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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		16.49		21.63	
	7.68	2.440	16.46	5.58	21.61	7.64
2,2-Dimethylbutane	0.486		1.369		1.989	
	0.476	0.164	1.369	0.469	1.988	0.684
Cyclohexane			2.723		3.907	
			2.715	0.918	3.898	1.329
Ethyl alcohol	16.76		21.48		24.51	
	16.67	3.51	21.38	4.71	24.70	5.59
Ethyl ether	19.35		25.18			
	19.34	6.54	25.22	8.96	28.50	10.43
p-Xylene			16.56		20.16	
			16.55	7.66	20.11	9.54
Mesitylene	13.51	6.89	20.27			
			20.20	10.72		
Perfluoroheptane	0.0026		0.0119		0.0179	
	0.0025	0.0038	.0118		.0188	
			.0120		.0180	
			.0121	0.0182	.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.

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[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.

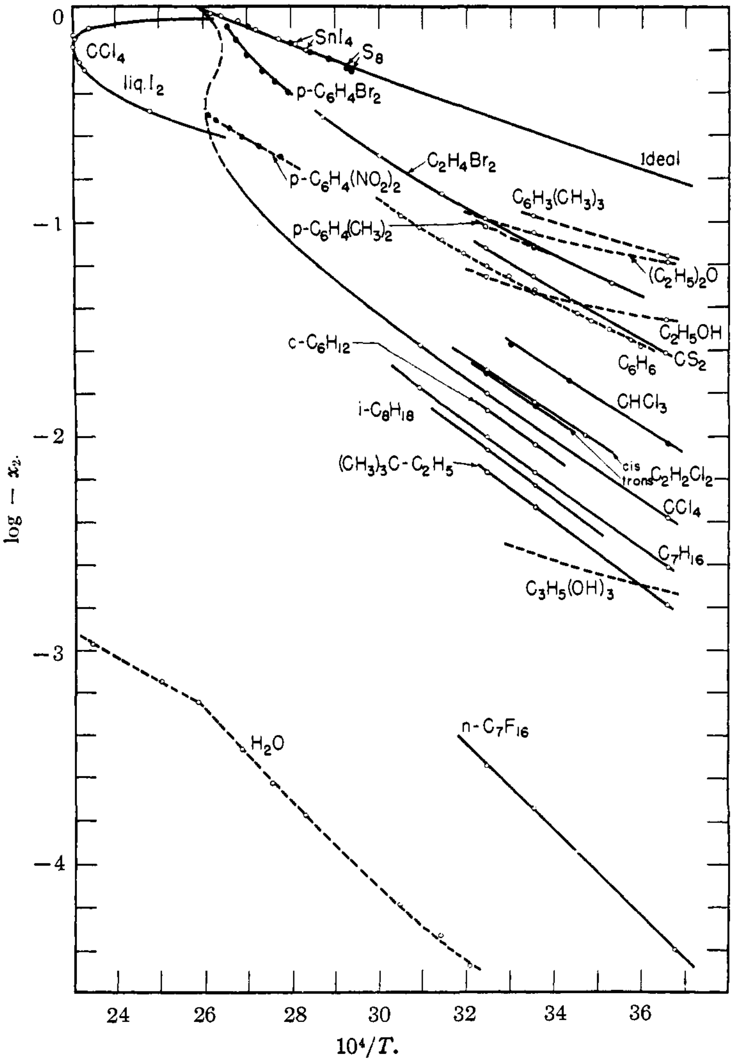

Fig. 1.—Solubility of iodine.

The results show, therefore, that in the series, benzene, *p*-xylene and mesitylene, iodine is increasingly solvated in the order given. This confirms the spectrophotometric evidence obtained by Benesi and Hildebrand,[1] who found that the solvation of iodine in its aromatic hydrocarbon solutions increases as the electron donor property of the solvent molecule increases, *i. e.*, as methyl groups are added to the benzene ring. As a quantitative comparison between the results of the spectrophotometric and the present solubility measurements, we have calculated the ratio of solvated to total iodine in its aromatic hydrocarbon solutions. The values of this ratio are listed in columns 4 and 6 of Table II. In view of the approximations made in their calculation, the agreement between the two sets of values is good.

