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Solubility of Iodine in Electron-Donating Solvents at Various Temperatures

Cheng-Zhang Jiang,[†] Fu-Juan Hsu,[‡] and Vojtech Fried*

Chemistry Department of the City University of New York, Brooklyn College, Brooklyn, New York 11210

The solubility of iodine in 18 aromatic solvents was measured at various temperatures. A successful attempt was made to correlate the solubility of iodine with the structure of the solvent molecule. The approximate method suggested by Hildebrand was employed for evaluating the degree of complexation—the stability of the iodine–solvent complex—from solubility data.

Introduction

Several workers (*1-6*) have attempted in recent years to estimate the solubilities in mixed solvents from known solubilities in single solvents. The Hildebrand-Scatchard regular solution theory and its various modifications (*4*, *6*, *7*) have been widely used in this connection. It is generally recognized that the regular solution theory provides good results if the solubility is relatively small and if no specific interactions between the solute and solvent—hydrogen-bonding and charge-transfer interactions—are present in the solution.

Hildebrand and co-workers (*6*, *7*) have shown in several articles that the solubility curves, plotted as ln S vs. $1/T$, where S is the solubility expressed in mole fraction of iodine, fall into two groups: (a) the group of violet solutions and (b) the group of solutions for which the color varies from yellow to reddish brown. Solutions of the first group are free of specific interactions (dispersion forces determine the behavior of the solution) and usually obey the regular solution theory reasonably well. Solutions of the second group are not free of specific interactions and usually do not behave as regular solutions.

It is the second group of solutions that is of interest to us. Our ultimate aim is to modify the regular solution theory so that it can predict with reasonable accuracy the solubility in mixed solvents from the solubilities in single solvents. We decided to investigate solutions of iodine in aromatic solvents. The reasons for selecting this group of systems are as follows: (a) The iodine-aromatic solvent complexes are relatively weak. (b) The large London forces of iodine molecules make iodine soluble in a variety of solvents. (c) The analytical technique is simple, precise, and accurate. (d) There is much information on the iodine-aromatic solvent systems available in the literature (*6*, *7*).

This paper deals (a) with the solubility of iodine as a function of temperature in 18 aromatic solvents, (b) with a method relating the solubility to the molecular structure of the solvent, and (c) with an approximate estimation of the complexed and free iodine in the various solutions. The adaptation of the regular solution theory to mixed solvents is the subject of our next paper.

Experimental Section

Fisher and Aldrich chemicals of the best commerical quality are used in this investigation. With the exception of the 1,2,3-, and 1,3,4-trimethylbenzenes and the 1,2,3,4-tetramethylbenzene, all chemicals were further purified by the usual methods, such as extraction, dehydration, distillation, and crystallization. Some of these procedures were repeated several times in order to achieve high-quality products. Gas-chromatography analysis, as well as physical properties such as density, freezing point, boiling point, and refractive index, proved that, except for the 1,2,3-trimethylbenzene (94%) and the 1,2,3,4-tetramethylbenzene (96%), the purified chemicals were of good quality (99% or better). Fisher spectrograde iodine was sublimed twice prior to each measurement.

Table I. Precision of the Measurements for the System Iodine-Benzene at 30 °C

run	precision/ mol %	run	precision/ mol %
1	5.507	7	5.504
2	5.506	8	5.490
3	5.500	9	5.500
4	5.497	10	5.497
5	5.506	av value (±SD) = 5.503 (±9 × 10^{-3})	
6	5.527		

Saturated solutions of iodine were prepared for all experiments by continuous stirring of the two-phase mixture under thermostated conditions for periods of 18-30 h, sometimes starting with unsaturated solvents and other times with solutions that had been saturated at a higher temperature. Replicate measurements showed no difference in the final iodine concentration after 15 h of continuous stirring (Table I).

The continuously stirred saturation vessel (with a magnetic stirrer) shown in Figure 1 was maintained at a constant temperature by the circulation of water from a large-capacity thermostat through the water jacket of the vessel. The temperature of the circulating water was measured at the inlet and the outlet with two mercury-in-glass thermometers, calibrated against an NBS standardized Pt-resistance thermometer. The vessel was insulated with glass wool and asbestos and its temperature was kept constant to 0.02 °C, with a maximum difference of inlet temperature above that of the outlet of 0.025 °C at 50 °C. After the attainment of saturation equilibrium, the stirring was stopped for about 2 h and samples were withdrawn via a preheated stopcock (to prevent the crystallization of iodine) for analysis. The sample was cooled by an ice-water mixture in order to prevent losses by evaporation.

