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Complexation of metal ions by azocrown ethers in Langmuir–Blodgett monolayers

Izabella Zawisza,[a] Renata Bilewicz,*[a] Elzbieta Luboch[b] and Jan F. Biernat[b]

[a] *University of Warsaw, Pasteura 1, 02-093 Warsaw, Poland. E-mail: bilewicz@chem.uw.edu.pl*
[b] *Technical University of Gdansk, Narutowicza 11, 80-952 Gdansk, Poland*

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Monomolecular films of amphiphilic derivatives of crown ethers bearing an azo group in the macrocycle were formed on the surfaces of pure water or aqueous solutions of metal cations and transferred onto a thin mercury film electrode using the Langmuir–Blodgett technique. The properties of the monolayer modified electrodes were studied by voltammetry. The azocrown molecules assembled in monolayers at the air–solution and electrode–solution interfaces were found to interact with selected alkali metal cations. This was revealed by the changes of the parameters of the surface–pressure and surface–potential isotherms recorded during the formation of monolayers at the air–solution interface, and by the electrochemical behaviour of the monolayer covered electrodes. The stability constants of the complexes formed by Na^+, K^+ and Ca^{2+} cations with the neutral (K_{ox}) and reduced (K_{red}) forms of the macrocyclic ligand in the monolayer, and the reaction coupling efficiency (K_{ox}/K_{red}), were calculated.

Introduction

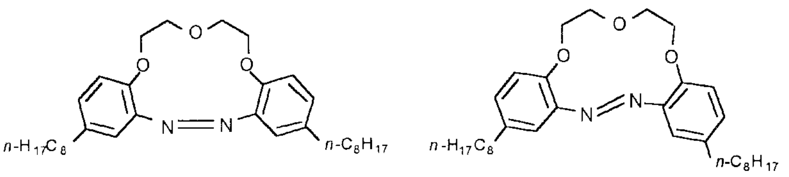
Azo compounds are used as photo- or redox-active components of films deposited on solid substrates by self-assembly or Langmuir–Blodgett methods.[1–13] In the solid phase the simplest such compound, azobenzene, exists in two isomeric forms: *Z* and *E*. The *trans* (*E*) form is flat[1,14] with a dipole moment equal to zero, while in the less stable *cis* (*Z*) form the phenyl rings are not coplanar and the dipole moment is 3.0 D.[15] Reversible *cis–trans* isomerization of azo compounds could be useful to construct molecular switches and especially the combination of the N=N group with a crown ether known for its complexing abilities may lead to useful materials for ion-sensing devices. Photoswitchable azobis(benzo-15-crown-5) ionophores were for example used as molecular probes for phase boundary potentials at ion-selective liquid membranes.[16] In earlier papers we described the synthesis and properties of crown ethers with an azo group in the macrocycle.[17–27] The electrochemical behavior of azocrown molecules in Langmuir-Blodgett monolayers on electrodes has been discussed recently.[23,26,27] We demonstrated that the size and structure of the azocrown ethers defined the ability of the molecules to bind cations inside the cavity.[21–25] In the solid state, in the presence of sodium iodide, L13 (Fig. 1) azocrown ligand was found to form a sandwich type complex of formula $Na(L13)_2{}^+I^-$ with *trans* orientation of the benzene residues.[21] Only the *trans* (*E*) form of the azocrown compounds was found suitable as a host for metal cations.

In the present paper we study the binding properties of 13-membered amphiphilic azocrown ether (L13-C8) molecules assembled in monolayers at the air–water and electrode–solution interface.[25] We used voltammetry to follow the complexation of cations by the neutral and reduced forms of the azo compound molecules assembled in monolayers on electrodes, and evaluate the binding constants from the changes in the formal potentials of the azo group observed in the presence of certain cations in the solution.

Experimental

All materials were of analytical grade. The synthesis of the azocrown ether and separation into *Z* and *E* isomers is described elsewhere.[25] The solutions of crown ethers were prepared daily. Distilled water used as the subphase was passed through a Milli-Q water purification system. Methylene chloride (Aldrich) was employed as the spreading solvent. The supporting electrolyte solutions were prepared using citrate

Parent crown ethers *Z* and *E* L13



Z-L13-C8 (*cis*) *E*-L13-C8 (*trans*)

Fig. 1 Structures of the compounds studied.

