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Dependence of the Electronic Absorption Spectra
of Aqueous Solutions of Iodine Monochloride
on the Conditions of Dilution and Storage Time

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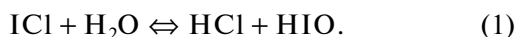
Abstract—The electronic absorption spectra of aqueous solutions of iodine monochloride ICl are studied. The spectra of as-prepared solutions display the absorption band associated with hydrated ICl molecules. An additional band indicating that molecular iodine was formed in the solution emerges in the spectrum as dissolution takes place. Only the band belonging to iodine monochloride remains in the absorption spectra, and no additional bands appear after chloride anions Cl^- are added to the solution. The absorption spectrum becomes more complex when ICl is dissolved in an alkaline medium. The band belonging to molecular iodine emerges in the spectra at low alkali concentrations, while being transformed to other shorter-wavelength bands at high alkali concentrations ($\text{pH} \geq 12$).

Keywords: iodine monochloride, electronic absorption spectrum

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INTRODUCTION

Iodine monochloride ICl is a compound consisting of two halogens that can change their valence from positive to negative in chemical reactions. It is generally acknowledged [1] that dissolution of iodine monochloride in cold water leads to formation of two acids in the solution, HCl and HIO:



Hypoiodous acid exists in extremely diluted solutions and exhibits amphoteric properties of both weak acid HIO and weak base IOH. It is extremely unstable and is easily decomposed in the presence of alkali or upon heating [2]. Hence, the question arises as to whether it is possible to detect hypoiodous acid in aqueous solutions of iodine monochloride according to its absorption spectra. There is no clear opinion regarding this problem in the literature. Mokhnach et al. [3–5] stated that there is an absorption band of the IO^- anion with maximum at 360 nm in aqueous solutions of molecular iodine and iodine monochloride, while in other studies this absorption band was ascribed to the complex triiodide anion I_3^- [6–8]. In addition, Kireev and Kuzema [9] reported no absorption of IO^- anion at 340–800 nm.

EXPERIMENTAL

Our absorption spectra were recorded by a PE-5400UV spectrophotometer (Ecochim, Russia) operating at 190–1000 nm in quartz cells with paths 10 mm long. The instrument recorded the absorbance of samples $A = \log(I_0/I)$, where I_0 is the intensity of the light that passed through a cell with the solvent, while I is the intensity of the light that passed through a cell with the solution under study. Pure water was used as our reference solution.

Bidistilled water and substances of pure for analysis grade without additional purification were used in this study.

The electronic absorption spectrum of the as-prepared aqueous solution of iodine monochloride ICl is shown in Fig. 1. The spectrum contains two bands. One band at 190–290 nm is very strong, while the second is less intense and has a maximum at 342 nm. According to reversible reaction (1), these bands can be ascribed to water molecules, molecules of iodine monochloride or hypoiodous acid, or Cl^- anions. Water molecules and hydrogen cation H^+ do not absorb light at the operating wavelengths of the spectrophotometer. The Cl^- chloride anion has a narrow absorption band in the short-wavelength portion of the spectrum with a maximum at 195 nm. We mea-

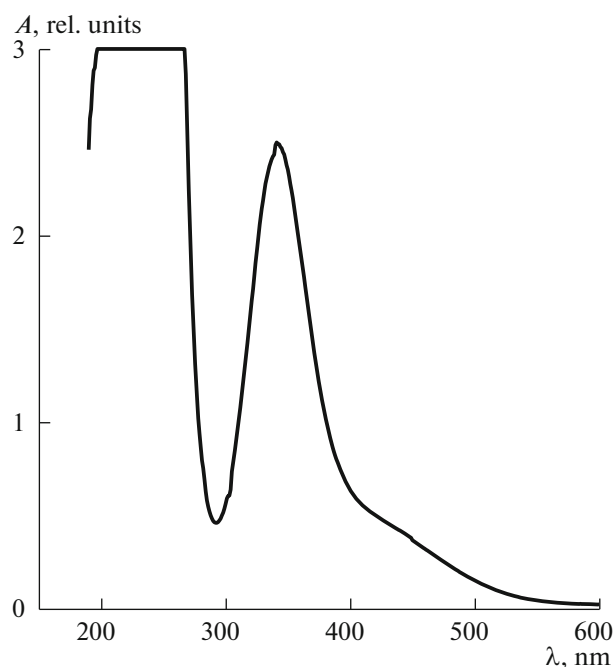


Fig. 1. Electronic absorption spectrum of an aqueous solution of ICl, recorded at a concentration of 0.8 wt %.

sured this by recording the electronic absorption spectrum of a diluted solution of hydrochloric acid HCl. Hence, the absorption band with the maximum at 342 nm could belong to undissociated iodine monochloride molecules, or to hypoiodous acid molecules, or hypoiodite IO^- anions.