TABLE II

SOLVATION OF IODINE AT 25°

	Solubility data			Spectral data	
Solvent	$[I_2]$ mole fr.	$[C]$ mole fr.	$[C]/[I_2]$	K	$[C]/[I_2]$
Benzene	0.0482[6]	0.025	0.52	1.10	0.67
p-Xylene	.0766	.062	.81	..	..
Mesitylene	.1072	.093	.87	1.56	0.88

The solubility of iodine is a direct measure of the total iodine concentration, $[I_2]$, listed in column 2. The concentration of the solvated or complexed iodine, $[C]$, is the difference between $[I_2]$ and the concentration of free iodine. The latter quantity was calculated by means of the "van Laar–Scatchard–Hildebrand" relationship (equation 2 in the following section), assuming that the free iodine concentration in a saturated aromatic hydrocarbon solution is equal to the iodine concentration calculated for a saturated, regular solution of iodine in the same solvent. The stoichiometric ratio, $[C]/[I_2]$, listed in the last column of Table II was calculated from the equilibrium constant, K, by means of the equation

$$K = \gamma_C[C]/(\gamma_I[I_2 - C]\gamma_A[A - C]) \quad (1)$$

where γ_C, γ_I and γ_A are the activity coefficients, and $[C]$, $[I_2 - C]$ and $[A - C]$ are the mole fraction concentrations of the iodine–aromatic hydrocarbon complex, iodine and aromatic hydrocarbon, respectively. The activity coefficients (defined as a/x, where a is the activity and x is the mole fraction concentration) in equation 1 were calculated from the "solubility parameters" of the three species by means of equation 2, given in a following section.

Prior to the development of the electron donor–acceptor theory of acids and bases by G. N. Lewis some years ago, the solvation of iodine in these aromatic hydrocarbon solvents, with its accompanying enhancement of solubility, could hardly have been foreseen, because all these species were regarded as typical non-polar, "normal" substances. The facts here brought to light suggest that in applying the theory of regular solutions one should be on the lookout for other similar, disturbing, acid–base or "chemical" interactions.

The solubility of iodine in ethyl alcohol has been measured by Delépine and Arquet.[7] These investigators were primarily interested in the effect of the addition of water on the iodine solubility in ethyl alcohol and therefore did not cover a wide temperature range. Iodine solubilities in ethyl ether from −180 to 0° have been determined by

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[7] M. Delépine and M. Arquet, *Bull. sci. pharmacol.*, **35**, 625 (1928).

Jacek.[8] Our investigation extends measurements of iodine solubilities in both of these solvents to cover the temperature range 0 to 35°.

Although the solubility of iodine in the oxygen-containing solvents cannot as yet be treated quantitatively, it is interesting to consider the enormous difference, for example, between ethyl alcohol and water in their behavior toward iodine as shown in Fig. 1. Hildebrand and Glascock[9] showed that certain oxygen-containing solvents form 1–1 complexes with iodine and in the one case where it had been calculated, the heat of formation of the complex was −3 kcal. per mole. Here again, iodine is probably acting as an electron acceptor, and the oxygen atom of the solvent as the electron donor. If this acid–base interaction is the predominating factor in their behavior toward iodine, the 2000-fold difference in solvent power for iodine between ethyl alcohol and water can be qualitatively explained by considering the availability of the unshared electron pairs in their oxygen atoms. In the case of pure ethyl alcohol, the ratio of OH hydrogen atoms to oxygen atoms is 1:1, which means that, at most, only one-half of the unshared electrons in the ethyl alcohol molecules could be utilized for hydrogen bond formation. In a solution of iodine in ethyl alcohol, therefore, at least one unshared pair of electrons will be available per alcohol molecule for donation to an iodine molecule. In the case of a solution of iodine in water, however, where there are twice as many potential hydrogen bonds as there are oxygen atoms, an iodine molecule and a hydrogen atom will directly compete with one another for one of the unshared electron pairs in a given water molecule.[10] The hydrogen bonds would be favored because of their higher heat of formation (−4.5 kcal. per mole[11]) and the result would account for the extremely low iodine solubility in water, if our explanation is the correct one.