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Table 1 Characteristics of the isotherms for *Z* and *E* isomers of L13-C8 azocrown ether on different subphases

Isomer	Subphase	$A_0 \pm 2$/Å^2	$\Pi_{\mathrm{coll}} \pm 1$/mN m^{-1}	$K_s \pm 3$/mN m^{-1}	$\mu \pm 0.04$/D
Z	Water	77	37	113	0.99
	0.1 M LiOH	76	40	105	0.95
	0.1 M KOH	76	40	118	0.98
	0.1 M NaOH	74	42	121	1.19
	0.01 M $Ca(OH)_2$[a]	76	40	125	1.24
E	Water	98	36	162	1.17
	0.1 M LiOH	97	37	149	0.97
	0.1 M KOH	93	38	165	0.91
	0.1 M NaOH	99	40	191	1.08
	0.01 M $Ca(OH)_2$[a]	102	39	170	1.30

[a] The concentration of $Ca(OH)_2$ solution was ten times lower because of the solubility problem.

buffer with pH and ionic strength brought to the desired value by addition of LiOH and LiCl, KOH or NaOH or Tris buffer acidified by adding $HClO_4$.

Surface pressure and surface potential *vs.* area per molecule isotherms were recorded using a KSV LB Trough 5000 equipped with two hydrophobic barriers, a Wilhelmy balance as a surface-pressure sensor and 5000SP surface potential meter (vibrating capacitor method). Software KSV-5000 was used to control the experiments. To protect the experimental set-up from dust it was placed in a laminar flow hood in which the temperature was kept constant at 20 ± 1 °C. Surface potential and surface pressure were recorded simultaneously as a function of molecular area. The accuracy of measurements was ± 2Å^2 molecule^{-1} for area per molecule, ± 0.1mN m^{-1} for surface pressure and ±5mV for surface potential. The procedures of cleaning the trough and monolayer spreading have been described earlier.[28–31] The substrate was thin mercury film on silver wire. The silver wire electrode was 0.05 cm in diameter and 3 cm long. The silver wire precleaned in concentrated perchloric acid was touched to a drop of mercury and cathodically polarized in 0.1 M KOH to obtain a shining and uniform layer of mercury, *ca.* 0.1 mm thick. Monolayers were transferred at surface pressure 20 mN m^{-1} by immersing the hydrophobic, thin mercury film electrode (TMFE) at a speed of 3 mm min^{-1}.

Voltammetry experiments were done in a three-electrode arrangement with a calomel reference electrode, platinum foil as counter and TMFE as working electrodes. An ECO Chemie Autolab system was used as the potentiostat. For high scan rate experiments *IR* compensation provided with this instrument was employed.

Results and discussion

Langmuir monolayers of *Z* and *E* isomers of L13-C8 on subphases containing metal cations

Monolayers of the amphiphilic derivative of the azocrown ether were recorded on pure water subphase and on subphases containing metal cations. The interactions with cations were demonstrated by the changes of surface pressure–area and surface potential–area isotherms recorded on the subphase containing these cations. Changes of the isotherms parameters area per molecule (A_0), compressibility modulus (K_s) and collapse pressure (Π_{coll}) were observed for the 13-membered azocrown on subphase containing Na^+ and Ca^{2+} cations. Fig. 2 compares the isotherms for the *E* isomer of L13-C8 on the water, LiOH, and NaOH subphases.

Table 1 presents the changes of A_0, Π_{coll} and K_s for the *Z* and *E* isomers of L13-C8 on subphases of different cations, when strongly alkaline solutions are employed. Owing to solubility problems the Ca^{2+} solutions were 0.01 instead of 0.1 M used in the case of other subphases; A_0 is the limiting molecular area in the monolayer and Π_{coll} is the monolayer collapse pressure. The compressibility factor is given by eqn. (1).[32] A = area per molecule and $\mathrm{d}A/\mathrm{d}\Pi$ = slope of the isotherm.

