THE NATURE OF IODINE SOLUTIONS

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The results of the more significant studies concerning the nature of violet and brown iodine solutions are summarized. Although molecular weight determinations show that iodine is present in the diatomic state in all solvents, other physicochemical data, e.g., heats of solution, cryoscopic and distribution behavior, indicate that brown solutions contain iodine chemically bound to the solvent, in equilibrium with free iodine. Each of the compounds which form brown solutions with iodine contains an element capable of acting as a donor in the formation of coördinate covalent bonds.

Iodine in brown solutions appears to be much more reactive than the presumably free iodine in violet solutions. The results of reaction between iodine and certain silver compounds are described.

It is well known that iodine solutions may be either violet or brown, the color depending upon the solvent. This variation of color with solvent has intrigued many chemists, and has been the subject of numerous intensive investigations on solutions of iodine. The results of the more significant studies which have led to our present concepts of the nature of such solutions are summarized in this paper. Aqueous solutions containing complex ions of the nature of I_3^- present a separate problem which will not be considered here.

SOME PHYSICAL PROPERTIES OF IODINE SOLUTIONS

It was first demonstrated by Lachman (22) that iodine solutions made with pure solvents fall into two classes according to color,—violet and brown. Violet solutions are formed with such solvents as hydrocarbons, chloro- and bromohydrocarbons, and carbon disulfide, whereas alcohols, ethers, ketones, organic acids, nitriles, nitrogen bases, and certain sulfur compounds dissolve iodine to form brown solutions. Brown solutions tend to become violet when heated, and revert to their original color on cooling (22, 27); similarly, the violet color of an iodine–carbon disulfide solution becomes brown when the solution is cooled in a dry ice–ether bath (29). Precise molecular weight determinations by Beckmann (3, 5) have proved that iodine is present in the diatomic state in all solvents investigated. The apparently higher molecular weights obtained in certain instances by other investigators were due, according to Beckmann, to their failure to take into consideration the volatility of the iodine. Correction for this factor gives values which are in excellent agreement with the molecular weight of the diatomic form.

The data just cited appear to minimize the possibility of the presence in solution of free iodine molecules of a greater degree of complexity than I_2, in any significant concentration. On the other hand, it may be relevant to mention here the work of Rabinowitch and Wood (26) on the effect of light on solutions of iodine. In the case of solutions in carbon tetrachloride and in hexane, they concluded, from a study of extinction coefficients, that dissociation of iodine molecules into atoms occurred to a measurable extent under intense illumination. The fraction of monatomic molecules, however, never exceeded 1 in 2200, and the rate of recombination of atoms is very high.

Even though iodine exists almost entirely in the diatomic state in all solutions, the physical properties of the brown solutions differ markedly from those of the violet. In the first place, iodine is much more soluble, in general, in solvents giving brown solutions than in others. The classical investigations of Hildebrand and his students (18) have shown that the violet solutions form a series of "regular solutions."[1] In these cases, the variation of the solubility of iodine with temperature may be represented fairly accurately by a regular family of curves corresponding to the equation

$$\log N_2 = 2.264 - [876.5 + k(1 - N_2)^2] \times \frac{1}{T}$$

in which N_2 is the mole fraction of iodine in a solution saturated at the absolute temperature T, and k is a parameter, approximately independent of temperature for each solvent, whose value depends upon the energy of vaporization of the solvent. When k is relatively small, the curves obtained by plotting log N_2 against $1/T$ are nearly linear except at temperatures approaching the melting point of iodine; as k becomes larger they take on a characteristic reversed S-shape. Approximate values of k for solutions of iodine in several solvents are as follows:

Solvent................	CS_2	$CHCl_3$	$TiCl_4$	CCl_4	C_7H_{16}	$SiCl_4$
k.....................	190	300	310	390	450	490

The fact that solubility curves for iodine in solvents in which it gives brown solutions do not fall in this family (nor, indeed, do they constitute a regular family of their own) indicates that new molecular species are formed in such solutions.

The distribution coefficient of iodine between its brown glycerol solution and its violet chloroform solution is influenced markedly by changes in temperature, whereas an approximately constant distribution coefficient is observed between two solvents in which iodine forms brown solutions (17). These facts are brought out in the data of tables 1 and 2. It is interesting to note in table 1 that the successive differences in the values of the distribution coefficients tend to become smaller as the temperature increases. This is not surprising, in view of the fact that brown solutions tend to become violet on heating.

The heats of solution of iodine in solvents giving brown solutions are much

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[1] Regular solutions are defined as solutions which are formed from their components with the same change in entropy as occurs in the formation of an ideal solution of the same concentration.

higher than the values for violet solutions (27). This fact is illustrated in table 3.

