Spectral studies of light-sensitive crown-containing dyes in solution and in polymolecular Langmuir—Blodgett layers

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A comparative spectral study of the complexation of two crown-containing dyes (structures **1** and **2**) with calcium in solution and in polymolecular Langmuir—Blodgett layers was carried out. The binding constants with Ca in solution were measured. The logarithms of the binding constants are 12.8 for structure **1** and 8.02 for structure **2** (the binding constant for the Ca—EDTA complex is 10.57). The complex of compound **1** with Ca is four orders of magnitude more stable in solutions than the complex of compound **2**. Therefore, the addition of EDTA results in dissociation of only the complex of **2** with Ca (the absorption band shifts to the initial position). The complex of **1** with Ca becomes less stable in polymolecular Langmuir—Blodgett layers due to the dissociation in EDTA solution when exposed to light with λ = 400 nm. The complex of **2** with Ca behaves almost the same way in polymolecular Langmuir—Blodgett layers and in solution.

Key words: crown-containing dyes, complexation.

Paper strips similar to the well-known pH-indicators are often used for simple and rapid chemical analyses. Strips of this type were recently developed for some cations and for some compounds of medicinal interest.[1,2] Ionophores capable of binding ions by reversible complexation play an important part in ion sensors.[3,4]

Selectivity and relatively high constants of complexation with particular ions, in combination with high rates of complexation, are the properties ionophores must have in order to be used in sensors.

One of the main requirements for ionophores in optical sensors is that binding of an ion should cause a noticeable change in the absorption spectra. Therefore, various chromoionophores and organic dyes that change color during complexation with ions are of interest.[5—13]

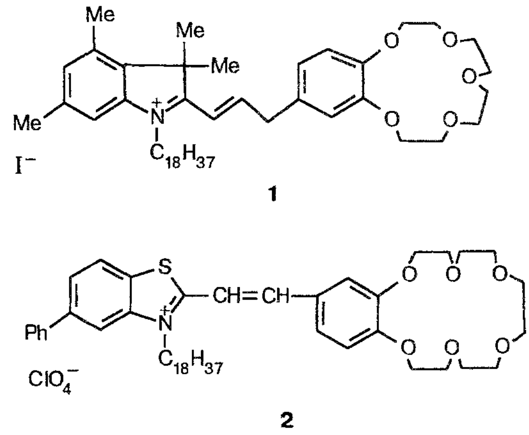
The present work deals with spectral studies of two compounds in solution and in polymolecular layers. The two compounds belong to the class of crown-ethers and contain light-sensitive chromophore fragments that can undergo photo-induced *trans-cis*-isomerization, and the studies were undertaken in order to determine if it is possible to use these compounds as sensors for Ca^{2+} ions.

Experimental

We studied crown-containing dyes **1** and **2** (Scheme 1).

Polymolecular Langmuir—Blodgett layers were obtained using a Joyce-Loeble (Great Britain) setup according to the previously described procedure.[14]

Scheme 1



A mixture of stearic acid and a crown-containing dye in a volume ratio of 1 : 3 (the initial molar concentrations of stearic acid and the crown-containing dye were equal) in chloroform was applied to the surface of a sub-phase containing $CdCl_2$ and $NaHCO_3$ at pH 6.9 and 18 °C. After removal of the chloroform, the mixture on the sub-phase surface was compressed at a pressure of 25 mN m^{-1}. The quality of the monolayers obtained was characterized by pressure (π) — square (*A*) isotherms (Fig. 1). The quality of the polylayers transferred to the surface of the sub-phase was determined from the transfer coefficient and the additive dependence of the optical density on the number of monolayers transferred. It should be noted that dyes **1** and **2** contain an aliphatic substituent, $C_{18}H_{37}$, which favors the formation of monolayers on a phase boundary, as judged from the π—*A* isotherms.