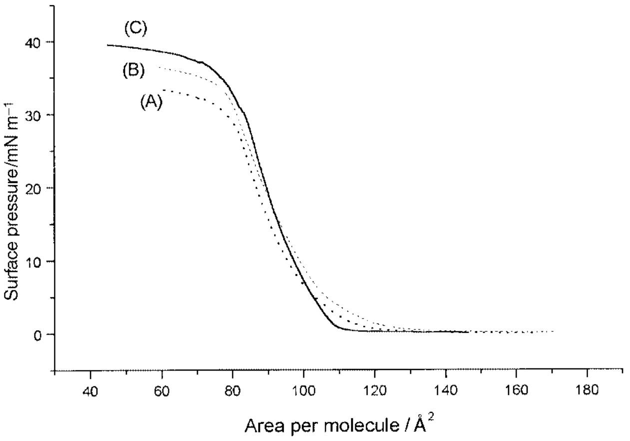

Fig. 2 Surface pressure–area isotherms for *E*-L13-C8 on different subphases: (A) water, (B) 0.1 M LiOH, (C) 0.1 M NaOH.

$$K_s = \left[-\left(\frac{1}{A}\right)\left(\frac{\mathrm{d}A}{\mathrm{d}\Pi}\right)\right]^{-1} \qquad (1)$$

The *E* and *Z* isomers can be recognized by the different value of the compressibility factor, K_s, calculated from the Langmuir monolayers. It was always higher for isomer *E*. For both isomers, the K_s values on water and on a 0.1 M solution of LiOH as subphases were almost identical. Upon addition of K^+, Ca^{2+} or Na^+, K_s and Π_{coll} increased indicating stabilization of the monolayer. This may be ascribed to the interaction with these metal ions in contrast to Li^+. The latter ion has a smaller radius compared to the size of the cavity of the macrocycle. As seen in Table 1, larger changes of K_s are observed for isomer *E* compared to isomer *Z*, since the structure of the former is appropriate for binding cations.

The surface potential measurements during the formation of monolayers at the air–water interface allow one to calculate the dipole moment in the monolayer,[25,33] eqn. (2), where μ is the

$$\mu = A_m \Delta V \varepsilon_0 \qquad (2)$$

effective dipole moment perpendicular to the water surface, A_m the area per molecule at the selected surface pressure, ΔV the surface potential corresponding to A_m and ε_0 is the permittivity in a vacuum.

In the presence of Li^+ cations the isotherms recorded for both *Z* and *E* isomers of L13-C8 are similar to isotherms obtained on the water subphase since the azocrown macrocycle is too big to accommodate small Li^+ cations. In the presence of Na^+ and Ca^{2+} the values of the compressibility factor and dipole moment were distinctly higher than in the absence of these ions in the subphase. Larger values of K_s and μ were observed for the *E* isomer since its structure is suitable for complexing cations. Formation of the charged complex on the air–water interface leads to the observed increase of dipole moment

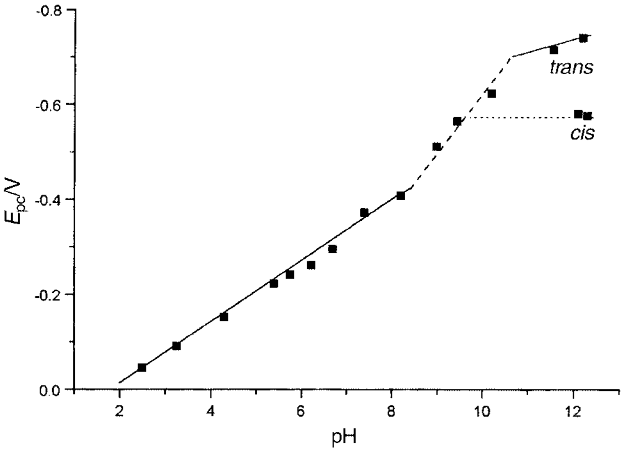

Fig. 3 Dependence of the potential of the reduction peak on pH, in citrate buffer/LiOH for pH range 2–7 and above 11, and 0.05 M Tris/$HClO_4$ for pH 7–10. $v = 0.1$ V s^{-1}.

in the monolayer. Somewhat higher values observed for the monolayer of *Z* isomer on subphases containing NaOH compared to water and 0.1 M LiOH can be explained assuming that Na^+ ions induce isomerization of the unstable *Z* to the *E* isomer during the experiment.

Properties of azocrown monolayer preformed on the water–air interface and transferred onto a mercury film electrode (TMFE)

The monolayers of azocrown ethers were transferred onto the surfaces of a hydrophobic thin mercury film electrode by immersing the electrode into the subphase through the monolayer covered air–water interface. During the transfer the surface pressure of the monolayer at the air–water interface was kept constant.

