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Ion-selective Dyes for the Complexation of Alkali and Alkaline Earth Cations

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The interactions of ion-selective dyes with alkali and alkaline earth cations in methanol have been investigated quantitatively. Both dyes examined are able to complex these cations selectively. From the spectral changes the stability constants of the complexes formed are calculated. The substituents at the nitrogen atoms of the diaza crown ethers obviously influence the stability of the complexes.

INTRODUCTION

In the literature a large number of ion-selective dye molecules has been described. The molecules contain a chromophor and a crown ether or cryptand moiety.[1] The syntheses of such ion-selective dyes often involves many steps because both chromophore and ligand have to be build. So dye molecules are obtained, which are able to form complexes with cations selectively and by this way induce some changes in the absorption behaviour of the dyes.

The number of ion-selective dyes is not limited, because all possible structures of dye molecules may be combined with each crown ether and cryptand. As a result the number of synthesized ion-selective dyes increases rapidly.[2] However, for a possible use of these dyes in optical sensors, they have to be made easily accessible.

Another strategy for the synthesis of ion selective dyes is to use macrocyclic ligands and combine them with dye molecules in one step. In the literature only a few dyes are described, which have been synthesized by this way.[3] It is known, that these dyes may be used for the detection of alkaline earth cations. However, up to now no quantitative results about the complexation of alkali and alkaline earth cations have been reported.

EXPERIMENTAL

The chemical structures of the synthesized dyes are given in Figure 1.

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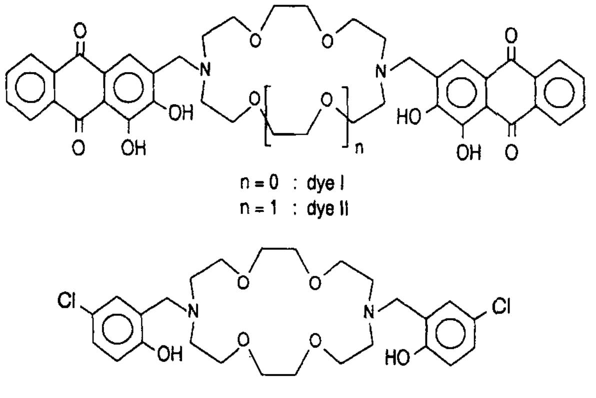

$22Ph_2$

FIGURE 1 Chemical structures of the synthesized ion-selective dyes and of 4-chlorophenol-substituted diaza-18-crown-6.

The dyes I and II have been synthesized according to the published procedure by the reaction of alizarine with the macrocyclic ligands diaza-15-crown-5 (Kryptofix 21, Merck) and diaza-18-crown-5 (Kryptofix 22, Merck).[3] Dye I is an oil and dye II a solid (m.p. 209°C).

The following salts $NaNO_3$ (Merck), KJ (Merck), $RbNO_3$ (Alfa), CsF (Ventron), $Ca(NO_3)_2$ (BDH-Chemicals), $SrBr_2$ (Ventron), $Ba(ClO_4)_2$ (Merck) and NH_4NO_3 (Fluka) were of the highest purity commercially available.

As solvents chloroform and anhydrous methanol (all Merck) have been used. The absorption spectra were recorded using a spectrophotometer Cary 5E (Varian). The dye solutions without salts look purple. Since more than one year all solutions containing dye I or dye II are stable in the light.

The measured absorbance A is related to the concentration of the uncomplexed dye [D] and to the concentration of the complex $[DM^{n+}]$ in the following way:

$$A = (\epsilon_D[D] + \epsilon_{DM}[DM^{n+}])\,d \qquad (1)$$

with ϵ_D and ϵ_{DM} as molar absorptivities of the dye and of the complex and d as the optical path

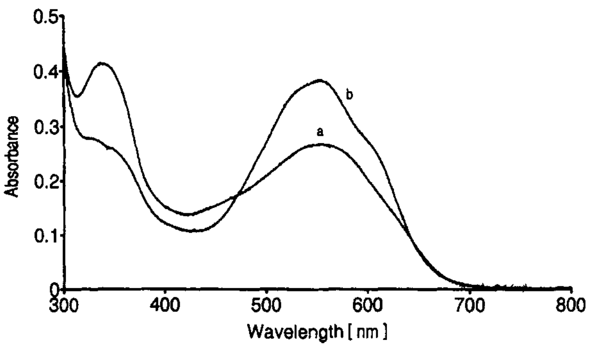

FIGURE 2 Absorption spectra of the dye II (a) and of its complex with $CaCl_2$ (b) in chloroform.

