Absorption Spectra of 1,4-Diaminoanthraquinone in Mixed Solvents of Carbon Tetrachloride and Ethyl Alcohol

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It was previously discussed by Arban1,2) that the absorption spectra of methylene blue in mixed solvents of water and organic solvents showed characteristic shifts which might be attributed to the change in aggregation states of the dye ion in the mixed solvents.

In this paper, characteristic changes in spectra of 1,4-diaminoanthraquinone (DAA) in mixed solvents are reported. The spectra were measured by means of a Hitachi recording spectrophotometer model EPR and all the measurements were carried out with the 1.0×10^{-4} mol./l. solution of DAA. As shown in Fig. 1, the spectrum of DAA in carbon tetrachloride has one absorption peak I at

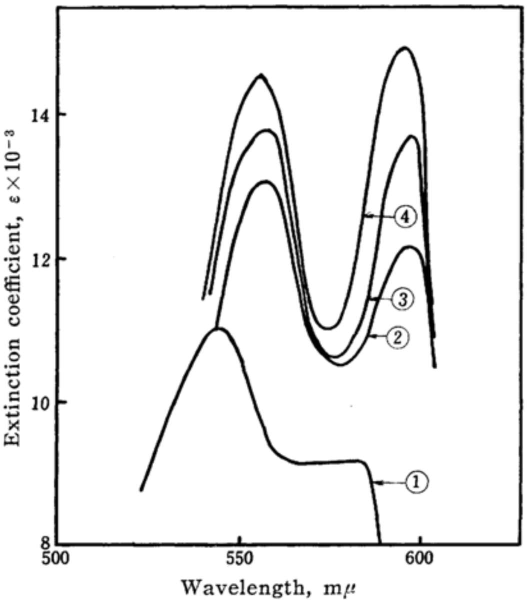

Fig. 1. Absorption spectra of 1,4-diaminoanthraquinone in mixed solvents; in CCl_4 ①, in CCl_4 80%: C_2H_5OH 20% ②, in CCl_4 40%: C_2H_5OH 60% ③, and in C_2H_5OH ④.

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1) Kh. L. Arban, *Izves. Acad. Nauk USSR, Series Phys.*, **22**, 443 (1956).

2) Kh. L. Arban and N. V. Ivanova, *Doklady Acad. Nauk USSR*, **114**, 1043 (1957).

544 mμ and one horizontal shoulder at 565$\sim$584 mμ. On addition of ethanol to the solution, the latter changes to the second peak II, and simultaneously a shift of the peak location occurs. With the increasing ethanol concentration, the extinction coefficient at peak II increases rapidly as compared with that at peak I, and consequently, the ratio of both coefficients $r=\varepsilon_{II}/\varepsilon_{I}$ increases. The spectral data of DAA in various organic solvents are given in Table I. Solvents which belong to the first group are non-polar and the spectra in these solvents show one maximum and one shoulder, and a small value of r. In contrast to this, the spectra in solvents of the second group which are polar and have hydrogen-bonding ability, show the two absorption peaks and a large value of r.

TABLE I. ABSORPTION SPECTRA DAA IN VARIOUS SOLVENTS

Solvents	Refractive Index	Absorption peak I mμ	r
The first group			
n-Hexane	1.38	534	0.83
Cyclohexane	1.43	539	0.82
Carbon tetrachloride	1.46	544	0.83
Benzene	1.50	545	0.85
The second group			
Methanol	1.33	551	0.98
Ethanol	1.36	554	1.03
Acetic acid	1.37	552	1.03
Glycerine	1.47	557	1.05
Pyridine	1.51	558	0.94

An addition of ethanol to pure solvent exerts another effect on the spectrum. When the concentration of ethanol is increased, the location of the peak shifts to longer wavelengths at first and via the point of the maximum shift return back to shorter wavelengths. Similar shifts are also observed with methanol and others. As examples, absorption curves in mixed solvents of carbon tetrachloride with methanol and ethanol are shown in Fig. 2.

This characteristic change can not be explained by the simple solvent-effect (Kundt's law) alone, because the law says only that the larger the refractive index of solvent is, the larger the degree of shift to longer wavelengths becomes. DAA satisfies Beer's law both in ethanol and in carbon tetrachloride, and disperses as the monomer or a uniformly aggregated particle. Arban's suggestion for methylene blue does not explain the case of DAA, if it can be assumed that dispersed particles are monomers in both solutions.

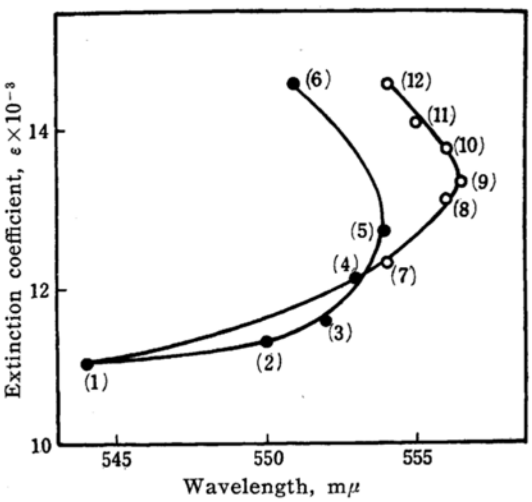

Fig. 2. Effects of solvent composition on wavelength and extinction coefficient at peak I.

—●— CH_3OH-HCl_4 mixtures
(1) 0 : 100, (2) 4 : 96, (3) 8 : 92
(4) 20 : 80, (5) 40 : 60 (6) 100 : 0
—○— C_2H_5OH-CCl_4 mixtures
(1) 0 : 100, (7) 6 : 94, (8) 20 : 80
(9) 40 : 60, (10) 60 : 40, (11) 80 : 20
(12) 100 : 0

Spectral differences such as a number of peaks, the ratio of extinction coefficients and characteristic changes of locations of peaks indicate that mutual interaction between DAA and carbon tetrachloride (the first group) differs from that between DAA and ethanol (the second group). The essential difference in the interaction has been studied by the present author from the view points of solubility. The detailed discussion on the results will be reproted elsewhere.

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