Consideration of the entropic factor should apparently diminish the difference between the hydration energies for the region near the electrode and the bulk of the solution. This is evidenced by numerous data from calculations of the potentials of the mean strength of various interacting systems in solutions [11].

LITERATURE CITED

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INFLUENCE OF ELECTROLYTES ON THE ASSOCIATION PROCESSES OF DISSIMILAR DYES

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The influence of an electrolyte on the association processes of dissimilar dye molecules has been investigated. It has been established that the degree of heterogeneous association depends on the concentration of LiCl. The bonding energy of the molecules in a complex has been determined from temperature measurements of the luminescence-spectroscopic characteristics of multiproportion dye solutions.

Multicomponent solutions of luminescent substances have been used to expand the energy and spectral ranges of the emission of dye lasers [1, 2]. The formation of nonluminescent associates of dissimilar dye molecules, which become fluorescence-quenching centers and worsen the lasing parameters, is possible in such systems [3]. The self-association pro-
cesses of solute molecules is strongly influenced by electrolytes [4]. Therefore, there is
interest in the study of heterogeneous association processes under conditions under which
changes in the strength of the local fields of the molecules participating in the complexation
processes and in energy of their interactions occur when an electrolyte is added.
In addition, the investigation of the influence of salts on the luminescence-spectroscopic
characteristics of multicomponent systems is of interest in connection with the wide use of
electrolytes in technology (electroluminescent and laser devices). In this communication we will present the results of an investigation of the influence of an electrolyte on the
development of the heterogeneous association processes occurring in two-component aqueous solutions of dyes. Aqueous solutions of cationic dyes [Rhodamine 6G (R6G), Rhodamine 3B (R3B), Methylene Blue (MB)] and an anionic dye [Brilliant Yellow (BY)] and mixtures of these dyes were investigated.

The absorption spectra of the solutions were recorded on a Specord M-40 spectrophotometer. The luminescence characteristics were investigated with the aid of an Hitachi MFP-4 spectrofluorometer. The electrolyte used was LiCl, since its ions have the smallest (in comparison with the ions of other salts) dimensions and can, therefore, more closely approach the dye molecules and more strongly increase the potential of the universal intermolecular interactions [5]. The addition of electrolytes to solutions of dyes can result in changes in the nature, composition, and structure of the solvation shells of their molecules and can, thereby, cause changes in the electronic spectra of solutions containing associates. This due to the strong influence of the structure of their solvation shells on the structure and composition of molecular aggregates of dyes [6].

The investigations carried out showed that the addition of the salt to one-component aqueous solutions of the dyes R6G, R3B, MB, and BY causes the intensity of the long-wavelength band (which characterizes the monomeric molecules) to decrease and the intensity of the short-wavelength absorption band, which corresponds to the absorption of the homogeneous associates, to increase. In the case of two-component solutions of the dyes, the introduction of the electrolyte also causes changes in their absorption spectra. It is seen from Fig. 1 that an increase in the concentration of the electrolyte causes an increase in the optical density of the solution and some changes in the form of its absorption spectra, which attest to the appearance of mixed associates in it. The hypothesis that mixed nonluminescent associates form is supported by the violation of the additivity of the absorption spectra of the interacting components (the absorption spectra of the dye mixtures differ from the sum of the spectra of the components). The presence of an isosbestic point in Fig. 1 indicates that the complexes formed in solutions of the dyes with the electrolyte

Fig. 1. Dependence of the absorption spectrum of an equimolar R6G + MB dye mixture in water (C = 5·10^{-4} M) on the concentration of LiCl: 1) 10^{-4}; 2) 1; 3) 4 M.

Fig. 2. Dependence of the absorption spectra of R6G (1-3) and of R6G mixed with BY (4-7) in water (C = 5·10^{-4} M) on the concentration of LiCl; 1, 4) 10^{-4}; 2, 5) 10^{-3}; 3, 6) 10^{-1}; 7) 1 M.