The analytical procedure consisted of weighing the sample to 5 × 10^{-4} g and titrating it with a standardized 0.001 N thiosulfate solution, a starch solution being used as an indicator. The size of the buret was chosen according to the size of the sample. The results shown in Table I for the iodine-benzene system at 30 °C indicate that the precision of the measurement is very good. The accuracy of the measurement is, however, not as good. Considering the errors due to the temperature fluctuation and temperature measurement, and the errors due to sampling and the analytical technique, we estimate the overall accuracy of the measurement to be ±0.4%. The error is smaller at lower temperature but increases with increasing temperature. To keep the overall error at ±0.4%, we disregarded all the measurements taken at temperatures higher than 50 °C. The measured data are in good agreement with liter-

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[†] Dalian Institute of Chemical Physics of the Chinese Academy of Sciences, Dalian, People's Republic of China.

[‡] Medgar Evers College of the City University of New York, Brooklyn, NY 11225.

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Table II. Solubility[a] of Iodine in Various Aromatic Solvents as Function of Temperature[b]

solvent	283.15 K	293.15 K	303.15 K	313.15 K	323.15 K
benzene	0.0319	0.0419	0.0551	0.0739	0.0965
toluene	0.0435	0.0554	0.0711	0.0930	0.1149
o-xylene	0.0549 (0.0568)	0.0688 (0.0703)	0.0873 (0.0876)	0.1103 (0.1111)	0.1374 (0.1346)
p-xylene	0.0554 (0.0554)	0.0682 (0.0681)	0.0846 (0.0846)	0.1050 (0.1073)	0.1304 (0.1300)
m-xylene	0.0586 (0.0611)	0.0730 (0.0744)	0.0905 (0.0915)	0.1132 (0.1148)	0.1415 (0.1381)
1,2,3-trimethylbenzene	0.0713 (0.0739)	0.0882 (0.0894)	0.1081 (0.1087)	0.1360 (0.1342)	0.1664 (0.1597)
1,2,4-trimethylbenzene	0.0705 (0.0725)	0.0875 (0.0872)	0.1076 (0.1057)	0.1324 (0.1304)	0.1641 (0.1551)
1,3,5-trimethylbenzene	0.0798 (0.0787)	0.0966 (0.0934)	0.1140 (0.1119)	0.1366 (0.1366)	0.1629 (0.1613)
1,2,3,4-tetramethylbenzene	0.0867 (0.0891)	0.1061 (0.1064)	0.1288 (0.1275)	0.1517 (0.1548)	0.1807 (0.1821)
ethylbenzene	0.0399	0.0513	0.0655	0.0822	0.1071
n-propylbenzene	0.0398	0.0506	0.0675	0.0832	0.1093
cumene	0.0377	0.0485	0.0628	0.6807	0.1037
n-butylbenzene	0.0373	0.0479	0.0612	0.0785	0.0978
isobutylbenzene	0.0324	0.0422	0.0535	0.0685	0.0867
tert-butylbenzene	0.0342	0.0437	0.0557	0.0716	0.0910
chlorobenzene	0.0202	0.0285	0.0390	0.0512	0.0690
bromobenzene	0.0350	0.0464	0.0620	0.0847	0.1108
trifluoromethylbenzene	0.00429	0.00529	0.00743	0.00980	0.0138

[a] The solubility is expressed in terms of mole fraction. [b] The results in the parentheses are the predicted values.

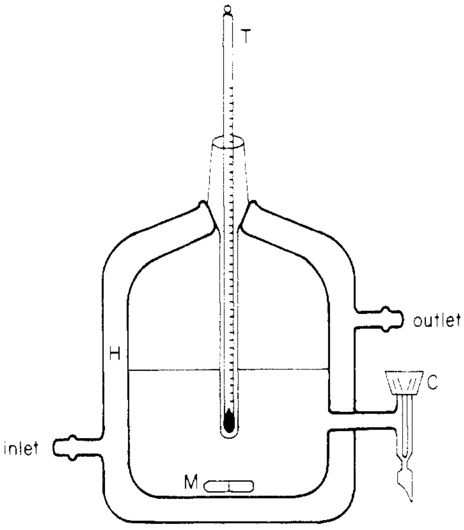


Figure 1. Saturation vessel: (T) thermometer, (H) heating jacket, (M) magnetic stirrer, (C) stopcock.

ature values where available (*6*, *7*).