A thorough analysis of the absorption spectra of aqueous solutions of iodine monochloride showed that they are very unstable. A short time after the solutions were prepared, they began to change strongly in color. While initially of a yellowish color, the solutions became deep brown after several minutes. Figure 2 shows the changes in the absorption spectra of these solutions over time. It shows only the portion of the spectrum that changed during our observations. It is clear from Fig. 2 that the intensity of the band with a maximum at 342 nm fell over time, but a band with a maximum at 452 nm emerged. The intensity of this band grew initially (up to curve 4) and then started to fall. A reddish brown precipitate formed on the bottom of the spectrophotometric cell at the end of the measurements. The formation of the precipitate was related to the reduced intensity of the bands in the absorption spectrum of ICl solutions (Fig. 2, curves 5 and 6).

Further observation of the spectra of ICl aqueous solutions showed that they change not only over time but also upon dilution. Figure 3 shows the spectra of several solutions with different concentrations of iodine monochloride. The spectrum of the solution with the highest ICl concentration (curve 1) contains

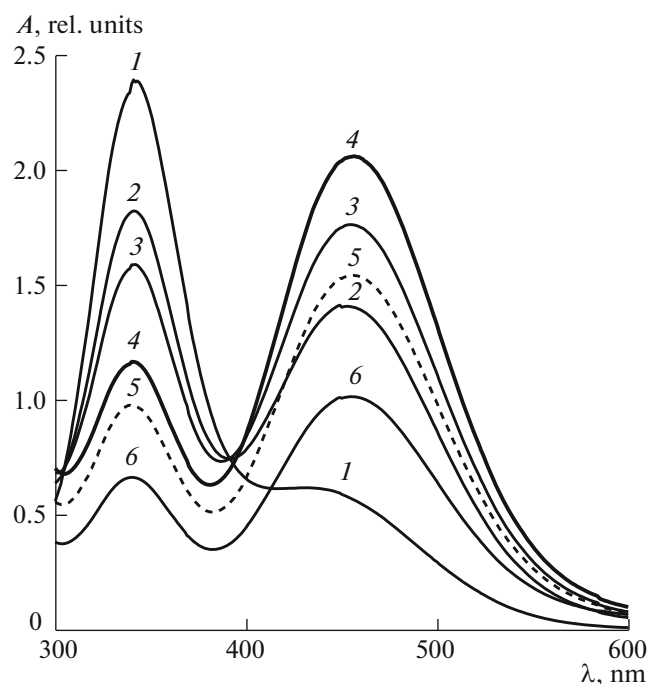


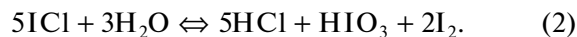
Fig. 2. Electronic absorption spectra of ICl in water, recorded at different times since the solution was prepared. The solution's concentration was 0.8 wt %. Spectrum 1 was recorded 5 min after the sample was prepared; spectrum 2, after 30 min; spectrum 3, after 60 min; spectrum 4, after 3 h; spectrum 5, after 5 h; and spectrum 6, after 7 days.

an intense band with a maximum at 342 nm. In less concentrated solutions, the intensity of the band at 342 nm falls, but a band at 452 nm emerges. The band at 342 nm disappears completely at a concentration of 0.1 wt % (curve 4), and only the band with the maximum at 452 nm is left. The broad band at 190–290 nm observed in the spectra of concentrated solutions becomes appreciably narrower with a maximum at 214 nm (curve 5) upon dilution.

RESULTS AND DISCUSSION

The variations in the absorption spectra of iodine monochloride solutions during storage and upon dilution are indicative of processes that change the chemical composition of these compounds. Based on the obtained data, we propose the following mechanism: ICl molecules start to dissociate once they are in water. This process is slow at room temperature, so at first the spectrum displays only the band belonging to iodine monochloride. More and more iodine cations I^+ accumulate in the solution as water molecules break ICl molecules into ions; these cations gradually form iodine molecules, as is indicated by the emergence of the band with the maximum at 452 nm. It was shown in [3–5] that this band is due to the absorption of hydrated iodine molecules I_2 . We believe the processes

that occur during the dissolution of ICl in water are determined by a different reversible equation, rather than by Eq. (1):



