Thermochromism in 5-Arylazo-8-quinolinols Diluted with Sodium Chloride

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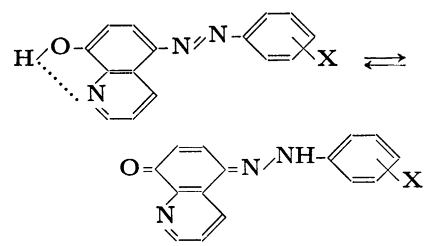
Our earlier work on the diffuse reflection spectra of 1-arylazo-2-naphthols diluted with sodium chloride disclosed that the compounds in this solid two-component system exist as mixtures of the azo and hydrazone tautomers.[1] The movement of the equilibrium upon an elevation of the temperature was well demonstrated by the change in the spectrum. However, no appreciable thermochromism was noted, because the absorption bands of the two tautomers are rather coalescent. Here, we wish to report that 5-arylazo-8-quinolinols;



the synthesis of which was described as early as 1888 by Matheus,[2] are distinctly thermochromic when diluted with sodium chloride.

The compounds were prepared by the usual diazo-coupling reactions with 8-quinolinol. The derivatives carrying one of the following substituents in the *o*-, *m*-, or *p*-position on the phenyl ring were synthesized: methyl, chloro, methoxy, and nitro. They were easily purified by vacuum sublimation. The method of measuring the reflection spectra was the same as that described in our previous paper.[1]

For example, pure 5-(*m*-anisylazo)-8-quinolinol is orange. It turns yellowish orange upon dilution with sodium chloride. As is shown in Fig. 1, the spectrum consists of three bands, located at about 360—70 mμ, 430—40 mμ, and 540 mμ; among those, the band at 440 mμ dominates at room temperature. Upon the elevation of the temperature, the relative intensity of this band is markedly diminished at a concentration of 0.01%. The mixture is red-colored at 100°C. The direction of the spectral change upon heating in 5-phenylazo-8-quinolinol and all the *m*- and *p*-substituted compounds examined is the same as has been mentioned above. Nevertheless, various spectral features are observed because of the large difference in the relative intensities of the bands. Among the *o*-substituted compounds, only 5-(*o*-anisylazo)-8-quinolinol shows an appreciable spectral change upon the elevation of the temperature. Here, the direction of the change is the opposite of that observed in the others.

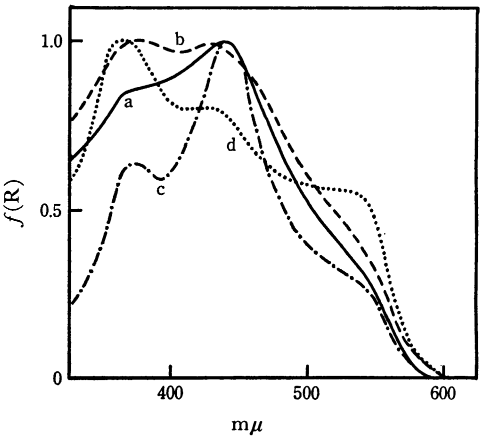


Fig. 1. Spectra of 5-(*m*-anisylazo)-8-quinolinol diluted with sodium chloride; (a) 1% at room temperature, (b) 1% at 100°C, (c) 0.01% at room temperature, and (d) 0.01% at 100°C. The maximum is arbitrarily taken as 1.00 in each spectrum.

It is likely that the azo tautomer is favored by the intramolecular hydrogen bond in the quinolinol part, the presence of which is suggested by the ease of vacuum sublimation. Therefore, the band outstanding in most of the room-temperature spectra may be ascribed to the azo tautomer. Further work is being planned to attempt a more conclusive assignment of the absorption bands to the possible tautomers.

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[1] C. Dehari, Y. Matsunaga, and K. Tani, This Bulletin, **43**, 3404 (1970).

[2] J. Matheus, *Ber.*, **21**, 1644 (1888).