Unsolvated Solutions of Iodine.—Figure 1 gives a qualitative picture of how well the solvents, carbon disulfide, 2,2-dimethylbutane, cyclohexane and perfluoro-*n*-heptane, fit into the family of curves representing the unsolvated solutions of iodine. The regularity of the shift of the slope and position of the solid curves from ideality with decreasing internal pressure of the solvent gave rise to the term, "regular solutions," proposed by the senior author.[12]

The solubility of iodine in carbon disulfide has been measured by Arctowski.[13] As we mentioned in a previous publication,[2] his solubility values when plotted scatter somewhat, those at the upper end of the temperature scale apparently being too high. We therefore redetermined the solubility of iodine in carbon disulfide and were gratified to find that our experimental values fell directly on the curve predicted in the earlier communication.

A quantitative comparison between the results of this investigation and those of previous investigations can be made by appropriate substitution of the experimentally determined quantities into the solubility equation[14]

$$4.576\, T \log (a_2/x_2) = \mathrm{v}_2\phi^2(\delta_2 - \delta_1)^2 \qquad (2)$$

where x_2 is the mole fraction of the solute in its saturated solution, a_2 is its activity (or ideal solubility), calculated from its heat of fusion, v_2 is the molar volume of the supercooled, liquid solute, ϕ_1 is the volume fraction of the solvent, and δ_1 and δ_2 are solubility parameters defined by the relation $\delta = (\Delta E^{V}/\mathrm{v})^{1/2}$ where ΔE^{V} is the molar energy of vaporization and v the molar volume of the pure component in the liquid state, both at the temperature, *T*. We have solved for δ_2, the solubility parameter of supercooled, liquid iodine, and have listed the resulting values for all of the available iodine solubility data in Table III.

TABLE III

SOLUBILITY PARAMETER OF IODINE CALCULATED FROM ITS SOLUBILITY IN REGULAR SOLUTIONS

Solvent	v (cc.)	$100x_2$	δ_1	δ_2
n-C_7F_{16}	225.5	0.0182	5.8	14.4
$(CH_3)_3CC_2H_5$	133.7	.469	6.7	13.1
iso-C_8H_{18}	166.1	.592	6.8	13.0
n-C_6H_{14}	131.6	.452	7.3	13.6
n-C_7H_{16}	147.5	.679	7.4	13.5
cyclo-C_6H_{12}	108.7	.918	8.2	14.0
$SiCl_4$	115.3	.499	7.6	13.9
CCl_4	97.1	1.147	8.6	14.2
$CHCl_3$	80.7	2.28	9.0	(14.1)
trans-$C_2H_2Cl_2$	77.4	1.417	9.0	14.5
cis-$C_2H_2Cl_2$	75.8	1.441	9.1	(14.5)
1,1-$C_2H_4Cl_2$	84.7	1.531	9.0	(14.4)
1,2-$C_2H_4Cl_2$	79.5	2.20	9.8	(14.9)
$TiCl_4$	110.5	2.15	9.0	14.1
CS_2	60.6	5.58	9.9	14.1
1,2-$C_2H_4Br_2$	86.6	7.82	10.4	(14.1)
$CHBr_3$	87.8	6.16	10.5	(14.1)
			Av.	14.0
I_2	59.0	25.8	$(\Delta E^{V}/\mathrm{v})^{1/2}$ =	13.6

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[8] W. Jacek, *Bull. intern. acad. sci. Cracovie*, A, 26 (1915).

[9] J. H. Hildebrand and B. L. Glascock, THIS JOURNAL, **31**, 26 (1909).

[10] In a strict sense, the hydrogen bond is not an acid–base interaction between an OH hydrogen atom and a free electron pair, for two electron pairs cannot be used simultaneously for covalent bond formation with a proton. The "bond" probably arises because of the electrostatic interaction between an extraordinary dipole (the OH group) and a highly polarizable site (an unshared electron pair of the oxygen atom). The OH group is an "extraordinary dipole" because its nearly bare proton allows its positive charge to come much closer to a second electronegative atom than in the case of an ordinary dipole, where the charge is buried. This viewpoint, however, does not alter the above discussion.

[11] L. Pauling, "Nature of the Chemical Bond," Cornell University Press, Ithaca, N. Y., **1945**, p. 304.

[12] J. H. Hildebrand, THIS JOURNAL, **51**, 66 (1929).

[13] H. Arctowski, *Z. anorg. Chem.*, **6**, 404 (1894).

