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Abstract

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Spectrophotometric Study of Iodine Compounds with One Positive Valence

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In the absorption spectrum of an aqueous iodine solution in the absence of iodide, absorption bands are observed with maxima at λ288–290 m , λ340–360 m , and λ460 m . Numerous investigators ($^{1-10}$) attribute the first two absorption bands to the complex anion J_3^-, and the band at λ460 m to the solvated molecule J_2. In these works we have not found convincing evidence for such an interpretation of the absorption spectra of iodine solutions. Nor is there any information in the foreign literature on the biological properties of iodine with positive valence.

Meanwhile, as we have shown ($^{11-13}$), iodine with positive valence is of special interest, since in this form, in contrast to J^-, it possesses high biological activity both in pure aqueous solutions and especially in solutions of natural and synthetic high polymers. Iodine-high-polymer complexes are at present acquiring ever greater importance and broad clinical application as nontoxic therapeutic preparations of antiseptic action (^{14}). Taking this into account, in order to obtain the spectral characteristics and identification of iodine with one positive valence, as well as some of its other forms, we decided to study the absorption spectra of aqueous iodine solutions in the range 220–800 m .

Experimental Part

Iodine solutions were prepared in twice-distilled water from an iodine preparation of "chemically pure" grade that had been subjected to double sublimation. Solutions of iodine chloride were obtained by the method described by Gengrinovich (^{15}). Starch solutions were prepared from soluble starch of the grade "Reagent OST 27, GOPKh 1866" in twice-distilled water. The acids H_2SO_4, $HClO_4$, and HNO_3 were of "chemically pure" grade. Dialysis was carried out through a cellophane membrane 40 m thick. All spectrophotometric studies were carried out at room temperature on an SF-4 spectrophotometer in the range 220–800 m .

To obtain the spectral characteristics of compounds containing J_2^{+1}, we studied the absorption spectra of solutions of KJO and JCl, in which the presence of iodine with one positive valence is beyond doubt. A KJO solution was obtained by the action of molecular iodine on a solution of caustic potash cooled to 0–5°

Fig. 1

Figure 1: Fig. 1

Fig. 2

Figure 2: Fig. 2

(with dilution of 0.01 M J_2 in a 2% KOH solution) according to the equation: $KOH + J_2 \rightarrow KJ + HJO$. As can be seen from Fig. 1, in the absorption spectrum of the solution obtained two absorption bands are distinctly expressed, with λ_{max}224–226 m and λ_{max}350 m . Since the band at λ224–226 m belongs, as is known, to J^- (^{16}), the absorption band at λ350 m should be attributed to JO^-.

The iodine chloride solution was obtained by us according to the equation:

$$KJO_3 + 6HCl + 2KJ \rightarrow 3JCl + 3KCl + 3H_2O$$

As is evident from this equation, the resulting JCl solution contains KCl, which, as is known, promotes the stability of JCl in aqueous solutions and gives no absorption in the range 220-800 mμ. In the absorption spectrum of this solution (Fig. 2) there are two absorption bands, with λ_{max}226 mμ and $\lambda_{max}\lambda$350 mμ. The first, at λ226 mμ, is explained by the presence of J^- (KJ). The second band, at λ350 mμ, appears as a result of hydrolysis of JCl with formation of JO^- according to the equation: $JCl + H_2O \rightarrow 2H^{\cdot} + Cl' + JO'$. Dilution of 0.1 N JCl to 0.005 N JCl causes the appearance in the absorption spectrum of a third absorption band at λ460 mμ (Fig. 2).