length. All measurements were performed at a constant concentration of the dye (dye I: $C_F = 2.3\ 10^{-4}$ mol/l, dye II: $C_F = 2.2\ 10^{-5}$ mol/l). Only the concentration of the salts was varied. The absorbance was measured at the wave length of the maximum absorption of the complex formed. The unknown molar absorptivity of the complex and the stability constant have been fitted to the experimental data.

RESULTS AND DISCUSSION

It is known from the literature, that the dye II can be used to extract Ca^{2+} from aqueous solutions to dichloroethane.[3] This dye also solubilizes $CaCl_2$ in chloroform. In Figure 2 the absorption spectra of the dye II and of its complex with $CaCl_2$ in chloroform are shown. The reported absorption spectra measured in dichloroethane are nearly identical.[3]

It has been reported that in methanol as solvent no complex formation of diaza-15-crown-5 and diaza-18-crown-6 with alkali ions can be observed.[4] Spectral changes of the dyes I and II in the presence of alkali and alkaline earth cations in methanol solutions are measured indicating a complex formation. Some absorption spectra of the dye II in the presence of sodium and potassium ions are shown in Figure 3. Similar spectra in methanol are measured with the dye I.

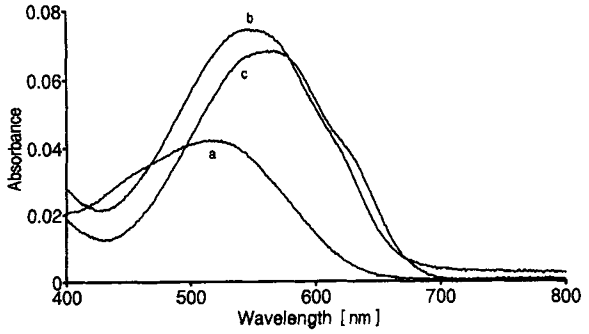

FIGURE 3 Absorption spectra of the ion-selective dye II (a) in the presence of Na^+ (b) and K^+ (c) in methanol at 25°C.

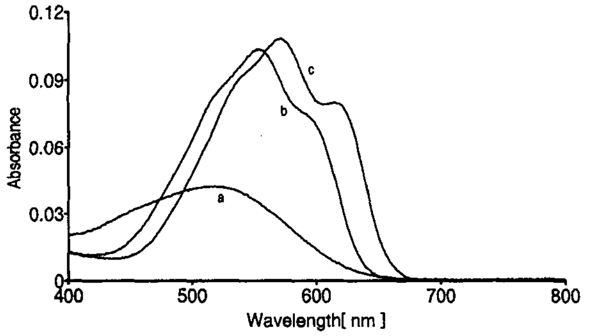

FIGURE 4 Absorption spectra of the ion-selective dye II (a) in the presence of Ca^{2+} (b) and Ba^{2+} (c) in methanol at 25°C.

The spectral changes of the dye II due to complexation of alkaline earth cations, see Figure 4, are much higher when compared with alkali ion complexes, see Figure 3.

In Table I the shifts in the maxima of absorption of the ion selective dyes due to the complex formation with alkali and alkaline earth cations in methanol as solvent are given. These results show, that the shift of the maximum of the absorption is influenced by the charge of the cation and by the size of the macrocyclic ligand within the dye molecule. If the cations are bigger than the cavities they are located outside of the cavities of the ligand molecule. Under these circumstances they interact mainly with just one of both chromophoric substituents.

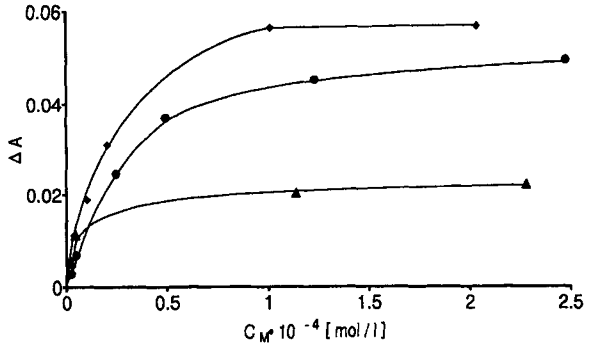

FIGURE 5 Changes of the absorbance A of dye II (2.2 10^{-5} mol/l) at a constant wavelength (529 nm) as a function of the concentration of alkaline earth cations (▲ Ca^{2+}, ● Sr^{2+}, ◆ Ba^{2+}) in methanol at 25°C.