Spectrophotometric studies give further interesting information concerning violet and brown solutions. The latter are transparent at the red end of the spectrum and absorb heavily in the violet, whereas the former absorb heavily in the longer wave-length portion of the visible spectrum and transmit both violet and all the infrared light beyond 1200 mμ (9). Violet solutions, moreover, have an absorption spectrum very similar to that of iodine vapor; and the spectrum of brown solutions at elevated temperatures, as would be expected, shows a shift in the absorption maximum toward the region of maximum absorption for violet solutions (21, 27). The work of Gróh (16) and particularly that of Getman (15) appears to indicate that for an iodine solution in a pure solvent at a fixed temperature only one of two colors is possible. Getman found, from measurements of the extinction coefficients in the visible spectrum of iodine solutions in purified solvents, that these solutions fall into two groups (table

TABLE 1

Distribution of iodine between glycerol and chloroform

t	CONCENTRATION IN GLYCEROL LAYER (c_1)	CONCENTRATION IN CHLOROFORM LAYER (c_2)	$c_1 + c_2$	$k = \frac{c_1}{c_2}$
°C.	*gram-moles/liter*	*gram-moles/liter*		
0	0.0119	0.0177	0.0296	0.675
10	0.0101	0.0198	0.0299	0.510
20	0.0084	0.0213	0.0299	0.410
30	0.0079	0.0217	0.0298	0.364
40	0.0077	0.0221	0.0297	0.349
50	0.0074	0.0226	0.0299	0.330

TABLE 2

Distribution of iodine between glycerol and ether

t	CONCENTRATION IN GLYCEROL LAYER (c_1)	CONCENTRATION IN ETHER LAYER (c_2)	$c_1 + c_2$	$k = \frac{c_1}{c_2}$
°C.	*gram-moles/liter*	*gram-moles/liter*		
0	0.00561	0.0270	0.0327	0.21
30	0.00544	0.0272	0.0326	0.20
30	0.00100	0.0051	0.0062	0.20

TABLE 3

Heat of solution of 1 g. of iodine in kilogram-calories

$CHCl_3$	CS_2	C_6H_6	$(C_2H_5)_2O$	C_2H_5OH	C_5H_5N
−21.52	−20.78	−18.36	−7.83	−7.58	+17.80
−21.65	−20.50	−18.51	−7.91	−7.75	+17.58

4): violet, with absorption maxima ranging from 520 to 540 mμ; and brown, with maxima from 460 to 480 mμ. The intensity of absorption also differs notably in the two groups. Getman also confirmed the observation of Ley and Engelhardt (23) that the absorption spectra of iodine solutions change with time.

The absorption spectra of solutions of iodine in several mixed solvents were studied by Weyl (28), whose results tend merely to confirm the earlier conclusions.

THE CONDITION OF IODINE IN BROWN SOLUTIONS

In order to account for the marked dissimilarities in properties between the brown and the violet solutions, it has been assumed by most investigators that the brown solutions contain iodine chemically bound to the solvent, in equilibrium with free iodine.[2] When the types of compounds which form brown solutions are considered in the light of our present knowledge of chemical binding, this assumption appears to be an altogether reasonable one. For it is readily apparent that each of these compounds contains an element, e.g., nitrogen, sulfur, or oxygen, capable of acting as a donor in the formation of coördinate covalent bonds.

TABLE 4

Absorption maxima and extinction coefficients of iodine solutions

VIOLET SOLUTIONS			BROWN SOLUTIONS		
Solvent	Absorption maximum	Extinction coefficient at maximum	Solvent	Absorption maximum	Extinction coefficient at maximum
	mμ			*mμ*	
n-C_6H_{14}	535	0.42	C_2H_5OH	480	0.30
C_6H_6	530	0.40	$(CH_3)_2CHOH$	480	0.27
$C_6H_5CH_3$	520	0.42	$(CH_3)_2CO$	460	0.23
CS_2	540	0.41	$CH_3COC_6H_5$	470	0.29
CCl_4	540	0.41	C_5H_5N	480	0.24
$CHCl_3$	535	0.41	H_2O	470	0.29
$C_6H_5NO_2$	500	0.42			

The case of iodine solutions in benzene is sufficiently anomalous to warrant special mention. Some observers have reported these solutions as brown, others as violet. It appears probable that the former statement was based upon

