SPECTROCHEMICAL STUDIES OF HYDROXYAZO-COMPOUNDS. PART VI.[1]

By **Taku UEMURA and Shozo TABEI.**

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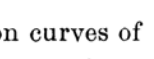
One of the writers[2] has already discussed on the tautomeric transformations of some hydroxyazo-compounds and assigned them different formulas which were derived from the results of alkaline reactions.

We have now to consider the position of the hydroxyl-group with regard to the azo-group, for in a previous report[3] we came to the conclusion that the shape of the absorption bands is probably altered by the insertion of the methyl-group into a benzene nucleus.

But we intend to take another point of view owing to the position of the hydroxyl-group which is included in these compounds. Though our last two papers described this assumption, we shall here again confirm this observation.

Experimental. m-Acetylamino-o-hydroxyazobenzene[4] clearly represents two bands in its absorption curve (Fig. 1). The auxochromic power of the amino-group is nearly lost by acetylation and this is easily understood in comparing the absorption curves of azobenzene  , p-acetylaminoazobenzene[5]  and

(1) Read before the Chemical Society of Japan, February 18, 1928.

(2) Uemura, Yokojima and Tan. this journal, **1** (1926), 260; Uemura, Yokojima and Endo, ibid., **2** (1927), 10 & 48; Uemura and Tabei, ibid., **2** (1927), 229 & 249.

(3) This journal, **2** (1927), 51.

(4) Hewitt and Ratcliffe, *J. Chem. Soc.*, **101** (1912), 1765.

(5) Berju, *Ber.*, **17** (1884), 1400.

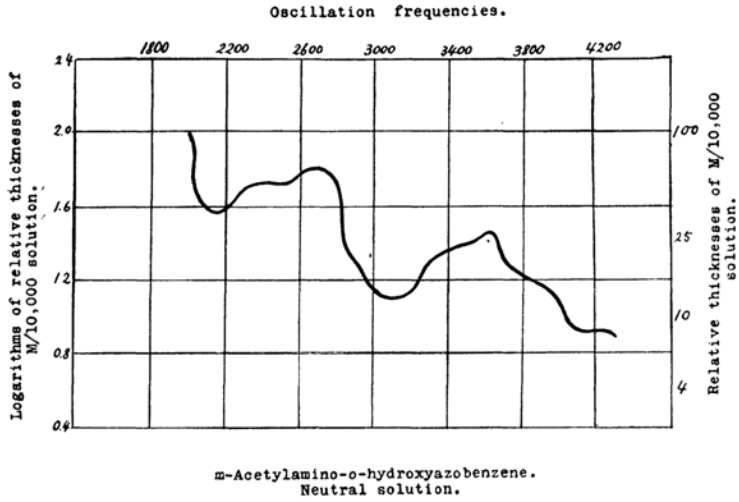
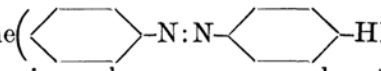


Fig. 1.

p-aminoazobenzene()(Fig. 2). The absorption curve of p-acetylaminoazobenzene approaches to that of azobenzene in the alcoholic solution, while on the contrary p-aminoazobenzene shows the considerable bathochromic influence in its curve. This proves that the auxochromic effect of the amino-group is remarkably weakened when acetylated.

Hence we may conclude that the absorption curve given by the neutral solution of m-acetylamino-o-hydroxyazobenzene is not caused by the acetylamino-group but by the hydroxyl-group. So far as the our studies are concerned, o-hydroxyl with respect to the azo-group has always two absorption bands.

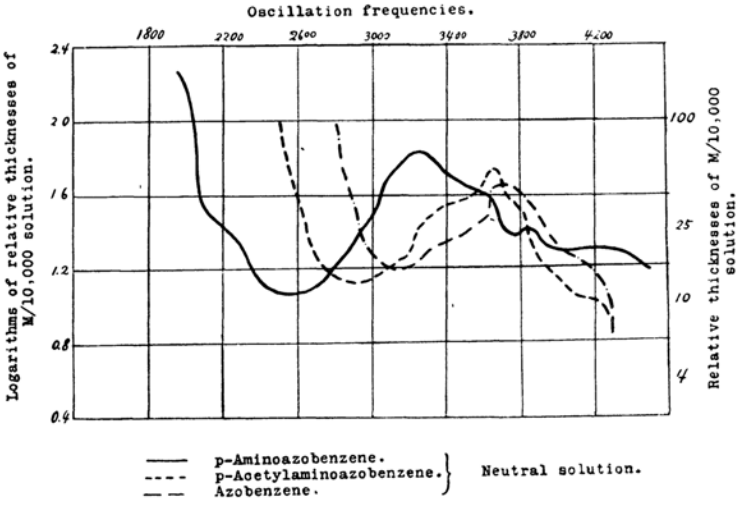


Fig. 2.

The following hydroxyazo-compounds, which appeared in previous papers, have two absorption bands on account of the o-hydroxyl-group with respect to the azo-group.

Benzeneazo-p-cresol.[1]
p-Nitrobenzeneazo-p-cresol.[1]
o-Tolueneazo-p-cresol.[2]
m-Tolueneazo-p-cresol.[2]
p-Tolueneazo-p-cresol.[2]
o-Nitrobenzeneazo-p-cresol.[3]
m-Nitrobenzeneazo-p-cresol.[3]

Summary.

1. The o-hydroxyl-group in hydroxyazo-compounds gives rise to two bands in their absorption curves.

2. The methyl-group shows perhaps no influence upon the shape of the absorption curves of hydroxyazo-compounds.

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Dyeing Department, Tokyo Higher Technical School.

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(1) This journal, **1** (1926), 262 & 265.
(2) Ibid., **2** (1927), 233 & 234.
(3) Ibid., **2** (1927), 256.