

EFFECT OF BINARY SOLVENT UPON THE LUMINESCENCE PROPERTIES OF 4-METHYL-7-DIETHYLAMINOCOUMARINE

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Absorption and fluorescence emission spectra of 4-methyl-7-diethylaminocoumarine were measured in the mixture of *n*-heptane and *n*-butanol. The large red-shift occurring in the spectra results from substantial change in the dipole moment and depends on the number of polar solvent molecules in the solvent shell. The spectral shifts are interpreted in terms of the theory of solvent shifts; the dielectric constant of the microenvironment and the interaction energy in the ground and excited states were calculated.

The solvent effect upon the spectra of organic compounds has been discussed in several papers. The problems concerning the influence of binary solvents upon these spectra are of particular interest [1—8]. Solvent shells are formed around the solute molecules. From spectroscopic measurements one can obtain information concerning the molecule investigated and the composition of the solvent shell. In the present paper the effect of binary solvent upon the luminescence properties of 4-methyl-7-diethylaminocoumarine was investigated.

Experimental

The substances investigated in water and the solvents used, *n*-heptane and *n*-butanol, were additionally purified before the measurements. The concentration of 4-methyl-7-diethylaminocoumarine was of the order of 10^{-6} M. Absorption spectra were measured with an Optica-Milano spectrophotometer, and the fluorescence emission spectra were recorded by a home-built set-up based on SPM-2 Zeiss monochromators.

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a) Investigation of solvent shells

The formation of solvent shells in the mixture of a nonpolar (I) and polar (II) solvent was investigated. According to DIMROTH [9, 10], the polar solvent molecules are first assembled around the solute molecule, and then such a complex is accommodated in the remaining (nonpolar) solvent. Based on [4, 1] the solvents are chosen so that the radii of the solvent molecules, as well as the solvent refraction indexes are equal, *i.e.*, ($r_I = r_{II} = r$) and ($n_I = n_{II} = n$), whereas the dielectric constants differ considerably ($\epsilon_I \neq \epsilon_{II}$). The mean filling-up degree of the solvent shell with molecules of polar solvent (II) is defined as [12, 13]:

$$\langle \gamma \rangle = \langle \gamma_{II} \rangle = 1 - \langle \gamma_I \rangle = \frac{z_{II}}{z_I + z_{II}} \quad (1)$$

where z_I and z_{II} denote the number of molecules of nonpolar and polar solvent in the solvent shell, respectively. Local dielectric constant is defined as:

$$\langle \epsilon_l \rangle = \epsilon_I \langle \gamma_I \rangle + \epsilon_{II} \langle \gamma_{II} \rangle \quad (2)$$

where ϵ_I and ϵ_{II} denote the dielectric constants for the nonpolar and polar solvent, respectively. By means of spectroscopic measurements the value of $\langle \epsilon_l \rangle$ for given solution can be determined. The shift of the absorption and fluorescence emission spectra in a binary solvent is given by:

$$\delta \tilde{\nu}_{A,F} = (\Delta \tilde{\nu}_{A,F}^{I+II} - \Delta \tilde{\nu}_{A,F}^I) = -C_{A,F} \left(\frac{2n^2 + 1}{n^2 + 2} \right) \left(\frac{\langle \epsilon_l \rangle + 1}{\langle \epsilon_l \rangle + 2} - \frac{n^2 - 1}{n^2 + 2} \right) \quad (3)$$

On solving equation (3) we obtain:

$$\langle \epsilon_l \rangle = \frac{n^2 - 2\Delta \tilde{\nu}_{A,F}}{1 + \Delta \tilde{\nu}_{A,F}} \quad (4)$$

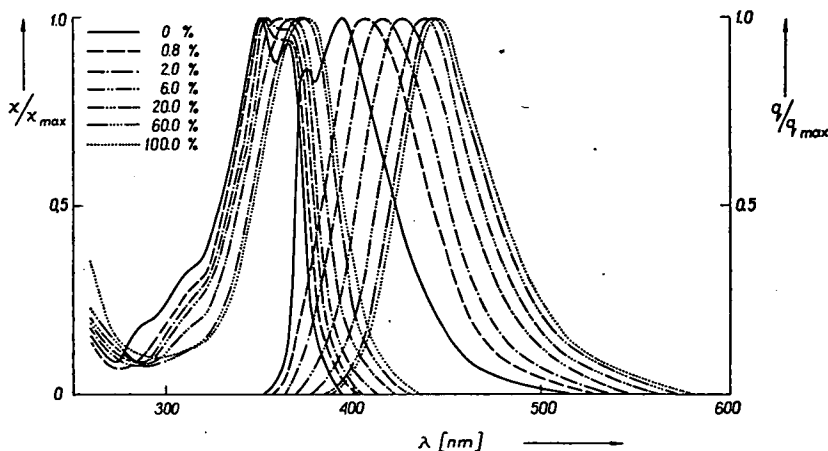


Fig. 1 Absorption and fluorescence emission spectra of 4-methyl-7-diethylaminocoumarin for various contents of polar solvent