Fig. 1. Absorption spectra of solutions: 1 –KJO (0.01 M J_2+2% KOH solution); 2 –0.01 M KJO_3; 3 –0.004 M KJO_4 (layer thickness 0.0063-5.00 cm)

Fig. 2. Absorption spectra of aqueous JCl solutions: a –0.01 N JCl; b –0.1 N JCl (layer thickness 0.0015-0.5 cm)

The absence in the spectra presented of a band at λ288–290 mμ indicates the possibility of the separate existence of absorption bands at λ288–290 mμ and λ350 mμ. We showed this further in the following way. An aqueous iodine solution containing 0.0083 g J_2 in 100 ml of water was subjected to dialysis through a cellophane membrane 40 μ thick. As can be seen from Fig. 3, in the absorption spectrum of the solution being dialyzed, 6 hr 40 min after the start of dialysis, two absorption maxima were observed at λ226 mμ and λ280 –282 mμ. The absorption maximum at λ350 mμ was entirely absent. In the spectrum of the dialysate, 5 hr after the start of dialysis, maxima were found at λ224–226 mμ and 282–284 mμ, as well as at λ440–455 mμ.

Fig. 3. Absorption spectra: a –aqueous J_2 solution subjected to dialysis; b –dialysate

Fig. 3

Figure 3: Fig. 3

Fig. 4. Absorption curves of systems: 1 –J_2–H_2O–H_2SO_4 (20%); 2 –J_2–H_2O –HNO_3 (15%); 3 –J_2–H_2O–$HClO_4$ (16%); 4 –J_2–H_2O–$HClO_4$ (8%), C_{J_2} –0.015% (layer thickness 0.0015-5.0 cm)

Figure 4: Fig. 4. Absorption curves of systems: 1 –J_2–H_2O–H_2SO_4 (20%); 2 –J_2–H_2O–HNO_3 (15%); 3 –J_2–H_2O–$HClO_4$ (16%); 4 –J_2–H_2O–$HClO_4$ (8%), C_{J_2} –0.015% (layer thickness 0.0015-5.0 cm)

The absorption band at λ350–360 mμ without the band at λ288–290 mμ was also obtained by us in the absorption spectrum of an aqueous iodine solution in the presence of starch taken in excess, which is in agreement with our data on the absorption spectrum of iodamylose solutions ([17]).

An absorption band with $\lambda_{\max}$350 mμ in the absence of a band at λ288–290 mμ was also observed by Gillam and Morton ([18]) in the absorption spectra of JCl solutions in acetic acid, chloroform, ethyl acetate, and HCl.

It follows from the above that absorption bands at λ288–290 mμ and λ350 mμ in the absorption spectra of iodine solutions and its compounds can exist separately. As our studies show in comparison with the literature data, $\lambda_{\max}$288 –290 mμ belongs to the complex anion J_3^-. The absorption band with $\lambda_{\max}$350 mμ, as shown above, is present in the spectra of solutions containing the complex anion JO^-, compris-

forming J^{+1}. The absorption band with $\lambda_{\max}$450-460 mμ in the absorption spectra of iodine solutions belongs, according to some assumptions ([7] and others), to the solvated iodine molecule; moreover, along with this band others are always present, which greatly complicates the interpretation of absorption at λ 450-460 mμ. In view of this, we decided to isolate in the absorption spectrum of an iodine solution the absorption band with $\lambda_{\max}$460 mμ. Taking into account that the reaction of interaction of halogens, in particular iodine, with water is reversible: $H_2O + J_2 \rightleftarrows HJ + HJO$, and that in an acidic medium there is a shift to the left with suppression of the formation of KJO_3, HJ, JO^-, etc., which create additional difficulties in deciphering the spectra, we investigated aqueous iodine solutions acidified with H_2SO_4, HNO_3, and $HClO_4$.