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[2] An entirely different explanation of the brown color of iodine solutions in certain solvents was proposed by Amann (1), who stated that such solutions contained particles of colloidal dimensions, visible in the ultramicroscope. More recently, Chirnoagă and Chirnoagă (7) have contradicted this statement, so far as the presence of ultramicroscopically visible particles is concerned. They present evidence, however, based upon cataphoretic experiments, of the existence of iodine in a subultramicroscopic colloidal state (which they designate as cryptocolloidal) in solutions of iodine in 96 per cent alcohol. Their extension of this hypothesis, merely by analogy, to all iodine solutions which exhibit a brown color seems to us entirely unwarranted.

observation of solutions in incompletely purified benzene, especially since a distinctly brown color is observed in thiophene solutions. Even in carefully purified benzene, however, the color is not a pure violet, at least at room temperature, but rather a violet-red, which changes to violet when the solution is heated. Hildebrand and Jenks (20) attribute the deviation of the solubility curve of iodine in benzene from its normal position in the regular family (18) to a slight degree of solvation, increasing with decreasing temperature. This hypothesis is supported by the work of Curti and Carbagnati (10), who infer the existence of a benzene–iodine complex from measurements of the dielectric constants of such solutions.[3]

TABLE 5

Solvent effect on the freezing point of iodine–bromoform solutions

(Cryoscopic constant for bromoform = 13.8)

WEIGHT OF $CHBr_3$	SOLVENT ADDED	WEIGHT OF SOLVENT ADDED	WEIGHT OF IODINE	MOLAL LOWERING
grams		*grams*	*grams*	
20.80	$C_2H_4Br_2$	0.960	0.2370	13.8
36.45	CS_2	0.442	0.0885	13.7
19.12	$C_6H_5CHCl_2$	0.471	0.1692	14.0
20.99	CCl_4	0.457	0.0654	13.7
19.21	C_2H_5OH	0.117	0.0570	11.0
20.13	$C_6H_5CH_2OH$	0.478	0.0691	11.4
19.55	$C_6H_5NO_2$	0.444	0.1242	13.2

The most convincing proof of the existence of solvated iodine in brown solutions comes from the work of Hildebrand and Glascock (19), who studied the change in

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[3] *Added in page proof:* The authors are greatly indebted to Professor Joel H. Hildebrand for the following private communication, which was received after this paper had been submitted for publication: "I have long wondered about the nature of the chemical interaction between iodine and benzene, evident from the shift of absorption of color away from the violet of unsolvated iodine. A possible explanation has appeared to lie in an acid–base interaction in the electron donor–acceptor sense such as we see in the union of I^-, the base, with I_2, the acid, to form I_3^-. Evidence of basic character in benzene is its union with BF_3, BCl_3, and with concentrated H_2SO_4. If this basic character is also responsible for its union with iodine, then the substitution of methyl groups should increase basic strength and ability to solvate iodine. That such a shift occurs in going from benzene to toluene solutions is shown in your table 4. As a further test, my collaborator, Dr. Hans A. Benesi, recently prepared iodine solutions of equal concentrations in benzene, toluene, xylene, mesitylene, and methylnaphthalene. We found that the color shifts stepwise in that order, ending with yellow. Dr. Benesi is at present engaged in measuring the absorption curves for these solutions. He has just found a strong absorption band for the benzene solution with a maximum at 3200 Å., which appears to correspond to a band with a maximum of 3530 Å. occurring in I_3^- solutions (W. R. Brode: J. Am. Chem. Soc. **48**, 1877 (1926)). The evidence at this moment appears to favor the acid–base explanation. The true explanation evidently is *not* to be found in dipole moments, because not only chloroform and 1,2-dibromoethane, but also 1,1- and 1,2-dichloroethanes and *cis*-dichloroethylene, recently investigated by Dr. Benesi (paper submitted for publication), all give violet solutions despite their considerable dipole moments."

the freezing point of solutions of iodine in an "inactive" solvent (i.e., one in which it gives a violet solution) brought about by the addition of a small amount of a third substance, itself either an "inactive" or an "active" solvent (i.e., one in which iodine gives a brown solution). In those cases in which the lowering is less than that calculated for the iodine on the basis of the dilute solution law, these authors conclude that there must be at least partial combination of iodine with the second solvent. The data of table 5 show that only with "active" solvents is a large deviation observed from the calculated freezing-point lowering.

By the same authors, the equilibrium for the reaction

$$I_2 + n(\text{“active” solvent}) \rightleftharpoons (\text{“active” solvent})_n \cdot I_2$$

was studied colorimetrically for various "active" solvents in several "inactive" media. The determination of free and bound iodine was based on the fact that violet solutions transmit violet light almost completely, while brown solutions absorb most heavily in this region of the spectrum. A mercury-vapor lamp was used as a source of light, and all red and green light was cut off from the box containing the colorimeter by means of appropriate filters. The amount of brown absorbing compound was determined in the presence of non-absorbing violet, by comparison of the intensity of the violet light transmitted by the mixture with that transmitted by a standard brown solution. A correction was made for the small amount of violet light absorbed by a violet solution.

