physics"[4] the purity of the alcohol was estimated to be 99.90 weight per cent., assuming that the impurity was water.

The 2,2-dimethylbutane and the cyclohexane were of "research grade" from the Philips Petroleum Co. The density of the former at 25° was 0.64446, in exact agreement with the value given by the Bureau of Standards[5]; the density of the latter was 0.77404 compared with 0.77389 by the Bureau of Standards. Both were used without further treatment.

The apparatus and procedure used in determining the iodine solubilities were those of Benesi and Hildebrand.[2]

Results

Solvated Solutions of Iodine.—The results of our iodine solubility measurements are summarized in Table I, and in Fig. 1 they are compared with solubility data obtained in previous investigations.[6] The solid curves in Fig. 1 fit into the family of "regular" curves previously found for all iodine solutions that are pure violet in color. The dashed curves represent solvated solutions of iodine and have slopes different from those of the "regular" solutions. The color of iodine in its solvated solutions ranges from red-violet in the case of benzene to brown in the case of ethyl ether.

TABLE I

SOLUBILITY OF IODINE

Solvent	0.0° Wt. %	0.0° Mole %	25.0° Wt. %	25.0° Mole %	35.0° Wt. %	35.0° Mole %
Carbon disulfide	7.70 7.68	2.440	16.49 16.46	5.58	31.63 21.61	7.64
2,2-Dimethylbutane	0.486 0.476	0.164	1.369 1.369	0.469	1.989 1.988	0.684
Cyclohexane			2.723 2.715	0.918	3.907 3.898	1.329
Ethyl alcohol	16.76 16.67	3.51	21.48 21.38	4.71	24.51 24.70	5.59
Ethyl ether	19.35 19.34	6.54	25.18 25.22	8.96	28.50	10.43
p-Xylene			16.56 16.55	7.66	20.16 20.11	9.54
Mesitylene	13.51	6.89	20.27 20.20	10.72		
Perfluoroheptane	0.0026 0.0023	0.0038	0.0119 .0118 .0120 .0121	0.0182	0.0179 .0188 .0180 .0200	0.0286

An examination of Fig. 1 shows that the solubility of iodine in mesitylene is higher than in any other common organic solvent, and that the solubility curve for *p*-xylene falls between the mesitylene and benzene curves. If no solvation occurred in these solutions, the solubility curves predicted by means of regular solution theory would be almost identical and would fall between the chloroform and carbon tetrachloride curves.

(1) H. A. Benesi and J. H. Hildebrand, THIS JOURNAL, **71**, 2703 (1949).

(2) H. A. Benesi and J. H. Hildebrand, *ibid.*, **70**, 3978 (1948).

(3) H. Lund and J. Bjerrum, *Ber.*, **64**, 210 (1931).

(4) "Handbook of Chemistry and Physics," 30th ed., Chemical Rubber Publishing Co., Cleveland, Ohio, 1947, p. 1675.

(5) U. S. Department of Commerce, "Selected Values of the Properties of Hydrocarbons," Circular of the National Bureau of Standards, C 461, Government Printing Office, Washington, 1947.

(6) (a) J. H. Hildebrand and C. A. Jenks, THIS JOURNAL, **42**, 2180 (1920); (b) G. R. Negishi, L. H. Donnally and J. H. Hildebrand, *ibid.*, **55**, 4793 (1933); (c) J. H. Hildebrand, "Solubility of Non-Electrolytes," Second Ed., Reinhold Publishing Co., New York, N. Y., 1936, pp. 153–157; (d) see ref. 2.