The changes of the absorbance for the dye II measured at constant wavelength as a function of the salt concentration in methanol due to the complexation of alkaline earth cations are shown in Figure 5. Using dye I and other cations similar curves are measured. From these curves it is possible to calculate the stability constants of the complexes using equation (1) and the mass bilances. The results with the ion-selective dyes and with 4-chlorophenol-substituted diaza-18-crown-6 (see Figure 1) are summarized in Table II. The ion-selective dye I with diaza-15-crown-5 as ligand forms the most stable complexes with the smallest cations (Na^+ und Ca^{2+}). The aza crown ether itself does not form complexes with alkali ions in methanol. Thus, the chromophoric substituents at the nitrogen donor atoms of the diaza crown ether influence the complexation behaviour. One or two of the hydroxyl groups of the dye molecules are directly involved in the complex formation. An increase of the stability constants of the alkali ion complexes formed with dye II is also observed, when compared with diaza-18-crown-6. In contrast, this effect is not observed for the complexation of alkaline earth cations with the exception of Ca^{2+}. The stability constants of the bis(chlorophenol)-substituted ligand diaza-18-crown-6 ($22Ph_2$) differ from that found for the dye II and the ligand (22). Thus, in the case of ion

TABLE I Shifts of the absorption maxima (in nm) of the ion-selective dyes I (536 nm) and II (529 nm) due to complex formation with alkali and alkaline earth cations in methanol at 25°C

Cation	dye I	dye II
Na^+	+8	+2
K^+	+8	+66
Rb^+	+8	+64
Cs^+	+4	+4
NH_4^+	+8	+12
Ca^{2+}	+17	-3
Sr^{2+}	+28	+2
Ba^{2+}	+39	+9

selective dyes the complete chromophoric substituents are obviously involved in complex formation.

These experiments clearly demonstrate, that the dyes I and II may be used in optical sensors to measure the concentration of alkali and alkaline earth cations in solution. The spectral changes during the complex formation are caused by the interaction of the chromophoric groups with the complexed cations.

Acknowledgements

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References

[1] Misumi, S. (1993) *Top. Curr. Chem.*, **165**, 163.

[2] Trend, J.E. and Kipke, C.A. (1995) *Eur. Pat. Appl. EP*, **649**, 848.

[3] Blair, T.L., Desai, J. and Bachas, L.G. (1992) *Anal. Lett.*, **25**, 1823.

[4] Buschmann, H.-J. (1986) *Inorg. Chim. Acta*, **125**, 31.

[5] Buschmann, H.-J. (1986) *J. Solution Chem.*, **15**, 453.

[6] Zhang, X.X., Bordunov, A.V., Bradshaw, J.S., Dalley, N.K., Kou, X. and Izatt, R.M. (1995) *J. Am. Chem. Soc.*, **117**, 11507.

TABLE II Stability constants (log K, K in l/mol) for the complex formation of the dyes I and II and the ligands diaza-15-crown-5 (21) and diaza-18-crown-6 (22) with cations in methanol at 25°C

Cation	dye I	(21)	dye II	(22)	($22Ph_2$)
Na^+	5.24	_[a]	3.41	–[a]	2.85[d]
K^+	0.97	_[a]	4.78	1.83[a]	2.76[d]
Rb^+	0.31	_[a]	4.87	<1[a]	
Cs^+	_[b]	_[a]	4.63	_[a]	_[d]
NH_4^+			6.00		
Ca^{2+}	5.88	2.56[c]	4.23	3.87[c]	4.48[d]
Sr^{2+}	1.29	3.14[c]	4.81	5.99[c]	<2[d]
Ba^{2+}	_[b]	2.72[c]	5.29	6.12[c]	3.52[d]

[a] from Ref. 4

[b] spectral changes to small for the calculation

[c] from Ref. 5

[d] from Ref. 6