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CHEMISTRY

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1960

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Abstract

Full Text

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V. O. MOKHNACH, S. N. ANDREEV, and E. V. STROGANOV

ON THE COLORATION OF IODINE SOLUTIONS IN OLEUM

(Presented by Academician I. I. Chernyaev, 3 IX 1959)

The coloration of iodine solutions in water and in organic solvents is the subject of numerous investigations. The study of the electronic absorption spectra of these solutions, which are very sensitive to changes in the chemical nature of the solvent, makes it possible to approach the question of the state in which J_2 molecules are found in the condensed phase.

Recently, aqueous solutions of J_2 having a blue coloration have been studied especially intensively. This coloration, due to the presence in the electronic absorption spectrum of iodine of a band with a maximum located at 580–650 mμ, is observed, as a rule, when organic high-polymer compounds are introduced into an aqueous J_2 solution. The works of Geyns ([1]), Freudenberg ([2]), and Kramer ([3]) make it possible to consider that the carriers of the blue coloration in such solutions are inclusion compounds formed through the interaction of J_2 molecules with molecules of high polymers.

The growing interest in blue iodine solutions is due not only to the fact that their investigation makes it possible to accelerate the development of the chemistry of compounds of the inclusion type, but also to the fact that the antimicrobial properties of iodine in the presence of high-polymer compounds are not only preserved, but often enhanced in comparison with those J_2 solutions in which the formation of inclusion compounds is excluded. This circumstance, as well as the practical nontoxicity of iodine–high-polymer compounds, determines the possibility of their external, peroral, and parenteral use as medicinal preparations of antiseptic action ([4]).

In some cases J_2 solutions have a blue coloration even in the absence of organic high polymers. In particular, J_2 solutions in oleum have a similar coloration. Symons ([5]) assumes that the blue coloration of J_2 solutions in oleum belongs to J^+ cations. The process of dissolution of iodine in oleum, according to Symons, is reduced to the oxidation of J_2 to J^+:

$$J_2 + SO_3 + 2H_2SO_4 = 2J^+ + 2HSO_4^- + SO_2 + H_2O.$$

If one takes into account that the electronic absorption spectrum of J_2 solutions

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Fig. 1. Absorption curves of iodine solutions in 96% H_2SO_4 and in oleum. Iodine concentration 0.0005 mol/liter. 1 –96% H_2SO_4; oleum contains: 2 –7% free SO_3, 3 –18% free SO_3, 4 –26% free SO_3, 5 –50% free SO_3; D_λ –optical density of the solution

Figure 1: Fig. 1. Absorption curves of iodine solutions in 96% H_2SO_4 and in oleum. Iodine concentration 0.0005 mol/liter. 1 –96% H_2SO_4; oleum contains: 2 –7% free SO_3, 3 –18% free SO_3, 4 –26% free SO_3, 5 –50% free SO_3; D_λ – optical density of the solution

in oleum is analogous to the absorption spectra of aqueous J_2 solutions in the presence of organic high polymers, then the interpretation of the coloration of blue J_2 solutions in oleum proposed by Symons should also be extended to aqueous iodine solutions. Thus, alongside Freudenberg and Kramer' s assumption that the carrier of the blue coloration in solutions is inclusion compounds, there arises a second interpretation of the coloration of these solutions: the carrier of the blue coloration is the J^+ cation.

The aim of the present work is to verify the correctness of the latter assumption. If, during the dissolution of J_2 in oleum, there occurs, as Symons assumes, oxidation of elemental iodine to J^+, and the carrier

the blue color is this cation, then the consequences of this should be: first, the evolution of SO_2 upon dissolution of metallic iodine in oleum; second, a decrease in the concentration of free SO_3 in the oleum after dissolving a weighed portion of iodine in it; third, invariance of the absorption spectrum of the iodine solution in oleum at varying SO_3 concentration, but at a fixed iodine concentration.

Indeed, if absorption of light with wavelength λ = 580–650 mμ occurs on J^+ cations, and the concentration of the latter in the solution is fixed as constant, then the optical density of the solution should remain practically unchanged when the concentration of free SO_3 is varied. A change in the concentration of SO_3 in oleum can lead only to a change in the weight amount of iodine capable of dissolving in a given weighed portion of oleum.

