EFFECT OF DIPOLE-DIPOLE INTERACTION IN A SOLVENT ON THE ELECTRONIC SPECTRA OF THREE-COMPONENT SOLUTIONS


Electronic spectra of three-component solutions are calculated on the basis of a model, which makes it possible to incorporate the interaction between the molecules of a polar solvent, including the case of dielectric saturation. It is shown that the use of the theory of three-component solutions, which disregards the interaction between the molecules of a polar solvent, can lead to an overestimation of the efficiency with which an activator interacts with the molecules of a polar solvent.

Keywords: electronic spectrum, three-component solution, nonspecific solvation, dielectric saturation.

In solutions of complex polar molecules, solvation phenomena can occur that are related to the effects of dielectric saturation (DS) [1-5]. DS manifestations in the electronic spectra of complex polar molecules can be observed in both polar [1-3] and nonpolar solvents [4]. Three-component solutions (TCS), i.e., a solution of a polar substance in a binary solvent (a mixture of polar and nonpolar solvents), appeared to be the most convenient objects for studying DS manifestations in the electronic spectra of complex molecules. In these solutions, at low concentrations of the polar component of a binary solvent, conditions can be realized where only one molecule of the polar solvent (PS) is present in the first coordination sphere of the activator molecule [6]. Such solvates do not display dipole-dipole interactions between PS molecules, which hinder the origination of a nonlinear orientational interaction between polar molecules of a dye and a solvent [7, 8]. Thus, DS effects manifest themselves clearly in the electronic spectra of TCS (at least at low PS concentrations). A theoretical description of the electronic spectra of TCS under the conditions of DS proved to be in good agreement with experimental data [3, 5, 7-11]. On the other hand, in earlier studies by N. G. Bakhshiev and Yu. I. Mazurenko (see, for example, [12, 13], the extensive experimental data agree well with the theoretical model, which disregards DS effects. Therefore, it is interesting to ascertain the role of the interactions between PS molecules in the formation of the electronic spectra of TCS, which, as has already been noted, can hinder the DS manifestation in the electronic spectra of complex molecules.

Previously [14], a statistical model was proposed for describing electronic spectra in TCS, which allows one to take into account the interaction of PS molecules, also under the conditions of DS. We will discuss the model in brief. Activator and solvent molecules are modeled by spheres with radii \( R \) and \( r \), respectively. Dipole moments of the activator and PS molecules are assumed to be pointlike and located at the center of the molecules. In the course of calculation, consideration is given to an activator molecule with the first coordination sphere, which consists of \( N \) molecules of polar and nonpolar solvents (a solvate). The entire remaining medium is regarded as a heat reservoir capable of exchanging the molecules of polar and nonpolar solvents with the solvate. Only dipole-dipole interactions of the solvent molecules with one another and with the acti-

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Fig. 1. $\langle J \rangle$ vs. the relative portion of PS with allowance for the dipole-dipole interaction between PS molecules (1, 2) and disregarding this interaction (3, 4); $\mu_g = 2.6$, the dipole moment of PS molecules is $\mu = 1.7$ D, $R = 3$ Å, $r = 1.5$ Å, $T = 250$ (1, 3) and 350 K (2, 4).

The shift of the electronic spectrum of absorption $\Delta \nu_a$ and emission $\Delta \nu_f$ of an activator molecule is determined in our case by the number of PS molecules that reside in a solvate and by the energy of the dipole-dipole interaction of these molecules with the activator

$$\Delta \nu_a = \sum_{j=0}^{N} \left[ \frac{X_j \langle E_j^0 \rangle}{N} \left( \frac{\mu_e}{\mu_g} \cos \varphi - 1 \right) \right], \quad \Delta \nu_f = \sum_{j=0}^{N} \left[ \frac{X_j \langle E_j^0 \rangle}{N} \left( 1 - \frac{\mu_e}{\mu_g} \cos \varphi \right) \right].$$

Here, $\mu_g$ and $\mu_e$ are the dipole moments of the activator molecule in the ground and excited states, respectively; $\varphi$ is the angle between the $\overrightarrow{\mu_g}$ and $\overrightarrow{\mu_e}$ vectors; $X_j$ is the portion of molecular subsystems (solvates) which contain $j$ molecules of the polar solvent; and $\langle E_j^0 \rangle$ is the mean energy of the interaction of PS molecules with the activator.

Likewise, for the mean number of PS molecules in the coordination sphere it is possible to write

*As the number of PS molecules in the solvate increases, the interaction between the solvent molecules hampers their alignment in the field of the activator molecule, thus decreasing the energy of the interaction of PS molecules with the activator.