The fluidity of mercury from 0 to 100° was determined as an incidental part of this investigation, using glass capillary No. 1.23. The values are a little higher at low temperatures than the mean values of earlier experimenters given by Erk,[5] and our values are somewhat lower than theirs at 40° and above. This slight change does not alter the conclusion that mercury is different from all other liquids yet studied in that its fluidity temperature curve is concave toward the temperature axis.

Summary

1. The suspicion that mercury exhibits slippage while flowing over unwet surfaces such as glass appears to be unfounded.

2. The fluidity of mercury from 0 to 100°, measured in a glass capillary viscometer with attention to recent corrections, was found to be not inconsistent with earlier determinations.

3. The rate of flow of mercury through a narrow copper capillary is irregular but decreases with time, particularly when the tube is well amalgamated. The values of the fluidity are quite untrustworthy. The effect is the indirect result of the very slight solubility of copper in mercury. Differential solubility of the crystals causes large crystals to build up on the surface of the capillary which interfere with the flow.

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[CONTRIBUTION FROM HILLSIDE LABORATORY]

THE COLOR OF IODINE SOLUTIONS[1]

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RECEIVED JULY 2, 1928 PUBLISHED NOVEMBER 6, 1928

The dependence of the color of solutions of free iodine upon the nature of the solvent has been the subject of numerous investigations, but notwithstanding the thoroughness of these studies the problem of the exact composition of iodine solutions yet remains to be solved completely.

As a result of their study of colors of iodine solutions, Gauthier and Charpy[2] concluded that four different colors may be distinguished, depending upon the nature of the solvent, as follows: (1) violet, as in chloroform; (2) red, as in ethylene bromide; (3) reddish-brown, as in toluene; (4) brown, as in ethyl alcohol. Although a number of solvents were found to conform to this classification, no satisfactory relation between the properties of the solvents and the colors of the solutions was discovered. Subsequent investigations by Rigollot[3] and by Krüss and Thiele[4] failed to establish any satisfactory connection between the chemical

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[1] In memory of Ira Remsen.

[2] Gauthier and Charpy, *Compt. rend.*, **110,** 1890; **111,** 645 (1890).

[3] Rigollot, *ibid.*, **112,** 38 (1891).

[4] Krüss and Thiele, *Z. anorg. Chem.*, **7,** 25 (1894).

behavior of the solvent and the color of the solutions. In 1903, Lachman,[5] after examining solutions of iodine in more than sixty carefully purified solvents, representative of twelve different types of organic compounds, was unable to distinguish more than two colors, namely, violet and brown. Furthermore, he formulated the following generalization between the color of the solution and the character of the solvent: saturated solvents give violet solutions, whereas solvents having an unsaturated character yield brown solutions. The differences in the colors of iodine solutions have been attributed by Krüss and Thiele,[4] Wiedemann and Ebert,[6] Loeb,[7] Beckmann[8] and others to differences in the molecular condition of the solute. Subsequent investigations, notably by Hildebrand and Glascock[9] Waentig,[10] Ley and Engelhardt,[11] and Dolezalek,[12] have confirmed this view and have furnished abundant experimental evidence to show that in the brown solutions the solute is more or less solvated, whereas in the violet solutions the solute consists solely of diatomic molecules of iodine. The compound, PyI_2, has actually been isolated by Waentig from a pyridine solution of iodine.

It has long been known that brown solutions of iodine tend to become violet when heated, while violet solutions become brown when sufficiently cooled. This change of color with temperature may be satisfactorily explained by assuming a displacement of the equilibrium between solvated and unsolvated iodine.

More recently, Amann[13] has put forward the view that while in some instances iodine, either free or solvated, may form true solutions, yet in other cases it forms colloidal solutions. He states that brown solutions of iodine contain ultramicroscopic particles, while violet solutions contain none.

Notwithstanding Lachman's statement that iodine solutions are either violet or brown, and that intermediate colors are never observed unless the solvents contain minute amounts of impurities, one finds repeated statements throughout the literature that solutions of iodine in certain solvents exhibit various colors such as blue-violet, red-violet, red and red-brown.

With the exception of the work of Coblentz[14] on solutions of iodine in carbon disulfide and ethyl alcohol, relatively few spectrophotometric

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[5] Lachman, THIS JOURNAL, **25**, 50 (1903).

