AN APPROXIMATE METHOD FOR DETERMINING THE OPTICAL CHARACTERISTICS OF DYE MOLECULES

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Abstract

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AN APPROXIMATE METHOD FOR DETERMINING THE OPTICAL CHARACTERISTICS OF DYE MOLECULES

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This paper proposes a method for calculating the optical characteristics of dye molecules: the refractive indices $n(\lambda)$ and the absorption indices $\chi(\lambda)$. Such data are practically absent in the literature, owing to the great experimental difficulties involved in studying dispersion in dye films ([1–4]).

The calculation method assumes the use of experimental dispersion curves of dilute solutions, the technique for studying which was developed in ([5]).

The calculation is based on the following assumptions:

1. The molecules, or aggregate groups formed from molecules, have a spherical shape and may be regarded as small spheres with dielectric permittivity ε_1.
2. For the absorption of incident radiation in a dielectric medium consisting of a mixture of two dielectrics, the macroscopic Maxwell theory is applicable. Therefore, absorption can be taken into account by introducing an imaginary part into the expression for the dielectric permittivity

$$\varepsilon_1 = \varepsilon_1' - i\varepsilon_1''.$$

3. In dilute solutions, the absorption of incident radiation, in the absence of negative absorption (induced emission), is determined by the Bouguer–Lambert–Beer law

$$I = I_0 e^{-knl},$$

where I_0 is the intensity of the incident light, I is the intensity of the light that has passed through a layer of thickness l; k is the molecular absorption coefficient or absorption cross section, and n is the number of molecules per unit volume.

In the electrodynamics of continuous media ([6]), for dilute binary solutions the following relation has been proved:

$$\varepsilon_p = \varepsilon_0 + 3N_1V_1\frac{\varepsilon_0(\varepsilon_1-\varepsilon_0)}{\varepsilon_1+2\varepsilon_0}, \tag{1}$$

which, in the optical-frequency region $\varepsilon = n^2$, has the form

$$n_p^2 = n_0^2 + 3N_1V_1n_0^2\frac{n_1^2-n_0^2}{n_1^2+2n_0^2}. \tag{2}$$

Substituting into this equation the complex refractive indices of the solution $n_p' = n_p - ik_p$ and of the dye particles $n_1' = n_1 - i\chi$, and taking into account that in the optical-frequency region the solvent does not absorb, we obtain equation (2) in complex form. It must be satisfied for both the imaginary and the real parts:

$$n_p^2 - n_0^2 - k_p^2 = 3N_1V_1n_0^2\frac{(n_1^2-\chi^2-n_0^2)(n_1^2-\chi^2+2n_0^2)+4n_1^2\chi^2}{(n_1^2-\chi^2+2n_0^2)^2+4n_1^2\chi^2},$$

$$n_pk_p = 9N_1V_1\frac{n_0^4n_1\chi}{(n_1^2-\chi^2+2n_0^2)^2+4n_1^2\chi^2}. \tag{3}$$

Taking into account that in weak solutions $n_p \approx n_0$, $n_p^2 - n_0^2 = (n_p+n_0)(n_p - n_0) \approx 2n_0(n_p-n_0)$, and also $n_p - n_0 \gg k_p^2$, equations (3) can be transformed to the form:

$$n_p - n_0 = \frac{3}{2}N_1V_1n_0\left[1 - 3\frac{2n_0^4+n_1^2n_0^2-n_0^2\chi^2}{(n_1^2-\chi^2+2n_0^2)^2+4n_1^2\chi^2}\right],$$

$$k_p = 9N_1V_1\frac{n_0^3n_1\chi}{(n_1^2-\chi^2+2n_0^2)^2+4n_1^2\chi^2}, \tag{4}$$

where n_0 is the refractive index of the solvent, n_1 is the refractive index of the dye particles, χ is the absorption coefficient of the dye particles, n_p is the refractive index of the solution, N_1 is the number of dye molecules per unit volume, and V_1 is the volume of the dye particles.

The molecular absorption coefficient k is related to k_p by the relation $k = 4\pi k_p/\lambda_0 N_1$, where λ_0 is the wavelength of the incident light in air.

At the maximum of the absorption band of the solution, the condition $n_p = n_0$ must be satisfied, i.e., in this region the absorption of the solution will be determined by the cross section for "soft" particles

$$\frac{4\pi}{\lambda_0 N_1} k_{pm} = \frac{4\pi}{\lambda_0} \chi_{mV} 1$$

or

$$k_{pm} = \chi_m N_1 V_1, \tag{5}$$

where χ_m is the value of the absorption coefficient of the dye particles under the condition $k_p = k_{pm}$.

Substituting (5) into equation (4), we obtain a system of two equations with the unknowns n_1 and χ:

$$n_p - n_0 = \frac{3}{2} \frac{k_{pm}}{\chi_m} n_0 \left[1 - 3 \frac{2n_0^4 + n_1^2 n_0^2 - n_0^2 \chi^2}{(n_1^2 - \chi^2 + 2n_0^2)^2 + 4n_1^2 \chi^2} \right],$$

$$k_p = 9 k_{pm} \frac{\chi}{\chi_m} \frac{n_0^3 n_1}{(n_1^2 - \chi^2 + 2n_0^2)^2 + 4n_1^2 \chi^2}, \tag{6}$$

For the absorption coefficient χ, from the system of equations (6) we obtain

$$\chi^6 - \chi^4 \cdot 4n_0^2 \left[1 - \frac{3}{4} \frac{ca}{a^2 + 4} \right] +$$

$$+ \chi^2 \cdot 4n_0^2 \left[1 - \frac{3}{2} \frac{ca}{a^2 + 4} - \frac{9}{4} \frac{c^2}{(a^2 + 4)^2} \right] + \frac{18 n_0^6 c^2}{(a^2 + 4)^2} = 0, \tag{7}$$

where

$$a = 3 \frac{k_{pm}}{k_p} \frac{n_0}{\chi_m} - \frac{2(n_p - n_0)}{k_p}, \qquad c = 3 \frac{k_{pm}}{k_p} \frac{n_0}{\chi_m}.$$

The value of χ_m for rhodamine C was taken from experiment (?). For other dyes, χ_m was calculated from the relation

$$\frac{k_{pm_1}}{k_{pm_2}} = \frac{n_1}{n_0} \frac{\chi_{m_1}}{\chi_{m_2}} \frac{\mu_2}{\mu_1},$$

where, respectively, n_1 and n_2 are the concentrations of different dyes, and μ_1 and μ_2 are their molecular weights.

Equation (7) was solved on an electronic machine using experimental curves obtained for weak solutions. The results obtained

Fig. 1. Calculated curves of the molecular absorption coefficient. A — rhodamine 6Zh, B —rhodamine C, V —crystal violet, G —malachite green. Solvents: a —water, b —chloroform

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are shown graphically in Fig. 1; moreover, on one and the same graph the curves for two different solvents (water and chloroform) are shown.

As can be seen from the graphs presented, the agreement with the experimental curves for solutions [5] is quite satisfactory. Comparison with the experimental curves for thin films [4] also confirms that the proposed approximate method gives reasonable results.

Fig. 1. Calculated curves of the molecular absorption coefficient.
A —rhodamine 6Zh, **B** —rhodamine C, **V** —crystal violet, **G** —malachite green.
Solvents: **a** —water, **b** —chloroform.

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Note: Figure translations are in progress. See original paper for figures.