The mechanism of the electrode process of the azo compound depends strongly on the pH. Lithium cations were used as the supporting electrolyte cations. The potentials for reduction and oxidation of the azocrown did not change with increase of Li^+ concentration in the solution which indicated the absence of interactions and allowed us to employ compounds of this cation to adjust the pH and ionic strength of the solution to desired values. In acidic and neutral media (pH values 2–7.5) the reduction is reversible and the slope of a plot of the potential *vs.* pH (Fig. 3, solid line) is 58 mV/pH unit. In the process of reduction $2e^-$ and $2H^+$ are consumed,[34] eqn. (3).

$$\text{–N=N–} + 2e^- + 2H^+ \longrightarrow \text{–NH–NH–} \qquad (3)$$

In acidic and neutral media the presence of Li^+, Na^+ or K^+ did not affect the position or shape of the voltammetric signals corresponding to electrode processes of the azo group, indicating lack of interactions of the azo compound with alkali metal cations under these conditions. In the pH range 7.5–11 the mechanism of reduction of the azo group changes, leading to the observed change of the slope of the plot of the reduction peak potential *vs.* pH (dotted line of Fig. 3).

In alkaline media the reduction potential of the azo group is not pH dependent and under these conditions the isomers *Z* (*cis*) and *E* (*trans*) can be distinguished by voltammetry.[26,27] The *cis* form is reduced at more positive potentials than the *trans* form (Fig. 3). Only isomer *E* of the azocrown was found to interact with metal cations, leading to a negative shift of the reduction potential. No differences in the *Z* (*cis*) peak position were found after addition of metal cations. Indeed, the size and steric structure of the macrocycle in *cis* form is not appropriate to complex metal cations.

In alkaline solutions the position of the voltammetric reduction peak for the *E* (*trans*) isomer depends on the concentration of sodium and potassium ions. The azocrown is reduced under these conditions according to eqns. (4) and (5),[34] where protons

$$\text{–N=N–} + 2e^- \longrightarrow [\text{–N–N–}]^{2-} \qquad (4)$$

$$[\text{–N–N–}]^{2+} + 2H_2O \longrightarrow \text{NH–NH–} + 2OH^- \qquad (5)$$

are abstracted from the solvent. In case of the reduced azocrown the ligand is in the neutral hydrazo form [eqn. (5)], which forms weaker complexes with metal cations than the original azocrown, as will be shown below. When, for comparison, NEt_4OH is used as the supporting electrolyte (despite its low stability in aqueous media and the known adsorbability of alkylammonium ion on mercury electrodes in water) instead of LiOH the formal potential for the azocrown was −0.703 V, which is clearly more positive than for 0.1 M NaOH (−0.743 V) and very similar to that in 0.1 M LiOH (−0.697 V). Therefore, we can conclude that the negative shift of the peak and formal potentials observed upon addition of Na^+ cations to a solution containing LiOH in aqueous media is due to the stronger complexation of the initial form of the ligand with Na^+ than with Li^+ or NEt_4^+ cations. The direction of the potential shifts also confirms that the complexation with the original ligand is always stronger than with the hydrazo compound obtained upon reduction in aqueous solutions.

Stability constants of Na^+, Ca^{2+} and K^+ complexes with the azocrown immobilized in a monolayer on electrodes

Monolayers of the *E* azo compound were transferred onto the mercury film electrode and the modified electrodes then immersed into solutions containing various concentrations of Na^+, Ca^{2+} or K^+ ions. The pH and ionic strength were kept constant. Fig. 4 presents voltammograms recorded using TMFE electrodes modified with Langmuir–Blodgett monolayers of *E*-L13-C8 azocrown in solutions of Na^+, Ca^{2+} and K^+. The reduction peak potential is clearly shifted to more negative values when the Na^+, Ca^{2+} and K^+ concentrations are increased. The widths of the peaks at half-height ($b_{1/2}$) also increase, revealing interactions in the monolayer. These observations indicate that the ligand studied forms more stable complexes with metal cations in its initial (neutral form of azocrown) than in the reduced state. The negative shift of potentials observed upon addition of Na^+ cations to a solution containing LiOH as the supporting electrolyte is in our system not surprising since the reduced form of the ligand is involved in stronger interactions with the H^+ ions abstracted from water and having larger affinity for the reduced azo bond than any other cation.