[14] This equation is a quantitative description of the solubility theory developed by van Laar, Hildebrand and Scatchard. A detailed discussion along these lines is given in the American Chemical Society Monograph: J. H. Hildebrand and R. L. Scott, "Solubility of Non-Electrolytes," 3rd ed., Reinhold Publishing Corp., New York, N. Y., 1950.

The iodine solubilities listed in column 2 have been measured in this Laboratory[6] with the exception of those in bromoform[15] and chloroform.[16] The solvent solubility parameters listed in column 4 have been constantly revised as better heat of vaporization data became available. The solubility parameters of cyclohexane and 2,2-dimethylbutane, which were added to the list as a result of the present investigation, were calculated from the recently compiled data on hydrocarbons.[5] In the case of perfluoro-*n*-heptane, the heat of vaporization was calculated from the vapor pressure data of Fowler, *et al.*[17] The correction for gas imperfection was calculated by means of the Berthelot relation from the critical temperature obtained by Fowler, *et al.*, and the critical pressure, which was estimated to be 16.4 atm. using the law of corresponding states. The bracketed values of δ_2 correspond to the polar solvents in the table. In a recent publication,[2] two of us have shown that iodine solubilities bear little or no relation to the dipole moments of the chlorinated hydrocarbon molecules listed in Table III and we have therefore included the bracketed figures in obtaining an average for the value of δ_2. We have also considered the effect on the entropy of mixing of differences in size between the solute and solvent molecules with the aid of the "Flory–Huggins" equation.[18] We find that the largest correction to δ_2 on account of unequal molal volumes amounts only to 0.3 unit. This is for the case, perfluoro-*n*-heptane, where the ratio of solvent and solute molar volumes is almost 4:1. Since this correction does not alter the conclusions that follow, we have retained the values calculated by means of the simplified relation given by Equation 2.

The agreement seen in Table III between the δ-values so calculated offers striking evidence of the usefulness of Equation 2, despite the enormous range of iodine solubilities. In the case of ethylene dibromide, which has the highest solvent power for iodine, the actual solubility is almost $^{1}/_{3}$ of the ideal solubility; while in perfluoro-*n*-heptane, which is at the other end of the solubility scale, the actual solubility is only $^{1}/_{1400}$ of the ideal solubility. The variations shown in the δ_2-values indicate the limitations to the accuracy of solubilities calculated by means of Equation 2. In the case of iodine in perfluoroheptane, for example, a change of 0.1 in either δ_1 or δ_2 would cause a change of 2.3% in log x_2 but this corresponds to 18% change in x_2. This point has been previously considered by the senior author.[19]

One interesting fact brought to light in Table III is the distinctly smaller values of δ_2 calculated for the branched hydrocarbons, corresponding to somewhat higher solvent power than Equation 2 would predict with $\delta_2 = 14.0$. We offer no explanation of this but regard it as inviting further study.

Acknowledgment.—We express our appreciation to the Office of Naval Research for the support of this research.

Summary

The solubility of iodine in mesitylene, *p*-xylene, ethyl ether, ethyl alcohol, cyclohexane, 2,2-dimethylbutane and perfluoro-*n*-heptane has been measured over a range of temperature.

The solvation in the case of mesitylene and *p*-xylene increases the iodine solubility over the values for regular solutions, the increase being greatest for mesitylene. The enhancement of iodine solubilities in these solvents is in good agreement with equilibrium data obtained from earlier spectroscopic measurements and therefore provides further evidence for the existence of an acid–base interaction (in the Lewis sense) between aromatic hydrocarbons and iodine.

Iodine solubilities (in unsolvated solutions) obtained in this and earlier investigations are in satisfactory accord with the behavior predicted from the internal pressures of the pure solvents.

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(15) A. Hantsch and A. Vogt, *Z. physik. Chem.*, **38**, 728 (1901).

(16) A. Jakowkin, *ibid.*, **18**, 590 (1895).

(17) R. D. Fowler, *et al.*, *Ind. Eng. Chem.*, **39**, 375 (1947).

(18) *Cf.* J. H. Hildebrand, *J. Chem. Phys.*, **15**, 225 (1947).

(19) J. H. Hildebrand, *Chem. Revs.*, **44**, 37 (1949).