In measuring the solubility of iodine in ethylbenzene, we encountered some unexpected difficulties. Namely, we were unable to reach the end point of titration. The blue color, indicating the presence of free iodine in the solution, reappeared in regular intervals. It took us some time to find out that the peroxides in the ethylbenzene are responsible for this strange behavior. With freshly distilled ethylbenzene, we were able to reach the end point of titration with great reproducibility. We cannot explain why this behavior has not been observed with some of the other solvents.

Results and Discussion

The measured solubilities of iodine, expressed in mole fractions, in the 18 mono- and polysubstituted benzene compounds, are presented in Table II. The data were fitted by a least-squares method to an equation of the form

$$\ln S = -A/T + B$$

The *A* and *B* constants obtained by this procedure are given in Table III. As the standard deviations indicate, the linear expression describes the solubility dependence on temperature, within the given temperature range, very well.

The *A* and *B* constants are related to the enthalpy of solution and the entropy of solution, respectively. We evaluated the enthalpy of solution of iodine in benzene from solubility data and compared it with the value obtained calorimetrically. The results were in large disagreement. The discrepancy, however, does not come as a surprise. We cannot expect that the enthalpy of solution evaluated from solubility data exactly reflects the endothermic solubilities of the iodine and the complex and the exothermic formation of the complex in the solutions. Calorimetric and spectroscopic measurements in combination with solubility data are required for the splitting of the total enthalpy change into the individual contribution. At present, we are engaged in such measurements.

Table III. Best-Fit *A* and *B* Constants for the Equation $\ln S = A/T + B$

	constants		$\pm\sigma \times 10^4$
solvent	*B*	$-A$	
benzene	2.397 92	1105.29	5
o-xylene	1.978 08	919.07	5
m-xylene	1.847 13	873.80	7
1,2,4-trimethylbenzene	1.791 69	834.85	7
1,2,3,4-tetramethylbenzene	1.504 55	726.68	3
n-propylbenzene	2.129 59	1001.61	7
n-butylbenzene	1.953 02	958.25	3
tert-butylbenzene	1.967 41	974.22	4
bromobenzene	2.609 85	1153.93	6
toluene	2.083 91	977.43	5
p-xylene	1.903 60	901.22	4
1,2,3-trimethylbenzene	1.826 87	843.77	7
1,3,5-trimethylbenzene	1.383 07	703.19	6
ethylbenzene	2.025 74	971.42	7
isopropylbenzene	2.146 23	1013.58	4
isobutylbenzene	1.946 60	973.69	3
chlorobenzene	2.575 41	1208.39	2
trifluoromethylbenzene	1.803 67	1188.19	1

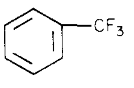
The following conclusions can be drawn from the measured solubility data: (a) In all the solvents employed in this study, the solubility of iodine increases with temperature. (b) The solubility of iodine in the monosubstituted benzenes is lower than in their respective polysubstituted isomers. This confirms the spectrophotometric evidence obtained by some researchers (*8*–*12*) who found that the solvation of iodine in its aromatic hydrocarbon solutions increases as the electron-donor property of the solvent molecules increases, i.e., as methyl groups are added to the benzene ring. (c) The chain length on the monosubstituted benzenes has very little effect, if any, on the solubility (see the solubilities of iodine in toluene, ethylbenzene, propylbenzene, and butylbenzene). (d) There is very little difference in the solubilities of iodine in the normal and iso solvents (see the solubilities of iodine in *n*-, iso-, and *tert*-butylbenzenes).

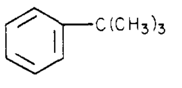
Table IV. Percent of Complexation of Iodine in the Various Solvents

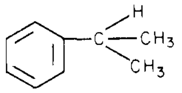
solvent	exptl solubility	δ^{*a}	δ^{b}	calcd solubility^{c}	complexation/%
benzene	0.0551	9.96	9.2	0.0271	51
toluene	0.0771	10.29	8.9	0.0199	72
o-xylene	0.0873	10.60	9.0	0.0216	75
p-xylene	0.0846	10.55	8.8	0.0178	79
m-xylene	0.0905	10.65	8.8	0.0178	80
1,2,3-trimethylbenzene	0.1081	10.94			
1,2,4-trimethylbenzene	0.1076	10.93			
1,3,5-trimethylbenzene	0.1140	11.03	8.8	0.0178	85
1,2,3,4-tetramethylbenzene	0.1288	11.25			
ethylbenzene	0.0655	10.21	8.8	0.0178	73
n-propylbenzene	0.0675	10.27	8.6	0.0143	79
isopropylbenzene	0.0628	10.17			
n-butylbenzene	0.0612	10.15			
isobutylbenzene	0.0535	9.99			
tert-butylbenzene	0.0557	10.04			
chlorobenzene	0.0390	9.59	9.5		0
bromobenzene	0.0620	10.13	9.9	0.0514	17
trifluoromethylbenzene	0.00743	8.05			
CCl_4	0.01313	8.53	8.6		0

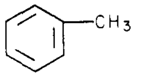
[a] Solubility parameters evaluated from experimental solubilities. [b] Solubility parameters taken from the literature. [c] Solubility calculated from the regular solution theory.