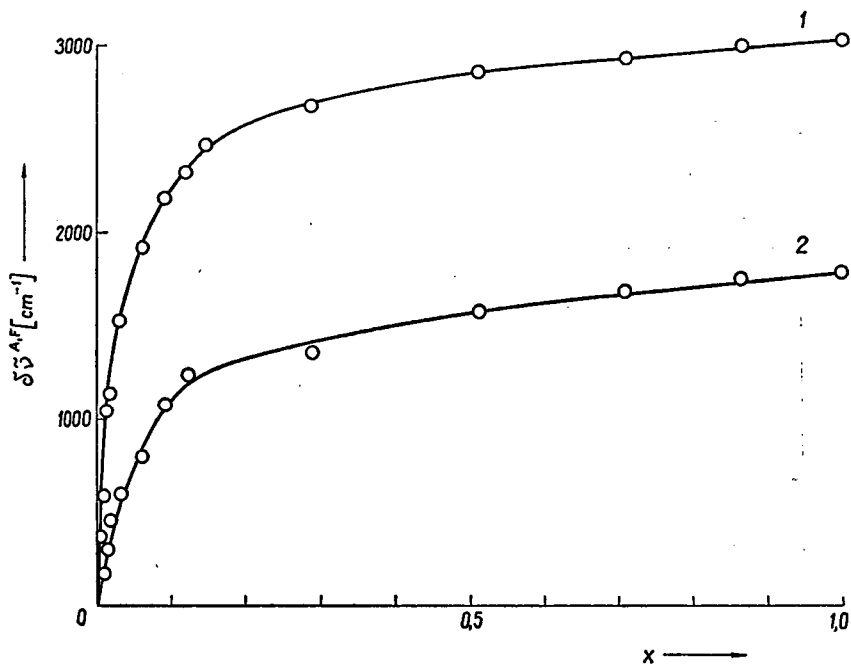


Fig. 2. Spectral shifts in the absorption and fluorescence emission spectra versus molar ratio of the polar solvent
1 — fluorescence, 2 — absorption

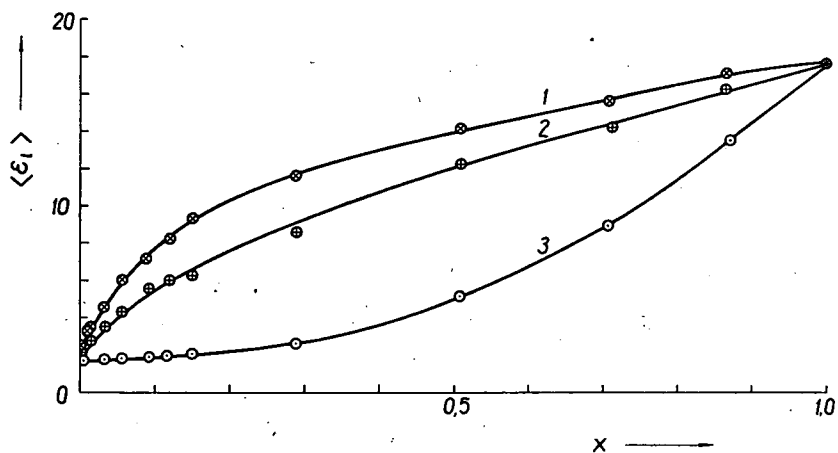


Fig. 3. Local and macroscopic dielectric constants versus molar ratio of the polar solvent 1 — excited state, 2 — ground state, 3 — macroscopic dielectric constant according to [11]

where

$$\Delta\bar{\nu}_{A,F} = \frac{\delta\bar{\nu}_{A,F}}{C_{A,F}} \frac{(n^2+2)^2}{3(2n^2+1)} \quad (5)$$

Fig. 1. shows the absorption and fluorescence emission spectra. The shift of the absorption and fluorescence emission spectra of the compound investigated, is shown in Fig. 2, the local dielectric constant as a function of molar ratio, x , of the polar solvent in Fig. 3. The mean filling-up degree of the solvent shell with molecules of a polar solvent is shown in Fig. 4.

