STUDY OF THE ACID IONIZATION OF CERTAIN REAGENTS – bis-azo derivatives of CHROMOTROPIC ACID


The acid ionization of mono- and bis-azo derivatives of chromotropic acid – well-known photometric reagents – is discussed in a number of studies [1-4]. However, the question of the sequence of ionization of the acid groups, in particular, the hydroxy groups of the naphthalene and benzene rings, upon the resolution of which depend the concepts of the mechanism of complex formation and the nature of the metallochrome properties of the reagents, remains in dispute [5, 6].

EXPERIMENTAL

The present work discusses the ionic states and electronic structure of certain bis-azo derivatives of chromotropic acid, both containing and not containing salt-forming substituents with the general formula

in their benzene rings. The resolution of the question raised was accomplished on the basis of spectro-photometric and potentiometric data, bringing in the simple MO LCAO method of Hückel for certain reagents [7]. This method had been used earlier for the reagent arsenazo (I) [8, 9]. The influence of the concentration of the solutions, the nature of the solvents, and the temperature on the absorption spectra of the reagents were also studied.

Fig. 1. Absorption spectra of reagent I in water at pH: 1) 3.1 and 7.1; 2) 8.5; 3) 9.0; 4) 9.9; 5) in 95% acetone at pH 2.3 and 7.2. [HR] = 2.24·10^{-5} M; cuvette 10 mm.

Fig. 2. Absorption spectra of reagent XI in water at pH: 1) 4.4; 2) 9.4; 3) 12.0; 4) in 30% NaOH. [HR] = 2.30·10^{-5} M; cuvette 10 mm.
Certain spectrophotometric characteristics of the reagents and the results of a potentiometric titration are cited in Table 1. As can be seen from Table 1 and Fig. 1, in the interval pH 1-8 the absorption spectra of the reagents are invariant and have two long-wave maxima. Such spectra are characteristic of the