TABLE 6

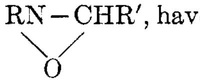
Study of the equilibrium $C_2H_5OH + I_2 \rightleftharpoons C_2H_5OH \cdot I_2$ *in carbon tetrachloride*

(c_1 = concentration of alcohol; c_2 = concentration of iodine; c = concentration of complex)

$$K = \frac{c}{c_1^n \times c_2}\ ;\ n = 1$$

c_1	c_2	c	K
0.595	0.00153	0.00114	1.25
0.527	0.00164	0.00104	1.26
0.383	0.00188	0.00083	1.15
0.194	0.00221	0.00052	1.21
0.130	0.00236	0.00039	1.27

On the assumption that $n = 1$, good concordance was obtained in the values of the equilibrium constants in each case. The data for a typical equilibrium are given in table 6.

The nature of such molecular addition compounds of iodine as have actually been isolated is in agreement with the evidence given above for chemical binding between solvent and iodine in brown solutions. In each case, the compound adding to iodine contains an atom which can act as a donor in a coördinate covalent bond. Thus addition compounds of iodine with $(C_6H_5CH_2)_2S$, $(CH_3)_2S$, $(C_6H_5)_3CSC_6H_5$, C_5H_5N, C_9H_7N, and various substances of the general formula  $\underset{\diagdown\, O\, \diagup}{RN{-}CHR'}$, have been prepared (4, 6, 8, 12, 14, 25, 27).

The precise nature of the binding between the iodine and the solvent molecule is not known in any instance. However, conductivity studies by Audrieth and Birr (2) have shed some light on the character of binding between iodine and pyridine. The electrical conductivity of solutions of iodine in pyridine increases with time. In very dilute solutions, however, a constant value is rapidly attained, the extremely high limiting value of approximately 130–132 units being found for the molecular conductance at infinite dilution. To explain the experimental data the authors postulate the gradual conversion of the initially formed non-conducting addition compound into a ternary salt, and believe it likely that solutions of iodine in pyridine contain the substances shown in the equilibria formulated below.

$$\mathrm{Py} + \mathrm{I_2} \rightleftharpoons \mathrm{IPy^+} + \mathrm{I^-} \rightleftharpoons \mathrm{Py^{++}} + 2\mathrm{I^-} \tag{a}$$

$$2[\mathrm{Py \cdot I_2}] \rightleftharpoons \mathrm{IPy^+} + \mathrm{I \cdot PyI_2^-} \tag{b}$$

Additional evidence in support of the hypothesis of such amphoteric behavior of iodine in brown solutions is to be found in the very recent work of Fairbrother (11) on the dielectric polarization of iodine in violet and brown solutions, respectively. The only results so far reported are given in table 7.

TABLE 7

Dipole moment of iodine in different solvents

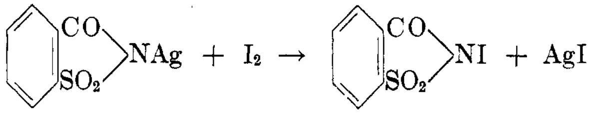
SOLVENT	COLOR OF SOLUTION	DIPOLE MOMENT OF IODINE (DEBYE UNITS)
C_6H_6	Violet-red	0.6
p-$C_6H_4(CH_3)_2$	Red	0.9
1,4-Dioxane	Brown	1.3
Diisobutylene	Red-brown	1.5

These results indicate that the formation of a red or brown solution is accompanied by polarization of the iodine molecule. It may be supposed that the proximity of an electron-donor stabilizes one of the possible ionic structures, I^-—I^+ and I^+—I^-, of an iodine molecule. Thus a partial ionization of the iodine takes place, the positive end of the molecule being stabilized by coördination with a molecule of the solvent.

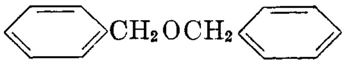
THE INFLUENCE OF SOLVENT ON THE REACTIVITY OF IODINE

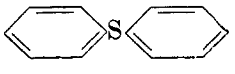
The bound iodine in brown solutions appears to be much more reactive than the presumably free iodine in violet solutions. It is possible, moreover, to activate the iodine in violet solutions by the addition of compounds which change the color of such solutions to brown.