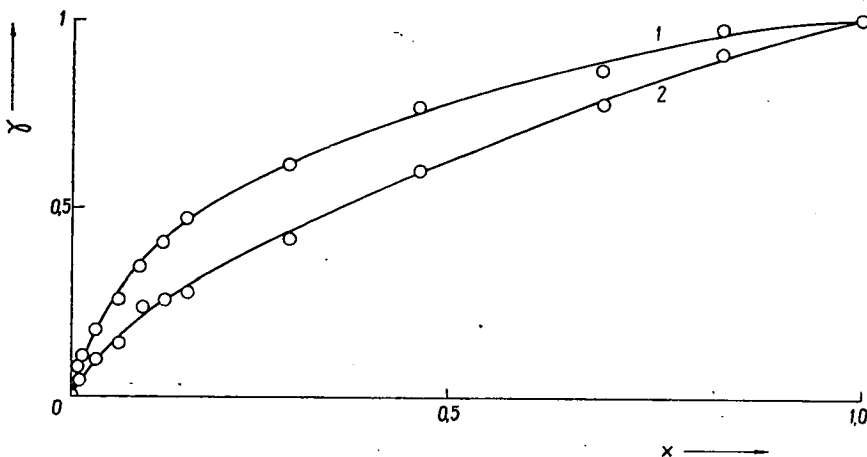


Fig. 4. Filling-up degree of the solvent shell with the polar solvent molecules versus molar ratio of the polar solvent
1 — excited state, 2 — ground state

b) Determination of the mean interaction energy and the solvent number N_m

A statistical model for a tricomponent solution has been elaborated by MAZURENKO [14, 17]. The model describes the interaction of the studied molecule with a binary solvent consisting of one polar and one nonpolar solvent. The probability distribution of the filling-up of the solvent shell with nonpolar and polar solvent molecules in the energy equilibrium state is described by the following expression:

$$\Phi^{eq}(N) = \frac{N!}{N!(N_m - N)!} (\theta^{A,F})^N (1 - \theta^{A,F})^{N_m - N} \quad (6)$$

where N_m is the number of nonpolar and polar solvent molecules in the solvent shell, N being the number of polar solvent molecules, and θ — the relative spectral shift defined by:

$$\frac{\theta^{A,F}}{1 - \theta^{A,F}} = \frac{x}{1 - x} \exp\left(-\frac{F_m^{A,F}}{kTN_m}\right) \quad (7)$$

with $\theta = \bar{N}/N_m$. The quantity $\theta^{A,F}$ is related to the spectroscopic parameters by the formula:

$$\theta^{A,F} = \frac{\tilde{\nu}_n^{A,F} - \tilde{\nu}_p^{A,F}}{\tilde{\nu}_n^{A,F} - \tilde{\nu}_p^{A,F}} \quad (8)$$

where $\tilde{\nu}_n^{A,F}$, $\tilde{\nu}_p^{A,F}$ and $\tilde{\nu}^{A,F}$ correspond to the location of the absorption and fluorescence emission spectra in nonpolar, polar, and binary solvent, respectively. While elaborating the experimental results it is more convenient to use the logarithmic form of expression (7):

$$\ln \frac{\theta^{A,F}}{1-\theta^{A,F}} = \ln \frac{x}{1-x} + \chi^{A,F} \quad (9)$$

Plotting $\ln \frac{\theta^{A,F}}{1-\theta^{A,F}}$ versus $\ln \frac{x}{1-x}$ we obtain straight lines which cut off a segment on the ordinate axis, corresponding to the quantity $\chi^{A,F} = F_m/kTN_m$. Having known $\chi^{A,F}$ we can estimate the number of molecules in the solvent shell:

$$N_m = \frac{hc(\tilde{\nu}_n^F - \tilde{\nu}_p^F + \tilde{\nu}_n^A - \tilde{\nu}_p^A)}{2kT(\chi^F - \chi^A)} \quad (10)$$

and then the energy of interaction between the molecule studied and the solvent shell:

$$-F_m^{A,F} = \frac{kT\chi^{A,F}N_m}{N_m} = kTN_m \quad (11)$$

The filling-up degree of a solvent shell can be determined more precisely if the polarizability of the solute molecule is taken into account. Thus we obtain [18]:

$$\theta^{A,F} = \frac{(n^2+2)^3(\tilde{\nu}_n^{A,F} - \tilde{\nu}_p^{A,F})}{(\epsilon_{II} - \epsilon_I)[3(2n^2+1)C_{A,F} - (n^2+2)^2(\tilde{\nu}_n^{A,F} - \tilde{\nu}_p^{A,F})]} \quad (12)$$

The plots of $\ln \frac{\theta^{A,F}}{1-\theta^{A,F}}$ versus $\ln \frac{x}{1-x}$, are shown in Fig. 5 and Table I summarizes the results obtained based on the theory presented.