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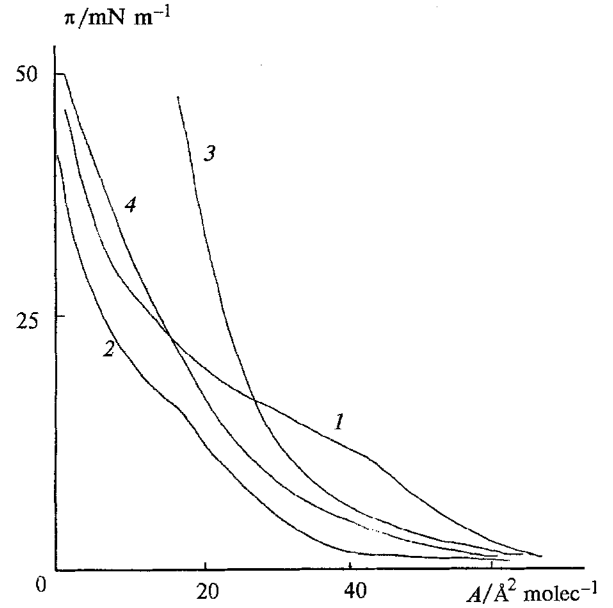

Fig 1. Pressure (π) — square (A) isotherms for individual crown-containing dyes **1** (*1*) and **2** (*2*) and mixtures of **1** (*3*) and **2** (*4*) with stearic acid (3 : 1).

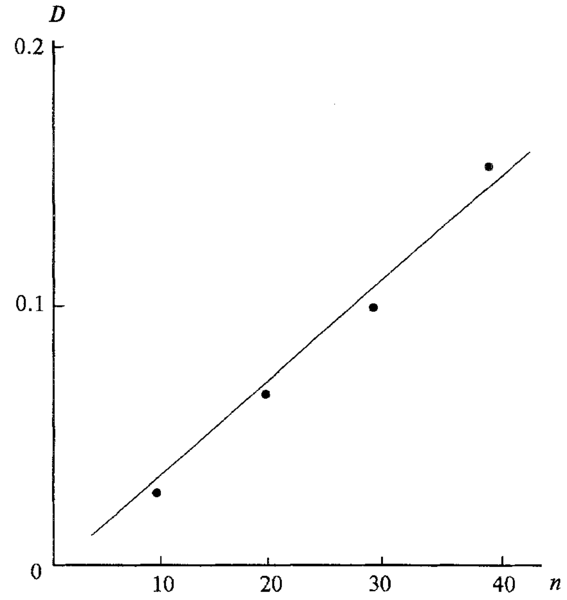

Fig. 2. Plot of optical density D *vs* the number of monolayers n.

The dyes were applied as a mixtures with stearic acid in the ratio of 3 : 1, which is optimal for the concentration of dyes in polylayers. The number of monolayers in all dye-containing samples was equal to 40, which is optimal according to the optical density at λ_{max} of the absorption of dyes **1** and **2** (Fig. 2). Absorption spectra were recorded on a Shimadzu UV-VIS-NIR 3100 spectrophotometer (Japan).

Results and Discussion

Spectral studies in solution

The results obtained for the two dyes are presented in Fig. 3. Dehydrated acetonitrile was used as the solvent. The addition of $Ca(ClO_4)_2$ at a concentration 100 times higher than that of the dye results in a shift of the absorption maximum of crown-containing dyes **1** and **2** to the short-wave region by 12 and 17 nm, respectively (Fig. 3, curves *1*, *1'* and *2*, *2'*). Exposure of the Ca-form of crown-containing dyes **1**, **2** to light at the absorption maximum for 15 min leads to additional hypsochromic shifts of the absorption maxima by 18 and 5 nm, respectively (Fig. 3, curves *1*, *1'*, *2*, *2'*, and *3*, *3'*), accompanied by a noticeable decrease (1.5—2 times) in optical density as compared with the starting and unexposed forms of dyes **1** and **2**.

Crown-containing dyes **1** and **2** can exist as *trans*- and *cis*-isomers, as well as mixtures of both isomers. Transitions from the *trans*- to the *cis*-form occur under light action. On illumination, the calcium complexes of the dyes studied form *cis*-substituted isomers, which have an additional hypsochromic spectral shift. However, it should be noted that the absorption bands of the initial, light-exposed calcium, and unexposed calcium forms overlap strongly and, therefore, one should speak of the existence of an equilibrium mixture of *trans*- and *cis*-isomers of these dyes and shifting of the existing equilibrium towards the *cis*-isomer (Fig. 3) with exposure to light. Since the study of the equilibrium of the *trans*-*cis*-transitions of crown-containing dyes **1** and **2** was not the purpose of our investigation, in the present work we shall assume that these isomers exist as mixtures.