(e) Chlorobenzene forms a less stable complex with iodine than bromobenzene. (f) From the four α,α,α-substituted aromatic hydrocarbons









toluene seems to form the most stable complex and (trifluoromethyl)benzene the least stable complex with iodine. As the hydrogens in the α,α,α position are replaced by methyl groups, the electron-donor ability and, consequently, the stability of the complex are reduced.

Next, we evaluate the concentration of the solvated or complexed iodine $[I_{2,c}]$ in the various solvents. We assume that this is given as the difference in the total iodine concentration, $[I_2]$, and the concentration of the free iodine, $[I_{2,f}]$, in the solution: $[I_{2,c}] = [I_2] - [I_{2,f}]$. The latter quantity is calculated by means of the Hildebrand–Scatchard equation (*6*, *7*)

$$\ln a_{I_2} = \ln x_{I_2} + V_{I_2} \phi_S^2 (\delta_{I_2} - \delta_S)^2 / RT$$

assuming that the free-iodine concentration in the saturated aromatic hydrocarbon solution is the same as it would be if the solution would obey the regular solution theory. The results, summarized in Table IV, follow the same order as the ones obtained from spectral data: (a) *o*-xylene forms a less stable complex with iodine than *p*- and *m*-xylene. (b) Toluene forms a more stable complex with iodine than benzene. (c) From all the solvents for which solubility parameters are available, the iodine–mesitylene complex seems to be the most stable one. Over 80% of iodine in this solvent is complexed. (d) No complexation is observed in chlorobenzene and carbon tetrachloride, and (e) the bromobenzene complex seems to be weak.

In the above equation, a_{I_2} is the activity of solid iodine (= 0.2582), V_{I_2} is the molar volume of supercooled liquid iodine (=59 cm^3/mol), and δ_{I_2} is the solubility parameter of iodine (=14.1 (cal/cm^3)$^{1/2}$). The solubility parameters of the various solvents taken from the literature (*6*, *7*, *13*) are in Table IV.

In the same table, we present the solubility parameters obtained from experimental solubility data, δ^*.

We made a relatively successful attempt in correlating the solubility of iodine with the molecular structure of the solvents. The procedure is based on the equation

$$S = S_T + xI_{op} + yI_{st} + zI_m$$

where S and S_T are the solubilities of iodine in a particular solvent and toluene, respectively. I_{op}, I_{st}, and I_m are the inductive- and steric-effect contributions to the solubility. x is the number of ortho- and para-substituted methyl groups, y is the number of ortho-substituted methyl groups, and z is the number of meta-substituted methyl groups. It is the steric effect that is responsible for the difference in the solubilities of the ortho- and para-substituted methyl groups. From the solubility of iodine in toluene and the three isomeric xylenes, we arrived at the following expressions:

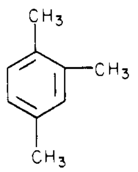
$$I_{op} = 0.0135 + (1 \times 10^{-4})(t - 30)$$

$$I_m = 0.0204 + (1.4 \times 10^{-4})(t - 30)$$

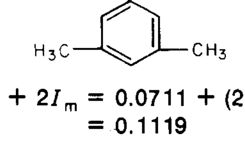
$$I_{st} = 0.0030 + (1 \times 10^{-4})(t - 30)$$

where t is the temperature in degrees Celsius.

Using these values, we estimated the solubility of iodine in 1,2,4- and 1,3,5-trimethylbenzenes at 30 °C.



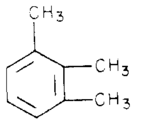
$$\begin{aligned}\delta &= S_T + 2[2I_{op} + I_m]/3 + I_{st} \\ &= 0.0711 + 2[(2)(0.0135) + 0.0204]/3 + 0.0030 \\ &= 0.1057\end{aligned}$$



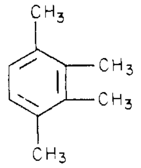
$$\begin{aligned}S = S_T + 2I_m &= 0.0711 + (2)(0.0204) \\ &= 0.1119\end{aligned}$$

The agreement between the measured and estimated solubilities at this temperature and all the other temperatures is very good.