From the differences of the formal potentials of the azo group in the presence of only Li^+ ions, and after addition of complex forming cations to the solution, the stability of the complex could be determined. Changes of the formal potential with the increase of metal ion concentration can be used for the calculation of the stability constants with the oxidized and reduced forms of the ligand according to eqn. (6),[35] where

$$E^0_{\mathrm{LM}} = E^0_{\mathrm{L}} - \frac{RT}{nF}\ln\left(\frac{1 + \Sigma\beta_{i\mathrm{ox}}[\mathrm{L}]_i}{1 + \Sigma\beta_{j\mathrm{red}}[\mathrm{L}]_j}\right) \qquad (6)$$

E^0_{L} = formal potential of the “free” ligand, E^0_{LM} = formal potential of the ligand in the complex, n = number of electrons exchanged in the process of reduction, F = Faraday constant, R = gas constant, $\beta_{i\mathrm{ox}}$ and $\beta_{j\mathrm{red}}$ are cumulative stability constants for complexes with oxidized and reduced forms of the ligands. For a 1 : 1 adduct the relationship between change of the potential and concentration of the metal cation is given in eqn. (7),[36]

$$\frac{1}{e^{-nF\Delta E/RT} - 1} = \left(\frac{1}{K_{\mathrm{ox}} - K_{\mathrm{red}}}\right)\left(\frac{1}{[\mathrm{M}]}\right) + \left(\frac{K_{\mathrm{red}}}{K_{\mathrm{ox}} - K_{\mathrm{red}}}\right) \qquad (7)$$