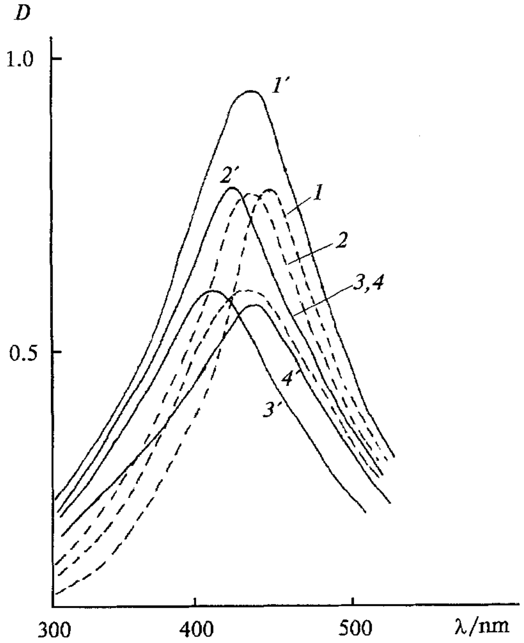

Fig. 3. Electronic absorption spectra of crown-containing dyes **1** (*1*—*4*) and **2** (*1'*—*4'*) in solution: *1*, *1'*, the initial form; *2*, *2'*, the Ca-form; *3*, *3'*, the Ca-form after illumination for 15 min; *4*, *4'*, exposed Ca-form in the presence of EDTA.

If the sodium salt of ethylenediaminetetraacetic acid (EDTA) (10^{-2} mol L^{-1}) is added to solutions of the Ca^{2+}-containing light-exposed form of crown-containing dyes **1** and **2**, the absorption maximum of dye **2** returns to the initial position practically immediately (for the initial dye, λ = 437 nm, Fig. 3, curve *4*), but this is not observed for dye **1**. This allows us to propose that the stability constant of the Ca—EDTA complex is higher than that of the complex of Ca with dye **1**. According to our calculations, the logarithm of the stability constant of the Ca—EDTA complex is 10.57,[15] that for the complex of Ca with dye **2** is 8.02, which is three orders of magnitude lower, and that for the complex of Ca with dye **1** is 12.8, which is two orders of magnitude higher. The method of isomolar series[16] was used to measure the stability constants; the determination was carried out at 25 °C using the spectral method. It is noteworthy that the addition of EDTA to Ca^{2+}-containing, unexposed forms of crown-containing dyes **1** and **2** affords similar results (see above).

We should therefore conclude that crown-containing dye **2** is a more effective sensor than crown-containing dye **1**.

Spectral studies in Langmuir—Blodgett polylayers

The isotherms of individual crown-containing dyes **1** and **2** and their mixtures with stearic acid are given in Fig. 1, curves *1* and *2*. The isotherms of dyes **1** and **2** are flat and have an inflection at the surface pressure 10—12 mN m^{-1}. Judging from these isotherms, the crown-containing dyes **1** and **2** do not form a solid-crystalline phase and, as a consequence, their monolayers are not closely packed and have many defects. The small area per molecule of dyes **1** and **2** (18—22 Å^2 mol^{-1}) in a monolayer, combined with the rather bulky structure of molecules **1** and **2** (see the structural formulas), also confirms the above concept. These low areas per molecule can probably be explained by the fact that the hydrophilic crown-ether moieties contained in these dyes are located in the bulk of the sub-phase rather than on the phase boundary during the formation of a monolayer. Therefore, the monolayers obtained from individual crown-containing dyes **1** and **2** have low coefficients of transfer to a quartz carrier, and the resulting polylayers are not additive.