Fig. 1. Absorption curves of iodine solutions in 96% H_2SO_4 and in oleum. Iodine concentration 0.0005 mol/liter. 1 –96% H_2SO_4; oleum contains: 2 –7% free SO_3, 3 –18% free SO_3, 4 –26% free SO_3, 5 –50% free SO_3; D_λ –optical density of the solution.

Experiments carried out by us with the aim of studying the mechanism of dissolution of iodine in oleum containing from 5 to 50% free SO_3 showed that dissolution of J_2 is not accompanied by a change in the concentration of free SO_3. Upon dissolution of J_2 in oleum, no evolution of gaseous products is observed, including sulfur dioxide. This makes it possible to reject Symons' s assumption that the process of dissolving J_2 in oleum is a process of oxidation of iodine. We studied the absorption spectra of J_2 solutions in oleum using an SF-11 spectrophotometer. To prepare the solutions, iodine obtained from

a commercial preparation by double sublimation was used. Oleum containing 50% free SO_3 was prepared by dissolving triply distilled SO_3 in 96% H_2SO_4 of chemically pure grade. Oleum with a lower SO_3 content was prepared by diluting the concentrated solution with sulfuric acid. The iodine concentration in the solution was kept constant—0.0005 mol/liter; the concentration of free SO_3 was varied from 5 to 50%.

The absorption curves of these solutions, measured at a solution layer thickness of 1 cm, are given in Fig. 1.

As can be seen from Fig. 1, an absorption band with a maximum at 645 mμ appears in the spectrum of iodine solutions in oleum only at a concentration of free SO_3 exceeding 7%. The intensity of this absorption band, at an unchanged iodine concentration in the solution, increases sharply with increasing SO_3 concentration. What has been said above gives grounds to draw the following conclusion: the process of dissolving iodine in oleum is not an oxidation-reduction process in the course of which J^+ ions could be formed. Upon dissolution of iodine in oleum, iodine is dispersed in the bulk of the solution in the form of J_2 molecules. The carriers of the blue color of these solutions are···

are, contrary to Saimons' s assumption, not J^+ ions, but J_2 molecules, present in a state close to that in which they are found in the presence of organic high polymers in aqueous solutions.

The sharp increase in the viscosity of oleum with increasing content of SO_3 in it, the process of dissolution of solid SO_3 in concentrated sulfuric acid, which resembles the process of dissolving gelatin in water and is accompanied by swelling of the sulfuric anhydride, make it possible to suppose that high-polymeric molecules of polysulfuric acids are formed in oleum. It is very probable that iodine dissolved in oleum forms inclusion compounds with these molecules, similar to the compounds formed in the case of organic high polymers.

As the concentration of SO_3 in the solution increases, the concentration of high polymers also increases, and the number of J_2 molecules involved in the reaction of formation of inclusion-type compounds grows. In this connection the optical density of the solution at $\lambda = 645$ mμ increases sharply, while at the same time the optical density at $\lambda = 460$–500 mμ decreases, which is most probably due to a reduction in the number of J_2 molecules not entering into inclusion compounds. It should be noted that the same picture is also observed in the spectra of aqueous iodine solutions when the concentration of organic high polymers in them is increased.

If one assumes, following Cramer ([3]), that in the inclusion compounds formed by iodine with high polymers the electron shell of the J_2 molecules is strongly loosened and drawn toward the high-polymer molecule, then it may be expected that iodine–high-polymer molecules can be donors of J^+ cations.

We tested the correctness of this assumption by observing the changes occurring during electrolysis of J_2 solutions in oleum. The experiments were carried out by

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us in a glass apparatus assembled according to the scheme used for determining transport numbers by the Hittorf method ([6]). The iodine concentration in the anode and cathode compartments was measured by determining the optical density of samples taken from the apparatus at the wavelength $\lambda = 645$ mμ.

In all the experiments we carried out, during electrolysis of J_2 solutions in oleum there was observed a decrease in the iodine concentration in the anode compartment and an increase in the J_2 concentration at the cathode. This migration of iodine into the cathode compartment can be explained only by the movement of the J^+ cation, split off from the inclusion compounds.

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Received
31 VIII 1959

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Note: Figure translations are in progress. See original paper for figures.

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