Absorption Spectra of Quinoline Adsorbed on Nickel Plates in an Aqueous Solution

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In a previous paper,[1] a remarkable decrease in the intensity of the absorption bands of thiourea and potassium iodide caused by the presence of nickel plates in aqueous solutions was observed and strong adsorptions on the metal was deduced. In the present investigation, the absorption spectrum of quinoline adsorbed on nickel plates was observed by means of the technique already reported.[1]

The absorption spectra of a solution of quinoline (b. p. 83.5—84.0°C/3 mmHg) in purified water, as measured with a reflection cell and a transmission cell, are shown in Fig. 1. In this figure, the absorption spectrum of an isooctane solution is also shown for purposes of comparison. The relative intensities of a peak at 220 mμ and shoulders at 233 mμ and 212 mμ evidently decreased the reflection measurements.

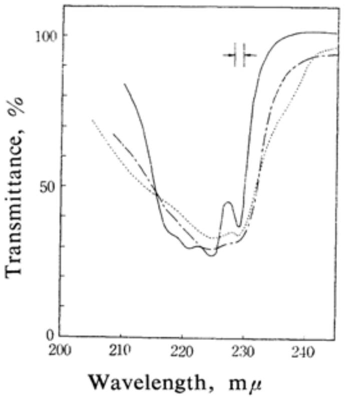

Fig. 1. Absorption spectra of quinoline in purified water measured with the reflection and transmission methods.
-·-· : reflection (concentration of quinoline: 1.70×10^{-5} mol./l.)
···· : transmission (concentration of quinoline: 1.70×10^{-1} mol./l.)
—— : in isooctane (concentration: 2.09×10^{-5} mol./l.)

The nickel plates were probably covered with oxide or hydroxide, which could dissolve in the aqueous solution because the water contained carbonic acid. In consequence, the concentration of hydrogen ions in the solution probably diminished as a result of the immersion of the nickel plates, and the decrease in the hydrogen ion concentration might produce an intensity reduction of some absorption bands.

The spectra of quinoline in aqueous solutions containing hydrogen ions at various concentrations were observed (Fig. 2). The shoulder at 233 mμ, decreased in relative intensity with the decrease in the hydrogen ion concentration and can be assigned to quinolinium ions. Furthermore, the absorption spectrum of aqueous solution of quinoline was measured after the withdrawal of nickel plates which had been dipped in the solution for about twenty minutes a relative intensity reduction of the shoulder at 233 mμ was found.

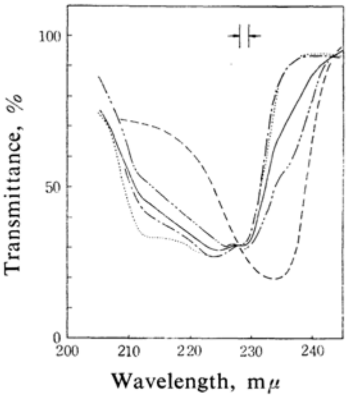

Fig. 2. Fffect of the hydrogen ion concentration on the spectrum of quinoline in aqueous solutions.
Concn. quinoline: 2.02×10^{-5} mol./l.
······ : in 1×10^{-2} N NaOH
-·-· : in 1×10^{-3} N NaOH
—— : in purified water
-··- : in 1×10^{-5} N HCl
--- : in 1×10^{-3} N HCl

On the basis of the results mentioned above, the intensity reduction of the shoulder at 233 mμ observed in the reflection measurement can be concluded to be due to the reduction of the quinolinium ion concentration in the solution as a result of the dissolution of nickel

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[1] W. Suëtaka, This Bulletin, 37, 1121 (1964).

oxide or hydroxide, accompanied by a decrease in the hydrogen ion concentration.

The experimental results reported in the preceding paragraphs indicate that the decrease in the relative intensity of the peak at 229 $\mathrm{m}\mu$ and more particularly that in the intensity of the shoulder at 212 $\mathrm{m}\mu$ observed in the reflection measurements cannot be explained on the basis of the decrease in the hydrogen ion concentration in the solution. Since the complex formation of quinoline with nickel salts has been reported,[2] it may be considered that the spectral change in question arises from the complex formation in the solution. The spectrum of quinoline in an aqueous solution containing nickel sulfate of a relatively high concentration (1.0 mol./l.)* has shown, however, only a slight increase in the relative intensity of the shoulder at 212 $\mathrm{m}\mu$. It must be added that the shape of the absorption band due to quinoline in water did not change with the dipping of nickel plates in the solution, except for the minor variation produced by the decrease in quinolinium ion concentration. The change in the spectrum observed in the reflection measurements, therefore, cannot be the result of the formation of a quinoline-nickel salt complex in the solution.

As a result of the investigation described above, the change in the shape of absorption band in question can be attributed to the overlapping of an absorption band of adsorbed quinoline and a band of the same compound in solution. The absorption band of adsorbed quinoline is assumed to have the shape shown in Fig. 3. In drawing the assumed band, the shape of the band due to quinoline in solution is supposed to be the same as that observed for the aqueous solution of quinoline after the withdrawal of the dipped nickel plates. The similarity in the band shape between the hypothetical absorption band of adsorbed quinoline and that of quinolinium ions is very interesting, because it suggests that the adsorption might occur at the acid center of the surface oxide on the nickel plates.

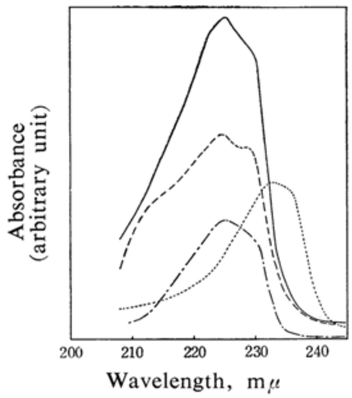

Fig. 3. Assumed absorption band of adsorbed quinoline.
——: absorption band observed with the reflection cell
- - -: quinoline in solution
-·-·-: adsorbed quinoline
······: quinolinium ion

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* The pH-value of the solution was adjusted to 5.0 by the addition of sodium hydroxide so as to reduce the quinolinium ion concentration.

[2] G. C. Bhattacharya and P. C. Sinha, *J. Indian Chem. Soc.*, **30**, 485 (1953).