[6] Wiedemann and Ebert, *Wied. Ann.*, **41**, 299 (1890).

[7] Loeb, *Z. physik. Chem.*, **2**, 606 (1888).

[8] Beckmann, *ibid.*, **17**, 107 (1895); **58**, 543 (1907).

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

[10] Waentig, *Z. physik. Chem.*, **68**, 513 (1909).

[11] Ley and Engelhardt, *ibid.*, **72**, 55 (1911).

[12] Dolezalek, *ibid.*, **64**, 727 (1908).

[13] Amann, *Z. Kolloid*, **6**, 235 (1910); *Kolloid Beihefte*, **3**, 337 (1912).

[14] Coblentz, *Phys. Rev.*, **16**, 35, 72 (1903); **17**, 51 (1904).

measurements of iodine solutions in the visible range of the spectrum have been recorded. It has seemed of interest, therefore, to undertake a series of spectrophotometric measurements of iodine solutions in typical solvents with a view to testing the validity of Lachman's statement relative to the colors of iodine solutions.

Apparatus.—The spectrophotometric measurements have been made with a Nutting photometer in conjunction with a Hilger wave length spectrometer. As a source of light a 15-watt Mazda lamp operating on the 110-volt a. c. circuit was employed. Absorption tubes of 10-cm. length were used throughout the entire series of measurements.

Materials.—Merck's resublimed iodine served as the solute in each of the solutions. Solvents of a high degree of purity were subjected to thorough dehydration and subsequent fractionation before being used in the preparation of the solutions. The following solvents were employed: ethyl alcohol, b. p. 78.4°, 760 mm.; *iso*propyl alcohol, b. p. 80.2–81.2°, 750 mm.; acetone, b. p. 56.6°, 755 mm.; chloroform, b. p. 61.0–62.0°, 757 mm.; carbon tetrachloride, b. p. 77.0°, 763.4 mm.; carbon disulfide, b. p. 46.0–46.2°, 752 mm.; *n*-hexane, b. p. 68.0°, 760 mm.; benzene, b. p. 80.0–80.2°, 757 mm.; toluene, b. p. 110.2–110.8°, 758 mm.; pyridine, b. p. 114.8–115.6°, 751.6 mm.; nitrobenzene, b. p. 209.2–209.4°, 753.5 mm.; acetophenone, b. p. 202–203°, 756 mm. The aqueous solutions of potassium iodide were prepared from a high grade of salt dissolved in conductivity water.

Results.—The values of the extinction coefficients,[15] ϵ, for the different solutions, as measured at intervals of 10 mμ throughout the visible spectrum from 680 mμ to 430 mμ, are given in Table I. Inspection of the data of the table shows that, if solutions in nitrobenzene be disregarded, the solutions may be grouped in two distinct classes as follows: (1) solutions resembling that of iodine in *n*-hexane (violet solutions), and (2) solutions resembling that of iodine in ethyl alcohol (brown solutions). Solutions in *n*-hexane, benzene, toluene, carbon disulfide, carbon tetrachloride and chloroform have absorption maxima ranging between 520 mμ and 540 mμ. On the other hand, solutions in ethyl alcohol, *iso*propyl alcohol, acetone, acetophenone and pyridine have absorption maxima ranging between 460 mμ and 480 mμ. All of the solvents belonging to the first group are saturated in character, whereas all of those belonging to the second group are unsaturated. While not differing essentially in the spectral character of their absorption, solutions of iodine in both acetone and pyridine are found to differ markedly from the other solutions belonging to the second group in the intensity of their absorptions. With the exception of these two solutions, and that of iodine in nitrobenzene already mentioned, very little difference is found to exist between the absorptive powers of the solutions within each group. The absorption

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[15] The extinction coefficient, ϵ, is defined by the equation $\epsilon = 1/d \log I/I_0$, where I_0 is the intensity of the light entering the solution and I is the intensity of the emergent light after having traversed d cm. of solution.