It was claimed in [1] that iodine monochloride can be dissolved in hot water via Eq. (2); however, an analysis of the spectra shown in Figs. 2 and 3 gives grounds for believing that the same reaction occurs at room temperature, albeit slowly. In order to verify this, we simultaneously recorded the spectra of two samples. The first sample was prepared by dissolving a small amount of iodine monochloride (0.8 wt %) in cold water at 5°C. As soon as the solution was prepared, we recorded its absorption spectrum. The resulting spectrum had the same form as the absorption spectrum of the as-prepared solution in room-temperature water that is shown in Fig. 1. The solution prepared in cold water was stored in a refrigerator at 5°C, and sampled for spectral measurements after certain periods of time. We recorded a series of these spectra, and they were identical to those shown in Fig. 2. The intensity of the band at 342 nm gradually fell in these spectra, while the band at 452 nm grew stronger.

We then prepared the second sample with the same amount of iodine monochloride dissolved in hot water at 80°C. This solution immediately became reddish brown; its spectrum was qualitatively the same as curve 4 in Fig. 3. Iodine monochloride is rapidly converted to molecular iodine in hot water.

An analysis of the absorption spectra of the solutions prepared in water with different temperatures showed that iodine monochloride dissolves via Eq. (2) rather than Eq. (1). Hydrated ICl molecules form first in the solution, followed by the formation of iodine ions whose accumulation in the solution produces molecular iodine I₂ and hypoiodic acid HIO₃. The absorption band of molecular iodine with a maximum at 452 nm emerges in the spectrum, while the intensity of the band at 342 nm belonging to ICl molecules falls. The spectra also contain bands belonging to Cl⁻ and IO₃⁻ ions. These ions absorb at 190–250 nm, and this band can be recorded in extremely diluted solutions. In Fig. 3, this band is visible in spectrum 5 as a short-wave component with the maximum at 214 nm.

We verified that the band at 342 nm belongs to undissociated molecules of iodine monochloride. It follows from the theory of solutions that the equilibrium of a chemical reaction can be shifted in either direction by changing its conditions. Since reaction (2) produces chloride anions Cl⁻, the equilibrium can be shifted to the left (i.e., the dissociation of ICl molecules can be slowed or stopped) by adding chloride anions Cl⁻ to the reaction mixture. In order to verify this, we prepared iodine monochloride solutions in a 0.1 M solution of hydrochloric acid HCl at different concentrations. The spectra of these solutions was sta-

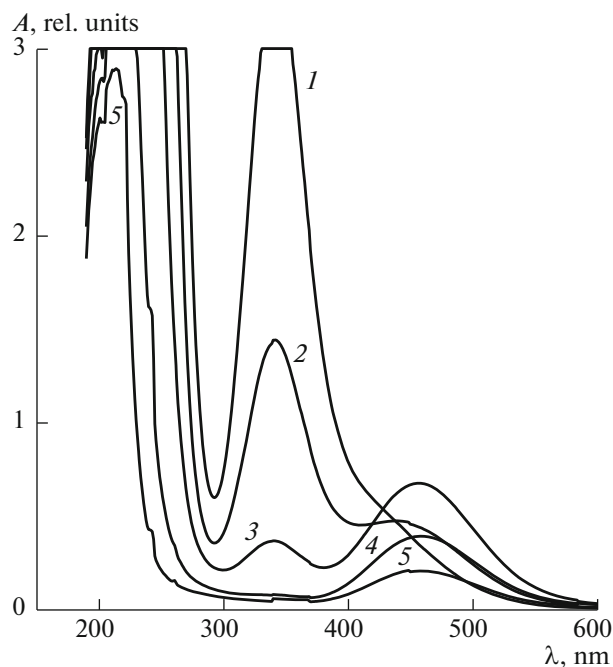


Fig. 3. Electronic absorption spectra of the as-prepared ICl solutions in water at concentrations of (1) 1, (2) 0.5, (3) 0.25, (4) 0.1, and (5) 0.05 wt %.

ble both over time and when diluted. In these spectra, the intensity of the band with the maximum at 342 nm falls, while no additional band at 452 nm emerges. This indicates that the equilibrium of reaction (2) shifts toward the left in a medium with a higher concentration of Cl⁻ anions and iodine monochloride does not dissociate into individual ions in these solutions. Inhibition of the dissociation of ICl molecules in solutions with greater concentrations of Cl⁻ anions is also observed in NaCl solutions. The absorption spectra of these solutions are similar to those of ICl solutions in hydrochloric acid. Hence, the hypothesis that the absorption band with the maximum at 342 nm belongs to undissociated molecules of iodine monochloride could be correct.