Fig. 4. Absorption curves of systems: 1 –J_2—H_2O—H_2SO_4 (20%); 2 –J_2—H_2O—HNO_3 (15%); 3 –J_2—H_2O—$HClO_4$ (16%); 4 –J_2—H_2O—$HClO_4$ (8%), C_{J_2}—0.015% (layer thickness 0.0015-5.0 cm)

As can be seen from Fig. 4, the absorption spectrum of the system J_2—H_2O—H_2SO_4 showed, as was to be expected, one absorption band with $\lambda_{\max}$465 mμ. In the spectrophotometric study of the system J_2—H_2O—HNO_3, two absorption bands were obtained with $\lambda_{\max}$300 mμ and $\lambda_{\max}$465 mμ. Since

λ_{max}300 mμ belongs, as is known ([19,20]), to the complex anion NO_3^-, this spectrum also gives an unambiguous solution to the problem. In the absorption spectrum of the third system, J_2—H_2O—$HClO_4$, at 8% acid content, two absorption bands were obtained with λ_{max}348 mμ and λ_{max}465 mμ. Since the absorption band at λ348 mμ, according to our data, belongs to the complex anion JO^-, we explained its presence in the spectrum by the insufficient concentration of $HClO_4$. Indeed, when the concentration of $HClO_4$ was doubled, then, as can be seen in Fig. 4, λ_{max}348 mμ disappeared completely, and in the spectrum there remained a single absorption band with λ_{max}460 mμ.

The obtaining in the absorption spectrum of an isolated absorption band at λ465 mμ is in complete agreement with the chemical reaction cited above and clearly establishes that the absorption band with λ460 mμ belongs to the J_2 molecule. Thus, the assumptions available in the literature ([7] and others) concerning the attribution of this absorption band to the solvated J_2 molecule receive experimental confirmation. In describing the absorption spectra of iodine solutions in all the works known to us on this question, the authors confine themselves to the formal attribution of the absorption band with λ_{max}460 mμ to the solvated J_2 molecule, supposedly possessing a symmetrical electronic structure. It seems to us that, for understanding the absorption spectra of iodine solutions, especially those that are colored, it is necessary to take into account the results of special studies of the polarization of the J_2 molecule in different solvents.

Dissociation of the iodine molecule has been assumed in a number of studies to explain experimental results (($\frown$21) and others). Of particular interest are data concerning iodine solutions in nonpolar solvents. Williams ($\frown$22, $\frown$23) obtained $\mu = 1.2$ for iodine in benzene and carbon disulfide. Fairbrother ($\frown$24), on the basis of determinations of μ for J_2 in various solvents, gives values of μ from 0.6 to 1.5 and concludes that the fact of polarization of J_2 in red and brown iodine solutions is beyond doubt. This is also confirmed by Kleinberg and Davidson ($\frown$25).

In view of the fact that the absorption band at λ460 mμ, isolated by us in the absorption spectrum of an iodine solution, can belong, as shown above, only to the J_2 molecule, and since only this single band accounts for the red-brown color of the solution, it may be concluded that the J_2 molecule in a 0.015% aqueous solution must be polarized. Since the biologically inactive ($\frown$11) complex ions JO_3^- and JO_4^-, containing J^{+5} and J^{+7}, respectively, do not absorb in the visible region of the spectrum ($\frown$13), just as the colorless compounds of trivalent iodine do not, it must be assumed that the J_2 molecule associated with the absorption band at λ460 mμ must contain J^{+1}. In that case the J_2 molecule in aqueous solutions should be represented in the form $n \cdot H_2O[J^{+1} \ldots J^{-1}]$. The absorption spectra of highly dilute aqueous solutions of JCl and JBr contain an absorption band at λ460 mμ, which also, apparently, is explained by the presence in the solution of polarized iodine molecules formed as a result of dissociation of dihalogen molecules.

Let us summarize the above: 1) in the spectra of solutions of iodine compounds, absorption bands with λ_{max}288–290 mμ and λ_{max}340–360 mμ may exist separately; 2) these absorption bands belong, respectively, to the complex anions J_3^- and JO^-; 3) the absorption band with λ_{max}460 mμ belongs to the polarized molecule $n \cdot H_2O[J^{+1} \dots J^{-1}]$; 4) solutions containing iodine compounds with valence $-1, +5, +7$ are colorless and devoid of biological activity; 5) the biological activity and coloration of iodine compounds are associated with the presence of iodine with one positive valence, J^{+1}.

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