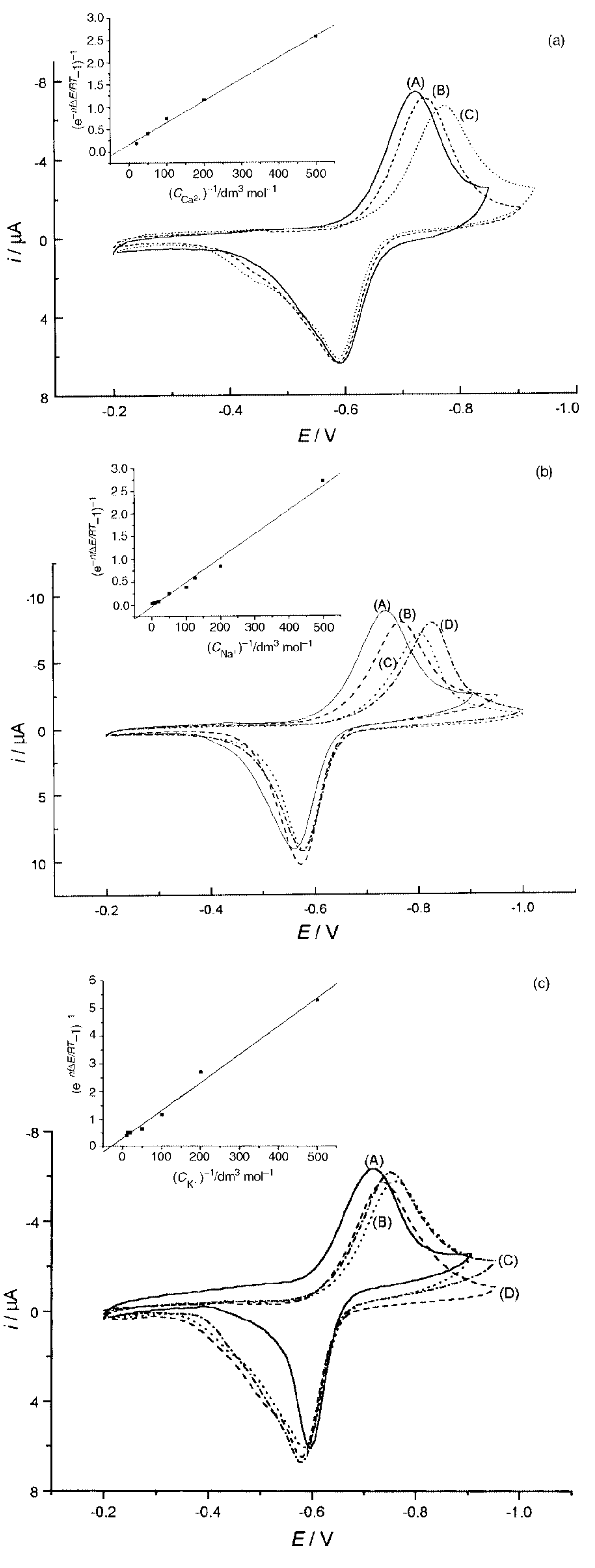

Fig. 4 Voltammograms recorded on *E*-L13-C8 monolayer modified TMFE in solutions of (a) Ca^{2+}, (b) Na^+ (c) K^+, pH 12.2. Concentrations of metal cations: (A) 0.0, (B) 5×10^{-3}, (C) 5×10^{-2} and (D) 0.1 M, $v = 0.1$ V s^{-1}. Insert: plot of $[e^{(-\Delta E nF/RT)} - 1]^{-1}$ *vs.* reciprocal of metal ion concentration in the solution.

where $\Delta E = E^0_{LM} - E^0_L$, K_{ox} = stability constant of the complex with the oxidized form of the ligand, and K_{red} = stability constant of the complex with the reduced form of the ligand.

Table 2 Stability constants for Na^+, K^+ and Ca^{2+} complexes with neutral (K_{ox}) and reduced (K_{red}) forms of L13-C8 azocrown ether in the monolayer on TMFE, pH 12.2 at 25 °C

Cation	K_{ox}/M^{-1}	K_{red}/M^{-1}	REC = K_{ox}/K_{red}	E^0_{LM}/V [±5 mV]
Ca^{2+}	241.4 ± 12.8	34.4 ± 2.6	7.0	−0.680[a]
Na^+	195.0 ± 8.4	5.4 ± 0.6	36.1	−0.700
K^+	127.0 ± 9.6	29.0 ± 2.1	4.38	−0.672

[a] For 0.05 M Ca^{2+} due to solubility problems.

A plot of $(e^{-nF\Delta E/RT} - 1)^{-1}$ *vs.* $[M]^{-1}$ for L13-C8 and Na^+, Ca^{2+} or K^+ is linear (Fig. 4). From the values of slope and ordinate intercept we estimated the values of stability constants for the complexes of Na^+ and K^+ with L13-C8 in oxidized and reduced forms. On the basis of our data eqns. (8)–(10) were

$$\frac{1}{e^{-nF\Delta E/RT} - 1} = 0.00483\left(\frac{1}{[Ca^{2+}]}\right) + 0.166 \quad \text{correlation} = 0.998 \tag{8}$$

$$\frac{1}{e^{-nF\Delta E/RT} - 1} = 0.00527\left(\frac{1}{[Na^{+}]}\right) + 0.028 \quad \text{correlation} = 0.996 \tag{9}$$

$$\frac{1}{e^{-nF\Delta E/RT} - 1} = 0.01021\left(\frac{1}{[K^{+}]}\right) + 0.0306 \quad \text{correlation} = 0.995 \tag{10}$$

obtained. Calculated values of the stability constants for complexes of Ca^{2+}, Na^+, and K^+ with *trans* L13-C8 immobilized in monolayers on TMFE are collected in Table 2.

The reaction coupling efficiency (REC) equal to K_{ox}/K_{red} may be calculated from eqn. (11).[37] Upon complexation, the formal

$$\frac{(E^0_L - E^0_{LM})nF}{RT} = \ln\left(\frac{K_{ox}}{K_{red}}\right) \tag{11}$$

potential of the complex is shifted to more negative values[23,26] which indicates that the initial form, neutral azocrown, binds the selected cation more strongly than the reduced form of the ligand. Sodium and Ca^{2+} cations fit well to the macrocycle cavity which explains the complexing abilities towards these cations. The shifts of peak potentials towards more negative values are most prominent in these two cases. The stability constants for the complex of Na^+ with L13-C8 in the neutral state is 36 times bigger than for the complex with the reduced form of the complex since the reduced form is bound to the protons from water.

The neutral form of the ligand binds strongest the Ca^{2+} cation for which the equilibrium constant, K_{ox}, is 241.4 M^{-1}; Na^+ cation is bound more strongly than K^+. The REC values show that upon reduction of the complex formed with Na^+ the complexation strength of the ligand is significantly decreased (*ca.* 40 times). It makes this system more interesting as a molecular switch than complexes of Ca^{2+} where the factor K_{ox}/K_{red} is only 7.0 or K^+ where it is only 4.3.