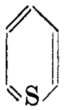
It has been shown by the determination of the iodine numbers of fats (24) that such compounds take up from violet solutions only about one-half the calculated quantity of iodine, whereas they take up from brown solutions the total amount theoretically possible. Furthermore, brown solutions of iodine in ether, alcohol, dioxane, cyclohexanol, and cyclohexene have been found to react with the silver derivative of saccharin to produce the theoretical quantity of silver iodide. When violet solutions of iodine in chloroform, benzene, carbon disulfide, carbon tetrachloride, and petroleum ether are treated with the same silver derivative, the first two behave, it is true, in the same manner as the brown solutions,[4] but the others react to a slight extent only (13). The reaction which takes place here is postulated to be the following:

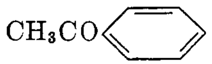


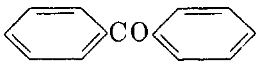
The activation of violet iodine solutions with respect to this reaction with the silver derivative of saccharin, by the addition of compounds which turn these solutions brown, has been investigated in some detail by Feigl and Bondi (12). Most of the compounds added markedly increase the reactivity of the iodine. Examination of the compounds which have been found to have little or no effect on the activity of iodine is of interest; they are

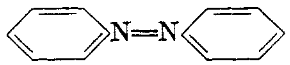












It is evident from the structures of these compounds that the potential donor atoms in the formation of coördinate covalent bonds with iodine would in these instances have but slight tendency to donate a pair of electrons. The deactivating influence of the benzene ring is a prime factor in this relative inability to form stable bonds. The observation has also been made that violet solutions of iodine in carbon disulfide are activated to a much smaller degree by methyl and benzyl ethers than by methyl and benzyl sulfides, respectively; this fact is in line with the lower electronegativity of sulfur.

REFERENCES

(1) Amann: Kolloid-Z. **6,** 235 (1910); Kolloid-Beihefte **3,** 337 (1912).
(2) Audrieth and Birr: J. Am. Chem. Soc. **55,** 668 (1933).
(3) Beckmann: Z. physik. Chem. **58,** 543 (1907).
(4) Beckmann: Ann. **367,** 271 (1909).
(5) Beckmann and Stock: Z. physik. Chem. **17,** 107 (1895).
(6) Chatelet: Ann. chim. [11] **2,** 12 (1934).
(7) Chirnoagă and Chirnoagă: Z. anorg. Chem. **218,** 273 (1934).
(8) Claus and Istel: Ber. **15,** 820 (1882).
(9) Coblentz: Phys. Rev. **16,** 35 (1903); **16,** 72 (1903); **17,** 51 (1903).

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[4] Evidence has been obtained in our Laboratory to show that the completion of certain reactions between silver salts of carboxylic acids and iodine is dependent on the presence of chloroform. Its rôle, however, has not yet been completely determined. (Unpublished results of Zingaro, Kleinberg, and Vander Werf.)

(10) Curti and Carbagnati: Rend. ist. lombardo sci., Classe sci. mat. nat. **73,** 403 (1939–40); Chem. Zentr. **1941,** II, 2299.
(11) Fairbrother: Nature **160,** 87 (1947).
(12) Feigl and Bondi: Monatsh. **53–54,** 508 (1929).
(13) Feigl and Chargaff: Monatsh. **49,** 417 (1928).
(14) Fromm: Ann. **396,** 92 (1913).
(15) Getman: J. Am. Chem. Soc. **50,** 2883 (1928).
(16) Gróh: Z. anorg. Chem. **162,** 287 (1927).
(17) Hantzsch and Vagt: Z. physik. Chem. **38,** 705 (1901).
(18) Hildebrand: *Solubility*, 2nd edition, pp. 153–7. Reinhold Publishing Corporation, New York (1936).
(19) Hildebrand and Glascock: J. Am. Chem. Soc. **31,** 26 (1909).
(20) Hildebrand and Jenks: J. Am. Chem. Soc. **42,** 2180 (1920).
(21) Krüss and Thiele: Z. anorg. Chem. **7,** 52 (1894).
(22) Lachman: J. Am. Chem. Soc. **25,** 50 (1903).
(23) Ley and Engelhardt: Z. anorg. Chem. **72,** 55 (1911).
(24) Margosches and Hinner: Chem. Zentr. **95, I,** 2648 (1924).
(25) Patein: Bull. soc. chim. **50,** 201 (1888).
(26) Rabinowitch and Wood: Trans. Faraday Soc. **32,** 547 (1936).
(27) Waentig: Z. physik Chem. **68,** 513 (1910).
(28) Weyl: Angew. Chem. **48,** 573 (1935).
(29) Wiedemann and Ehert: Wied. Ann. **41,** 299 (1890).