Encouraged by these results, we estimated the solubilities of iodine in 1,2,3-trimethylbenzene and 1,2,3,4-tetramethylbenzene.



$$\begin{aligned} S &= S_T + 2[2I_{op} + I_m]/3 + 2I_{st} \\ &= 0.0711 + 2[(2)(0.0135) + 0.0204]/3 + (2)(0.0030) \\ &= 0.1087 \end{aligned}$$



$$\begin{aligned} S &= S_T + 3[4I_{op} + 2I_m]/6 + 3I_{st} \\ &= \\ &\quad 0.0711 + 3[(4)(0.0135) + (2)(0.0204)]/6 + (3)(0.0030) \\ &= 0.1275 \end{aligned}$$

To test the accuracy of these predicted values, we measured the solubility of iodine in these solvents at various temperatures. As the data in Table II (in parentheses) prove, the agreement is very good.

The application of the regular solution theory to solubility of iodine in mixed solvents is the subject of our next paper.

Acknowledgment

We thank Professor Paul Haberfield for his interest in this work.

Registry No. I_2, 7553-56-2; benzene, 71-43-2; toluene, 108-88-3; *o*-xylene, 95-47-6; *p*-xylene, 106-42-3; *m*-xylene, 108-38-3; 1,2,3-trimethylbenzene, 526-73-8; 1,2,4-trimethylbenzene, 95-63-6; 1,3,5-trimethylbenzene, 108-67-8; 1,2,3,4-tetramethylbenzene, 488-23-3; ethylbenzene, 100-41-4; *n*-propylbenzene, 103-65-1; cumene, 98-82-8; *n*-butylbenzene, 104-51-8; isobutylbenzene, 538-93-2; *tert*-butylbenzene, 98-06-6; chlorobenzene, 108-90-7; bromobenzene, 108-86-1; trifluoromethylbenzene, 98-08-8.

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Solubility of Iodine in Mixed Solvents

Cheng-Zhang Jiang,[†] Carolyn S. Birbaum, and Vojtech Fried*

Department of Chemistry of the City University of New York, Brooklyn College, Brooklyn, New York 11210

The solubility of iodine in 10 two-component and 2 three-component solvent mixtures is measured at 30 °C. A method is suggested for predicting the solubilities in multicomponent solvents from known solubilities in single-component solvents. The agreement between the measured and predicted solubilities is very good.

Introduction

There have been several methods proposed for predicting solubilities in mixed solvents from known solubilities in single-component solvents (*1*–*12*). The methods based upon the solubility parameter theory were introduced by Hildebrand (*1*, *2*), the methods using the Margules equation by Prausnitz et al. (*3*), and the methods employing the concept of local volume fractions by Hildebrand et al. (*2*) and by Walkley et al. (*5*). Methods based on other concepts were employed by Bertrand (*8*, *11*), Nitta (*6*, *7*), and Kehiaian (*12*). The reliability of the individual methods and the accuracy of their prediction depend on the physical and chemical nature of the solute and solvent under investigation. Usually, the accuracy varies from good to satisfactory for systems in which the solute is a gas; it is, however, less satisfactory for systems in which the solute is a solid. The discrepancy is larger for systems with high solubilities and for solutions whose behavior is determined by specific interactions (hydrogen-bond and charge-transfer interactions).

In this study, we made some adjustments in the Hildebrand regular solution theory, so that it can cope better with solutions whose behavior is determined by specific interactions. The theory, in its modified version, is also able with better accuracy to predict the solubility of a solute in multicomponent solvents from known solubilities in single-component solvents. The reasons for employing iodine as a solute and the aromatic hydrocarbons as solvents have been given in our previous study (*13*).

Experimental Section

The purification of the employed chemicals as well as the method for measuring the solubility, its reproducibility, and accuracy were described previously (*13*). The accuracy of the measurement in multicomponent solvents is, however, not as good as in single-component solvents. The solvent components are usually of different volatilities—have different vapor pressures at the temperature of the experiment—and, consequently, exhibit different rates of evaporation. This leads to composition changes in the mixed solvent during the process of sampling. We estimated this composition change from Raoult's law and concluded that the error due to the different volatilities is about ±0.1%. This increases the overall error in the measurement to about ±0.5% (*13*).

[†] Dalian Institute of Chemical Physics of the Chinese Academy of Sciences, Dalian, People's Republic of China.

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