Determination of Na^+ ions and interferences of different cations present in the solution

The monolayer of *E*-L13-C8 was used as a sensing unit for Na^+ ions. The reduction peak of the azo group of L13-C8 assembled in a monolayer responded to Na^+ ion concentrations in the range 1×10^{-3} to 0.5 M. The potential of the reduction peak can be used to evaluate the concentration of Na^+ cation in solution [Fig. 5]. Larger concentrations of K^+ and Ca^{2+} will affect the potential of the reduction peak and hence will interfere in the determination of Na^+ ions based on the position of the azo group reduction signal. The presence of K^+ in the

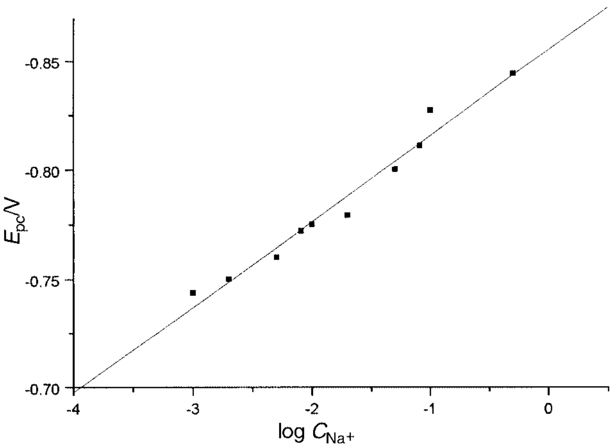

Fig. 5 Dependence of reduction peak potential on log C_{Na^+}, for a monolayer of *E*-L13-C8 on TMFE, $v = 0.1$ V s^{-1}.

solution interferes at concentrations larger than 10^{-2} M. The potential of the reduction peak is shifted to more negative values. For a Na^+ concentration 8×10^{-3} M the potential of the reduction peak is shifted from $E^0 = -0.772$ to $= -0.793$ V in the presence of 1×10^{-2} M K^+. 5×10^{-3} M Ca^{2+} leads to an additional shift of the anodic signal while the cathodic part is not affected. Above 8×10^{-3} M Ca^{2+} the cathodic peak also starts to shift to more negative potentials. This may be ascribed to higher stability of the Ca^{2+} complexes with the reduced form of the ligand compared to the Na^+ complexes, while the complexes with the oxidised form of the ligand are similar. Magnesium cations, do not interfere since magnesium hydroxide is precipitated at the high pH used for the determination of Na^+. This precipitation did not affect the shape of the voltammogram.

Conclusion

Amphiphilic derivatives of 13-membered azocrown ethers organized in monolayer assemblies were found to bind Ca^{2+}, Na^+ and K^+ in contrast to Li^+. The shape and size of the cavity of the azocrown is suitable for binding Ca^{2+} and Na^+ when the ligand is in its *trans* (*E*) form. Formation of the charged complex on the air–water interface is revealed by an increase of compressibility factor and dipole moment in the monolayer.

The electrochemical behaviour of the azocrown monolayers on thin mercury film electrodes was also found to depend on the presence of certain metal cations in the solutions. From the dependence of the azo group formal potential on the concentration of selected metal ions, the binding constants of the cations to the oxidised and reduced forms of the ligand were calculated. Calcium ion and the ligand in its initial form exhibited the strongest interactions. On the other hand, the largest difference between the complexing abilities of the initial azocrown and its reduced hydrazo form were found for the Na^+ cation. In this case, upon electrochemical switching from the reduced to the oxidised form, the complexation of the metal cation was strengthened almost 40 times which makes the system interesting as a molecular switch suitable for aqueous media. Most of the molecular switching studies reported so far gave the opposite result: reduced ligand interacted with the cation stronger than the initial form.[38,39] However the latter studies were performed in non-aqueous, aprotic media and no protons were available to neutralize the dianion produced in the reduction process. The anionic form obtained upon reduction was not neutralized in the reaction with protons. In the aprotic solvents the enhancement of binding upon reduction was due to a combined effect of crown binding and ion pairing with dianion. On the other hand, in aqueous media the dianion is immediately converted into the hydrazo form, which has weaker complexing abilities towards metal cations compared to the initial azocrown as demonstrated in this paper.

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