TABLE I

ABSORPTION OF LIGHT BY 0.0005 *M* IODINE SOLUTIONS

Wave length λ(mμ)	Extinction Coefficients													
	n-Hexane	Benzene	Toluene	Carbon disulfide	Carbon tetrachloride	Chloroform	Ethyl alcohol	*Iso*propyl alcohol	Acetone	Acetophenone	Nitrobenzene	Pyridine	0.01*M* KI	0.1*M* KI
680	0.048	0.049	0.043	0.069	..	0.055	0.044	0.022	0.022	0.040	..	0.037	0.027	..
670	..	.051	.044	.071	..	.057	.038	..	.024	..	..	.038	.030	..
660	..	.053	.045	.076	..	.060	.036	..	.027	..	..	.039	.033	..
650	.049	.058	.047	.083	0.065	.064	.037	.031	.029	.043	0.038	.041	.035	0.043
640	.054	.061	.048	.088	.070	.068	.041	.032	.030	.045	.045	.043	.037	.045
630	.064	.066	.050	.103	.079	.075	.044	.033	.031	.048	.048	.045	.038	.048
620	.083	.075	.055	.120	.094	.087	.046	.034	.033	.050	.050	.047	.039	.051
610	.103	.082	.066	.150	.110	.101	.052	.036	.034	.053	.056	.050	.043	.054
600	.132	.104	.083	.190	.143	.119	.055	.038	.035	.056	.068	.053	.048	.058
590	.175	.132	.105	.24	.180	.150	.061	.042	.037	.059	.084	.057	.051	.062
580	.23	.156	.134	.29	.23	.190	.066	.046	.038	.062	.108	.061	.056	.067
570	.29	.21	.180	.34	.28	.25	.072	.053	.040	.065	.142	.064	.064	.073
560	.36	.28	.24	.38	.37	.30	.082	.062	.042	.070	.180	.070	.073	.076
550	.40	.32	.28	.40	.40	.40	.094	.071	.044	.076	.22	.075	.081	.083
540	.42	.38	.33	.41	.41	.41	.105	.087	.047	.083	.26	.084	.090	.088
530	.42	.40	.40	.40	.40	.41	.126	.106	.050	.090	.33	.095	.099	.093
520	.40	.38	.42	.38	.38	.40	.15	.127	.054	.099	.37	.110	.115	.105
510	.36	.36	.37	.35	.35	.38	.18	.165	.064	.116	.40	.130	.129	.120
500	.32	.34	.33	.31	.31	.35	.23	.20	.083	.140	.42	.165	.150	.147
490	.25	.31	.29	.26	.26	.30	.27	.26	.116	.183	.38	.21	.20	.190
480	.18	.28	.26	.22	.22	.25	.30	.27	.155	.25	.32	.24	.28	.26
470	.12	.23	.23	.17	.18	.22	.27	.26	.195	.29	.25	.22	.29	.32
460	.07	.19	.18	.12	.12	.15	.21	.22	.23	.24	.17	.19	.23	.26
450	.04	.14	.15	.09	.08	.10	.17	.18	.17	.18	.07	.15	.19	.23
440	.03	.09	.09	.06	.06	.07	.13	.16	.13	.13	..	.13	.14	.19
430	..	05	..	..	.04	..	.09	..	..	..	..	.08	.09	.15

curves for solutions of iodine in *n*-hexane, ethyl alcohol, acetone and pyridine, as plotted from the data of Table I, are shown in Fig. 1.

The intensity of absorption is seen to be decidedly different in the two groups of solvents. The maximum intensity is found with the solvents of the first group, that is, with saturated solvents. Furthermore, the intensity of the absorption with saturated solvents is nearly identical. On the other hand, the intensity of absorption with solvents of the second group is markedly less than that with solvents of the first group. While the intensity of absorption with saturated solvents is practically constant, it varies widely amongst the different unsaturated solvents studied. These facts are clearly brought out by the data of Table II, showing the absorption maxima of the solutions examined.