The isotherms of mixtures of **1** and **2** with stearic acid (Fig. 1, curves *3*, *4*) differ from each other. The mixture of **1** with stearic acid (Fig. 1, curves *3*), unlike that of **2** with stearic acid (Fig. 1, curve *4*), forms a solid-crystalline phase, which affects the coefficient of transfer of mixtures into the polylayers. This transfer coefficient is higher for the mixture involving **1**. The optical density of 40 layers of the mixture of **1** with stearic acid is 0.15, and is 1.5 times lower for the mixture of **2** with stearic acid.

The spectral data obtained in polymolecular Langmuir—Blodgett layers are given in Fig. 4 (*a* and *b*). The absorption maxima of 40 layers of crown-containing dyes are at 456 nm (**1**) and 442 nm (**2**). These are close to λ_{max} in solution, which are 452 and 437 nm, respectively.

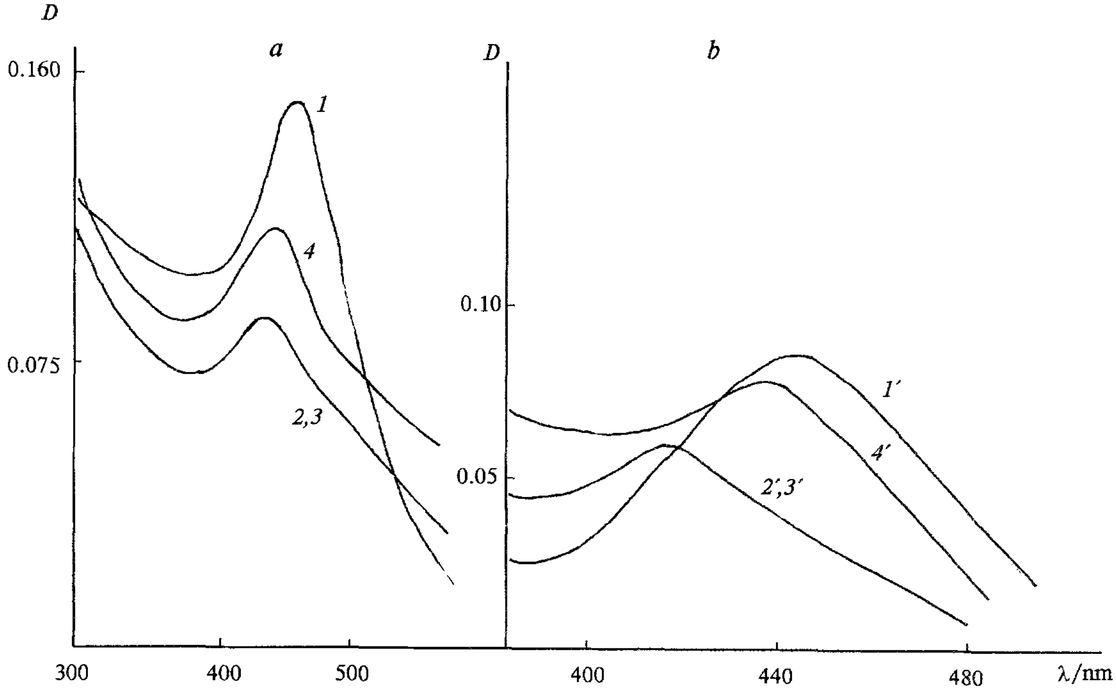

Fig. 4. Electronic absorption spectra of crown-containing dyes **1** (*a*) and **2** (*b*) in Langmuir—Blodgett polylayers: *1*, *1′*, the starting film; *2*, *2′*, the Ca-form; *3*, *3′*, exposure to light at the absorption maximum for 15 min in EDTA solution (10^{-2} mol L^{-1}); *4*, *4′*, in EDTA solution after illumination for 60 min.