The equilibrium of Eq. (2) can be shifted to the right in order to accelerate the dissociation of iodine monochloride. This can be done by adding a compound that binds chloride anions formed during the dissociation of ICl, thus reducing their concentration in the solution. An alkali can be one such compound. KOH added to an aqueous solution of iodine monochloride yields KCl salt and shifts the equilibrium of reaction (2) to the right. This results in additional dissociation of ICl molecules and an additional release of molecular iodine. Figure 4 shows the spectra recorded for these solutions. Curve 1 shows the absorption spectrum of an aqueous solution of ICl at a concentration of 0.8%. In features the absorption band belonging to hydrated ICl molecules and a small

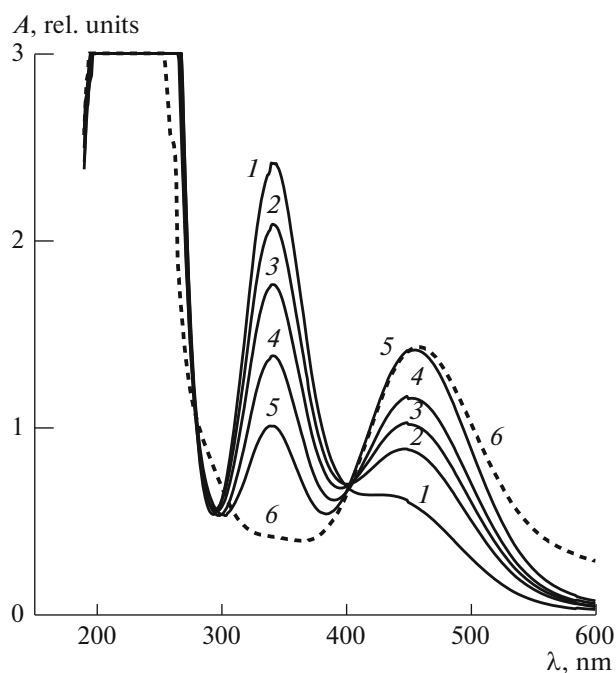


Fig. 4. Electronic absorption spectra of an aqueous solution of ICl with 0.1 M KOH solution added at different concentrations: (1) 0.8 wt % ICl with no added alkali; ICl with (2) 1/20, (3) 1/8, (4) 1/4, (5) 1/3, and (6) 1/2 vol fraction of alkali.

shoulder at the wavelengths where molecular iodine absorbs. Curve 2 corresponds to a solution 1/20 wt fraction of added 0.1 M KOH solution. Curves 3–6 are the absorption spectra of solutions with increasing alkali content. It follows from the graphs in Fig. 4 that greater alkali concentrations accelerate the dissociation of iodine monochloride and its conversion to molecular iodine. This is indicated by the falling intensity of the band with the maximum at 342 nm and the growth of the band at 452 nm. Curve 6 shows that almost no ICl molecules remained in the solution.

A solution with a high alkali content (50 wt %) was set aside so we could monitor its stability over time. The absorption spectra of the solution are shown in Fig. 5. Approximately 5 min later, one more band emerged in the spectrum of this solution in addition to the absorption band belonging to molecular iodine (452 nm) (Fig. 5, curve 2), and two bands emerged 45 min later (Fig. 5, curve 3). The newly emerged bands had maxima at 287 and 352 nm. None of these bands belonged to the absorption of iodine monochloride, whose maximum is at 342 nm (Fig. 5, curve 5). The newly emerged bands coincide with the absorption spectra of the complex triiodide anion I_3^- reported in [6–8]. The molecular iodine that forms in an alkaline medium thus gradually dissociates into I^- ions