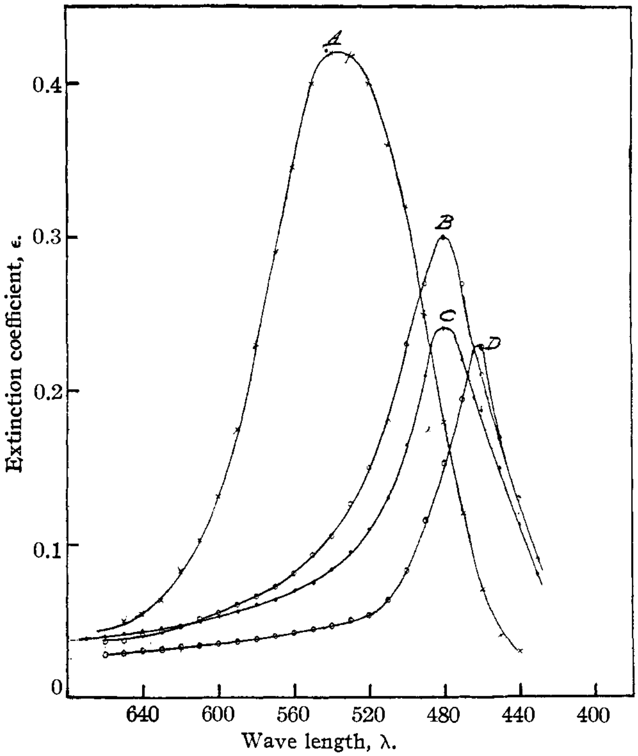

Fig. 1.—*A*, 0.0005 *M* I_2 in *n*-hexane; *B*, in ethyl alcohol; *C*, in pyridine; *D*, in acetone.

In this table λ_m denotes the wave length corresponding to the absorption maxima as determined from large scale plots of the data of Table I, while ϵ_m denotes the corresponding values of the extinction coefficients. The last column of the table gives the number of the group to which each solvent belongs.

TABLE II

ABSORPTION MAXIMA OF SOLUTIONS

Solvent	$\lambda_{m\mu}$	ϵ_m	Group	Solvent	$\lambda_{m\mu}$	ϵ_m	Group
n-Hexane	535	0.42	I	Ethyl alcohol	480	0.30	II
Benzene	530	.40	I	*Iso*propyl alcohol	480	.27	II
Toluene	520	.42	I	Acetone	460	.23	II
Carbon disulfide	540	.41	I	Acetophenone	470	.29	II
Carbon tetrachloride	540	.41	I	Pyridine	480	.24	II
Chloroform	535	.41	I	Water	470	.29	II
Nitrobenzene	50	.42					

The foregoing facts appear to substantiate Lachman's generalization that when iodine is dissolved in a saturated solvent the resulting solution is violet in color, whereas when it is dissolved in an unsaturated solvent the solution is brown in color. While in the case of saturated solvents iodine may be fairly assumed to form true solutions, its behavior with unsaturated solvents is by no means as clear. Although in the presence of an unsaturated solvent it is possible that the iodine molecule may undergo solvation, with equal probability it may be assumed to undergo association and give rise to a solution possessing a distinctly colloidal character. This latter possibility is in agreement with the view put forward by Amann[13] that brown solutions of iodine contain ultramicroscopic particles, whereas violet solutions are optically void.

It was pointed out by Ley and Engelhardt[11] that the absorption spectrum of iodine solutions changes with time, and that the differences between their results and those of Waentig[10] and of Crymble, Stewart and White[16] were to be traced to the failure of the latter observers to examine their solutions immediately after preparation. While the alteration in the character of the absorption spectrum of an iodine solution which occurs on standing is more pronounced in the ultraviolet than in the visible region of the spectrum, care has been taken throughout the present investigation to measure each solution immediately after it was prepared. The most pronounced example of the change in color with time which we have observed was furnished by solutions of iodine in *iso*propyl alcohol and acetone. Within a few hours after the solutions were prepared, the original brown color had faded to a light amber, and within a few days the solutions became absolutely colorless. This is undoubtedly due to a chemical reaction between the components of the solutions.

It is well known that solutions of iodine in aqueous potassium iodide darken on exposure to light. Recently the increase in the ultraviolet absorption of aqueous solutions of potassium iodide on exposure to light has been measured by Brode[17] and shown to be due to the presence of free iodine in the solutions. When a fixed weight of iodine is dissolved

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[16] Crymble, Stewart and White, *Ber.*, **43**, 1183 (1910).