Table 1. Dispersion of reproducibility and the confidence interval at the absorption maxima of crown-containing dyes **1** and **2**

Dye	λ_{max}	$S_e^2 \cdot 10^{-4}$	M_x
1	456	7.580	0.108±0.043
	413	1.770	0.068±0.021
	444	0.655	0.097±0.008
2	442	1.070	0.071±0.016
	415	0.856	0.041±0.014
	435	1.484	0.060±0.019

Note: S_e^2 — dispersion of reproducibility, M_x — confidence interval; $S_e^2 = \Sigma(x_q - x_m)^2/f$, where x_q is the sampling of the experimental values; x_m is the arithmetic mean of the sampling; f is the number of degrees of freedom; $f = n-1$; n is the number of measurements (in our case, it is 4); $M_x = x_m + (t\ S_e)/(n^{1/2})$; t is the Student criterium, the tabulated value at significance level 95% is equal to 3.18;[17] S_e is the mean square deviation.

The reproducibility of the results for Langmuir—Blodgett polylayers of **1** and **2** near λ_{max} is illustrated in Table 1.

Filling the Langmuir—Blodgett polylayers obtained with a solution of $Ca(ClO_4)_2$ (10^{-3} mol L^{-1}) for 1 day in the dark at 25 °C in both cases results in a noticeable shift of λ_{max} to the short-wave region by 30 nm (Fig. 4, curves *2, 2″*). The exposure of Ca^{2+}-containing layers to light at the absorption maximum of the Ca-complexes of **1** and **2** for 15 min does not change their absorption spectra (Fig. 4, curves *3, 3′*). A comparison of these results with those in solutions allows one to note that a strong bathochromic shift of the absorption maximum occurs immediately after the filling Langmuir—Blodgett polylayers of **1** and **2** even without exposure to light, whereas the same shift of λ_{max} of the Ca^{2+}-form in solution occurs only after 15 min of exposure to light. We explain this fact by a shift in the *trans—cis*-equilibrium toward the formation of the *cis*-isomer (Fig. 2, curves *3, 3″*, and Fig. 4, curves *2, 3,* and *2″, 3″*). Thus, it can be assumed from the above that dyes **1** and **2** are located in the stearic acid matrix primarily in the *cis*-form, which is probably more compact than the *trans*-form.

An experiment to return the filled Ca^{2+}-forms of **1** and **2** to the initial state was also carried out. Strips with deposited mixtures of the dyes with stearic acid were put into a solution of the Na-salt of EDTA (10^{-2} mol L^{-1}) and kept for 60 min at 45 °C. After that, a spectral study showed that under these conditions Ca did not pass out into solution in the case of dye **1** (the spectrum did not change, Fig. 4, curve *3*), and the white precipitate of a Ca—EDTA complex was formed on the strip in the case of dye **2**. After the removal of the complex by treatment in hot water at 75 °C, the absorption maximum of **2** shifted to the long-wave region by 20 nm (415—435 nm), but, as can be seen from Fig. 4 (curve *4*), it did not return to the initial position (442 nm). The strip with dye **1** in the EDTA solution was exposed to light with λ 400 nm for 60 min at 45 °C, then the λ_{max} of the layers containing dye **1** was shifted (after the removal of the Ca—EDTA complex) to the long-wave region by 30 nm (413—444 nm) but also did not return to the initial state (456 nm). It may be proposed that some of the Ca ions remained in the layers and, therefore, λ_{max} did not reach its initial value, and the optical density did not reach its initial value either. There are good reasons to believe that the amount of Ca in the layers should increase and the optical density should decrease as the cycles are repeated.

The results obtained reveal the difference in the behavior of crown-containing dyes in solution and in Langmuir—Blodgett polylayers, especially for dye **1**. We were not able to return the Ca-form of this dye to its initial state in the presence of EDTA and under illumination due to the high constant of complexation of dye **1** with Ca (see above). Its behavior changes in Langmuir—Blodgett polylayers: exposure to light at λ 400 nm in an EDTA solution at 45 °C results in the liberation of Ca from its complex with dye **1**, which may be due to a decrease in the constant of complexation when passing from the solution to a solid matrix. It should also be noted that dye **1** is more light-sensitive than **2**, which makes it possible to control the process with light as shown in this work.

The advantage of dye **2** is its ability to bind Ca relatively quickly and to release it rapidly in the presence of excess EDTA, whose binding constant is higher than that of the dye.

Thus, in our opinion, the crown-containing dyes studied in our work show promise for use as sensors.

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