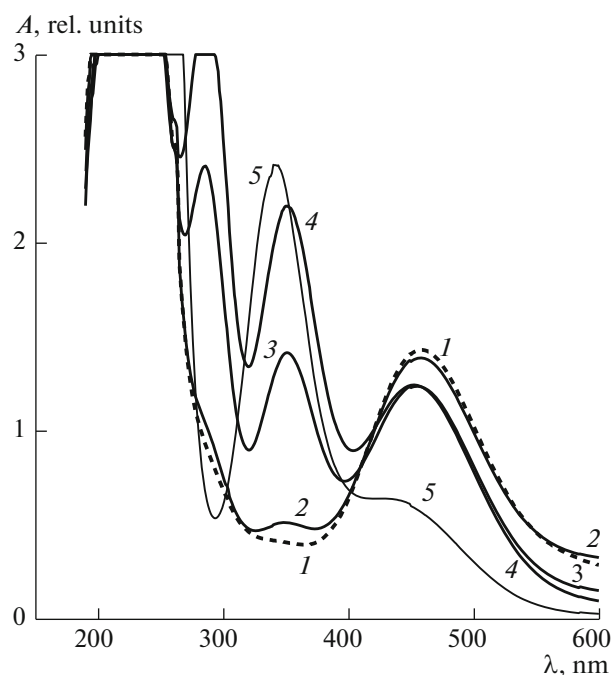


Fig. 5. Electronic absorption spectra of an aqueous solution of ICl with 1/2 vol fraction of 0.1 M KOH solution added, depending on the storage time: (1) at the time of preparing, (2) after 5 min, (3) after 45 min, (4) after 1.5 h, and (5) reference sample of 0.8 wt % of ICl with no added alkali.

that interact with iodine I_2 molecules to form complex triiodide I_3^- anions.

The situation is even more interesting if iodine monochloride is dissolved in alkali of higher concentrations. As ICl is diluted with KOH solution having pH 12, the solution first turns reddish brown (almost black), then gradually becomes lighter as the solution turns yellow-brown and eventually becomes virtually transparent after several minutes. The absorption spectra of these solutions go through several stages. In the beginning, they feature absorption bands with the maxima at 287 and 352 nm. These bands become less intense over time and eventually disappear. Only one short-wave band associated with the absorption of IO_3^- anions remains. We may hypothesize that the dissolution of iodine chloride in a strongly alkaline medium results in the rapid formation of molecular iodine, which then interacts with iodide I^- anion to produce triiodide anion I_3^- . The iodides are then oxidized to become iodates IO_3^- , whose absorption spectrum lies in the UV region at approximately 210 nm, and this is why the solution becomes lightly colored.

We made comparative measurements of the absorption spectra of ICl and molecular iodine in water and CCl_4 in order to verify the absorption band with the maximum at 342 nm that emerges in aqueous

Wavelengths (nm) corresponding to the maxima of the absorption bands of iodine and iodine monochloride molecules in water and carbon tetrachloride

Solvent	Water	Carbon tetrachloride
I ₂	452	515
ICl	342	455

solutions belongs to undissociated molecules of iodine monochloride. Carbon tetrachloride is a neutral solvent for these compounds; hence, we would expect that spectral bands belonging to virtually free molecules (such as molecules in gas state) emerge in it. Indeed, the spectra of ICl and I₂ in CCl₄ feature one absorption band each and are very similar. The parameters of these spectra are listed in the table. The absorption spectra of aqueous solutions of these compounds have a more complex structure but contain bands that are responsible for the absorption of hydrated molecules. These bands in water are shifted to shorter wavelengths compared to those in ICl, since polar water molecules affect the forces of interaction between valence electrons and the nuclei of the atoms of which they consist. In addition, the absorption spectra of ICl solutions are additionally shifted to shorter wavelengths due to the stronger binding of paired electrons in ICl molecules, compared to that in I₂ molecules (see table). A comparison of the absorption spectra of molecular iodine and iodine monochloride thus provides additional arguments for stating that the band with the maximum at 342 nm in aqueous solutions of iodine monochloride belongs to hydrated ICl molecules.

CONCLUSIONS

Aqueous solutions of iodine monochloride were studied spectroscopically. The resulting spectral characteristics of these solutions allow us to describe the mechanism of dissolution of iodine monochloride in water: First, hydrated ICl molecules form in the solution and gradually dissociate into I⁺ and Cl⁻ ions. The

accumulation of I⁺ cations in the solution leads to their association and the formation of molecular iodine. Iodine monochloride is converted to molecular iodine as a result of the gradual release of chlorine from the solution. This process can be slowed or inhibited completely by adding chloride anions Cl⁻ to the reaction mixture from an external source. Conversion can also be accelerated by heating the solution or adding an alkali. In alkaline environments, iodine monochloride is first converted to molecular iodine and then to triiodide I₃⁻, which is subsequently oxidized to iodate IO₃⁻.

Our study also gives grounds for stating that the dissolution of iodine monochloride in water takes place according to Eq. (2). The absorption band with the maximum at 342 nm that emerges in the solution is due to hydrated molecules of iodine monochloride ICl rather than to IO⁻ anions, as was erroneously suggested in [3–5].

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