

SHORT
COMMUNICATIONS

A Study of Electrooptical Properties of Hydrogen-bonded Complexes by the Electrochromism Method

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Abstract—The action of an external electric field on chemical equilibrium, namely, on proton transfer in the alizarin–piperidine complex at the stage when the molecular complex is converted to the ionic one, is considered. The problem of measuring the dipole moments of the solution components involved in the chemical reaction is discussed. The results of the measurement are compared with those obtained by calculation.

An external electric field F , which acts on a solution containing polar molecules, may be considered as a state parameter of the thermodynamic system. The electric field has a particularly pronounced effect on media containing molecules with large dipole moments and polarizabilities. In this case, dielectric polarization is accompanied by dichroism of solutions, which can be detected by optical methods. As distinct from p , V , and T , the electric field F is a vector. Varying the mutual orientation of the electric field F in a medium and the polarization vector of a probing light beam e of a spectrophotometer, one can measure the dipole moments and the polarizabilities of the molecules in the ground and electronically excited states and find their relative directions [1].

The aim of this work is to study proton transfer in a hydrogen-bonded complex and to refine the method of electrochromism as one of the techniques of molecular electron spectroscopy of solutions subjected to the electric field [2].

The electric field influences the equilibrium constant of a chemical reaction K if the molar dipole moment of a solution ΔM changes as equilibrium is shifted [3]:

$$\partial \ln K / \partial F = \Delta M / RT \text{ at } p, V, T = \text{const.}$$

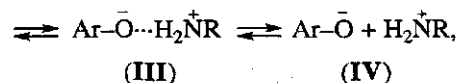
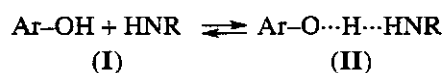
The electric field is a weak energy factor compared to p , V , and T ; therefore, a shift of equilibrium can be detected only using sensitive spectral equipment, which records an increment of absorption (the optical density) in the absorption bands, picking out the useful signals from the background noise. Denoting the absorption spectrum of a solution by $A(\lambda)$ (where λ is the wavelength), we obtain the spectrum of the increment of the absorption in the field $\Delta A(\lambda)$, which we name the spectrum of electrochromism. As was shown earlier, effects of a certain nature contribute to electrochromism, the most important of them forming the

overall electrochromism spectrum [2]

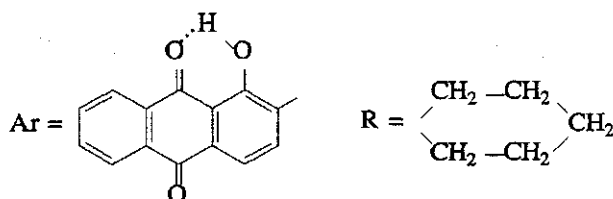
$$\Delta A(\lambda) = \Delta A_1(\lambda) + \Delta A_2(\lambda) + \Delta A_3(\lambda) + \Delta A_4(\lambda) + \Delta A^{\text{CH}}(\lambda). \quad (1)$$

Spectrum (1) and the $A(\lambda)$ spectrum are the basic sources of information on the action of the field on solutions. The values of the $\Delta A(\lambda)$ signals are normally on the order of 10^{-4} – 10^{-5} units of absorption in the field of 10^4 – 10^5 V/cm. The $\Delta A_{1-4}(\lambda)$ spectra, reflecting certain electrooptical properties of a solute, and the ΔA^{CH} spectrum, if chemical reactions proceed in a solution, can be separated from (1) with regard to particular nature of the effects that determine spectrum (1) and to the additivity of absorption.

In this work, the hydrogen-bonded complex between a proton donor (alizarin) and an acceptor (piperidine) is studied.



where



Thermodynamic studies based on analysis of the electron and IR spectra show that equilibrium between II and III (the equilibrium constant K is equal to 0.25–0.5) is dominated in toluene at 293–335K. This stage is chosen to avoid the treatment of diffusion processes (transport and orientation of interacting molecules), because this stage corresponds to proton transfer in ready complexes.

The equation for the chemical effect was obtained in [4]

$$\frac{\Delta A^{\text{CH}}}{A} = \frac{1}{9(1+K)} \left(\frac{F}{kT} \right)^2 [\mu_3 - \mu_2 \mu_3 \cos(\hat{\mu}_2 \mu_3)], \quad (2)$$

where A and ΔA^{CH} are the absorption and electrochromism bands corresponding to complex III.