[17] Brode, THIS JOURNAL, **48**, 1877 (1926).

in aqueous solutions of potassium iodide of increasing concentration, it has been found that the ultraviolet absorption increases with the concentration of the potassium iodide. In order to determine whether a similar increase in absorption occurs in the visible portion of the spectrum, 0.0005 *M* solutions of iodine in 0.01 *M* and 0.1 *M* potassium iodide have been measured. As will be seen from the last two columns of Table I, the more concentrated solution possesses slightly greater absorbing power.

The photochemical decomposition of iodine solutions has been studied by Stobbe and Schmidt.[18] They point out that solutions of iodine in alcohols slowly undergo transformation into solutions of periodides, such as hydrogen tri-iodide or other addition compounds. This reaction is accelerated by spongy platinum as well as by light. While the absorption spectrum of true solutions of iodine reveals but a single band in the visible portion of the spectrum, the ultraviolet absorption spectra of periodide solutions are found to resemble each other and to be characterized by two bands having wave lengths of 357 mμ and 290 mμ. Stobbe and Schmidt state that during the change of an iodine solution into a solution containing periodides, solutions of mixtures are formed which exhibit three absorption bands. In the solutions of iodine whose absorption spectra have hitherto been described by earlier observers, Stobbe and Schmidt have estimated that from 5 to 100% of the iodine present had undergone transformation into periodides. Furthermore, Stobbe and Schmidt found upon irradiating solutions of iodine in chloroform or benzene for twenty-four hours with a quartz mercury lamp, that the solutions became yellow on diluting with the respective solvents instead of acquiring the reddish color which unilluminated solutions of iodine assume when similarly diluted.

It seemed of interest, therefore, to carry out a few qualitative experiments on the stability of some of our solutions in ultraviolet light. To this end, 0.0005 *M* solutions of iodine in ethyl alcohol, *n*-hexane and carbon disulfide were irradiated in quartz flasks with ultraviolet light from a quartz mercury lamp for a period of six hours, after which their absorption curves were again determined spectrophotometrically. On comparing the resulting curves with those of the freshly prepared solutions, it was found that some change had occurred, the alcohol solution showing the most and the hexane solution the least photolysis. This is what might be expected with solvents containing oxygen which are known to decompose when exposed to ultraviolet radiation. Carbon disulfide on exposure to ultraviolet radiation has likewise been found by both Berthelot[19] and Bruhat and Pauthenier[20] to undergo partial decomposition, the walls of the containing vessel becoming coated with a

[18] Stobbe and Schmidt, *Z. wiss. Photochem.*, **20**, 57 (1920).

[19] Berthelot, *Ann. chim. phys.*, (VII) **19**, 150 (1900).

[20] Bruhat and Pauthenier, *Compt. rend.*, **178**, 1536 (1924); **180**, 1018 (1925).

brown deposit. A similar deposit was observed in the present series of experiments. Hexane appears to be quite stable when exposed to ultraviolet radiation and the solution of iodine in this solvent was found to be equally stable. The behavior of iodine solutions on exposure to ultraviolet radiation, as far as our few experiments have been carried, appears to confirm the view put forward by Lachman that unsaturation in the solvent is a factor of considerable importance in determining not only the color but other properties of iodine solutions.

Summary

1. The extinction coefficients of iodine solutions in a series of carefully purified solvents have been measured at intervals of 10 mμ throughout the visible spectrum.

2. The solutions may be divided into two distinct groups, as follows: (*a*) solutions in *n*-hexane, benzene, toluene, carbon disulfide, carbon tetrachloride and chloroform give violet solutions with absorption maxima ranging from 520 mμ to 540 mμ; (*b*) solutions in ethyl alcohol, *iso*propyl alcohol, acetone, acetophenone and pyridine give brown solutions with absorption maxima ranging from 460 mμ to 480 mμ.

3. The first group of solvents are saturated compounds, while the second group of solvents are unsaturated compounds.

4. The intensity of absorption differs markedly in the two groups. The maximum intensity of absorption is found with the saturated solvents of the first group, and is practically constant throughout the group. The intensity of absorption varies appreciably between the unsaturated solvents of the second group and is in every case less than with saturated solvents.

5. Solutions of iodine tend to undergo change on standing, this change being accompanied by a corresponding change in their absorption spectra.

6. The color and stability of iodine solutions on exposure to ultraviolet radiation appear to be more or less dependent upon the degree of saturation of the solvent.

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