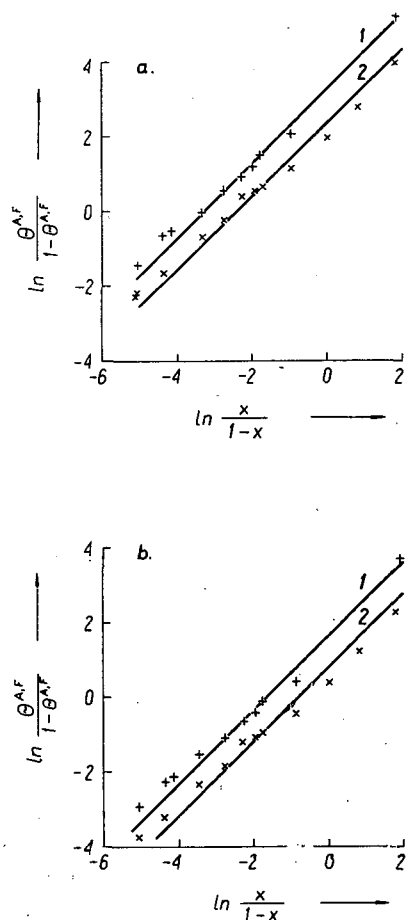


Fig. 5. $\ln \frac{\theta^{A,F}}{1-\theta^{A,F}}$ versus $\ln \frac{x}{1-x}$
 a — $\theta^{A,F}$ calculated according to formula (8) b — $\theta^{A,F}$ calculated according to formula (12)
 1 — absorption, 2 — fluorescence

Table I

Values of $\chi^{A,F}$, $F_m^{A,F}$ and N_m for 4-methyl-7-diethylaminocoumarine in the mixture of *n*-heptane and *n*-butanol

No.	Compound	Spectrum	$\theta^{A,F}$ calculated from eq. (8)				$\theta^{A,F}$ calculated from eq. (12)		
			$\chi^{A,F}$	$F_m^{A,F}$ [cm ⁻¹]	$F_m^F - F_m^A$ [cm ⁻¹]	N_m	$\chi^{A,F}$	$F_m^{A,F}$ [cm ⁻¹]	$F_m^F - F_m^A$ [cm ⁻¹]
	4-methyl-7-diethylaminocoumarine-	fluoresc. absorption	3.20	651	183	13	1.65	336	173
			2.30	468			0.80	163	

Discussion

The absorption and fluorescence emission spectra of 4-methyl-7-diethylaminocoumarine display large red-shifts in *n*-heptane, as compared to those obtained in *n*-butanol (Fig. 2), which is due to the difference in the dipole moment in the ground and excited state, and the formation of solvent shells around the molecules studied. This is confirmed by the value of local dielectric constant and the filling-up degree of the solvent shell with polar solvent molecules (Figs. 3 and 4). Local dielectric constant differs considerably from the macroscopic dielectric constant (Fig. 3).

In Table I the values of the interaction energy, $F_m^{A,F}$, calculated on the basis of the theory proposed by MAZURENKO and KAWSKI et al. [16—18], are given. The energy values differ considerably, whereas the difference of the interaction energies, $(F_m^F - F_m^A)$ calculated on the basis of the above theories are comparable within the error. The values of $F_m^{A,F}$ calculated from formula (12) seem to be more probable, since θ was calculated more precisely.

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ВЛИЯНИЕ БИНАРНЫХ РАСТВОРИТЕЛЕЙ НА ЛЮМИНЕСЦЕНЦИЮ 4-МЕТИЛ-7-ДИЭТИЛАМИНОКУМАРИНА

Й. Чайко и Л. Козма

Измерены спектры поглощения и люминесценции 4-метил-7-диэтиламинокумарина в смесях *n*-гептана и *n*-бутанола. Значительный красный сдвиг, наблюдаемый в спектрах связан значительным изменением дипольного момента и зависит от числа полярных молекул находящихся в сольватной оболочке. Спектральный сдвиг объяснен на основе теории сольватации; диэлектрические константы микроскопического окружения и энергия взаимодействия в основном и возбужденном состояниях определены расчётами.