To find the direction of proton transfer, which is determined by the $\hat{\mu}_2 \mu_3$ angle, there is a need to measure the dipole moments μ_2 and μ_3 . This is a challenging task for conventional dielectric methods, which requires, at best, rough approximations. The reason is that these methods are nonselective and give no way of distinguishing the components of orientational polarization relating to molecules II and III and to the slightly polar solvent, toluene.

To determine μ_2 and μ_3 , we used the electrochromism method [5]. The dipole moments are found from the ΔA_1 spectra [equation(1)] in the corresponding absorption bands of the solution. The regions where the bands do not overlap are preferable for our purposes. Toluene has no absorption bands in the visible region, where the bands of molecules II and III are found; therefore, the contribution of the solvent is insignificant, as is shown in [2]. Thus, the selectivity of the method is achieved.

To avoid difficulties connected with the measurements of the absolute values, the method of relative measurements with the use of the standard 4-N,N-dimethylamino-4'-nitroazobenzene is applied. This compound has a significant dipole moment $\mu^* = 8 \times 3.33 \times 10^{-30}$ C m and an electrochromism spectrum that is among the most intense in the visible region. The dipole moments of components II and III were found by the formula

$$\mu_{2,3} = \mu^* \left(\frac{\Delta A_{2,3} A^*}{\Delta A^* A_{2,3}} \frac{1 - 3 \cos^2 \gamma^*}{1 - 3 \cos^2 \gamma_{2,3}} \right)^{1/2},$$

where the asterisk denotes the standard, and γ is the angle between the directions of the transition and dipole moments. Because the above formula contains the ratio of the electrochromism signals, one can determine the $\Delta A_{2,3}$ values in any chosen arbitrary units, if conditions of the measurements are kept unchanged. This method is also used when ΔA^{CH} is measured for the calculation of the $\hat{\mu}_2 \mu_3$ angle. Note that the factor accounting for the local field of a solvent is excluded in this approach.

To divide the overall spectrum of electrochromism and differentiate the ΔA^{CH} spectrum, ΔA_1 was eliminated from (1) by choosing the direction of polarization of the indicator beam with respect to F such that $\Delta A_1 = 0$. The contribution of ΔA_2 was subtracted from (1), and those of the ΔA_3 and ΔA_4 spectra were negligibly small.

The following values are obtained for the alizarin-piperidine complex: $\mu_2 = 2.8 \times 3.33 \times 10^{-30}$ C m, $\mu_3 = 8.6 \times 3.33 \times 10^{-30}$ C m, $\hat{\mu}_2 \mu_3 = 150^\circ \pm 30^\circ$. The magnitude and the direction of the dipole moment in the

II-to-III conversion reflect not only proton transfer, but also a redistribution of the electron density and changes in the configuration of the complex and in its solvation. Thus, the directions of μ_2 and μ_3 correspond to the tangents to the coordinate of the chemical reaction of proton transfer in its initial and terminal points.

The ΔA^{CH} spectrum proved to be very intense and substantially exceeded the spectrum of the standard. The reason is that the overall change in the dipole moment of the complex with consideration for the antiparallelism of the μ_2 and μ_3 moments is equal to $11.4 \times 3.33 \times 10^{-30}$ C m. Owing to the squareness of the electrochromism signals, we obtain $\Delta A^{\text{CH}} = 2\Delta A^*$, all other factors being equal.

Some fine effects of proton transfer in the complex were established by performing the quantum-chemical calculations of the complex structures using the PCMODEL (4.0) program. The redistribution of the electron density due to proton transfer was shown to encompass only a small volume of the complex, including the nitrogen and oxygen atoms and two $-\text{CH}_2-$ groups bonded directly to it. This volume is substantially screened by the alizarin and piperidine rings, so that the deep penetration of the large solvating molecules of the solvent (toluene) into the hydrogen bond region is made difficult. Nevertheless, the replacement of slightly polar toluene with the dipole moment of $0.4 \times 3.33 \times 10^{-30}$ C m by benzene with the zeroth dipole moment significantly shifts the equilibrium to the left owing to a decrease in the solvation energy that stabilizes the polar complex.

The calculated values of the dipole moments for the free molecules of the complex in a vacuum are equal to $\mu_2 = 2.6 \times 3.33 \times 10^{-30}$ C m and $\mu_3 = 11.3 \times 3.33 \times 10^{-30}$ C m. The latter value exceeds the experimental one by $2.3 \times 3.33 \times 10^{-30}$ C m. This fact appears to be explained by a field-induced orientation of the solvate complex as a whole, including the solvate shell.

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