

# Properties of Monolayers of Crown Ethers Bearing an Azo and Azoxy Group in the Macrocycle

ELZBIETA MUSZALSKA and RENATA BILEWICZ\*

*Department of Chemistry, University of Warsaw, ul. Pasteura 1, 02093 Warsaw, Poland*

ELZBIETA LUBOCH, ANNA SKWIERAWSKA and JAN F. BIERNAT

*Department of Chemical Technology, Technical University of Gdańsk, 80952 Gdańsk, Poland*

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**Abstract.** Two methods are described for preparing monomolecular layers of crown ethers with an azo or azoxy group in the macrocycle. When the molecules used to build the monolayer are soluble in aqueous solutions, adsorptive preconcentration on mercury electrodes was used to prepare the monolayer coating. The monolayer was electroactive due to the presence of the azo or azoxy unit in the molecules. Monolayers of crown ethers bearing an azo group in the macrocycle were shown to recognize alkali metal cations present in the solution. Changes of the parameters of the voltammetric reduction peaks – peak potential and peak width, served as an indication of specific interactions of the monolayer of 13-membered and 16-membered azocrown ethers with  $\text{Na}^+$  and  $\text{K}^+$  cations, respectively.

The monolayers capable of recognizing cations have also been prepared on the aqueous solution–air interface, using the Langmuir technique. In this approach, amphiphilic derivatives of the azocrowns were synthesized and the monolayer has been assembled on the subphase containing metal cations. Binding of the cation by the macrocycle has a stabilizing effect on the monolayer and higher collapse pressures are achieved than on the pure water subphase. The monolayer was transferred from the air–water interface on the solid substrate using the Langmuir–Blodgett technique. Thin mercury film electrodes on the Ag substrate, or Au films evaporated on glass slides were employed as the electrode substrates. The former gave monolayer modified electrodes of higher stability.

**Key words.** Monolayers, azocrowns, crown ethers, Langmuir monolayer.

## 1. Introduction

Azo compounds have been studied for over 40 years. Increased interest in azo compounds in recent years is due to their applications as elements of optical memories and molecular switches [1–3]. The first synthesis of a crown ether with an azo group was described by Shiga and co-workers [4,5]. In the present study both azoxy and azocrowns are obtained using the procedures introduced by Biernat *et al.* and described in previous publications [6–8]. Introduction of an azo or azoxy group into the macrocycle makes the crown ether electroactive, and thus opens the possibility of studying them using electroanalytical techniques. In

\* Author for correspondence.

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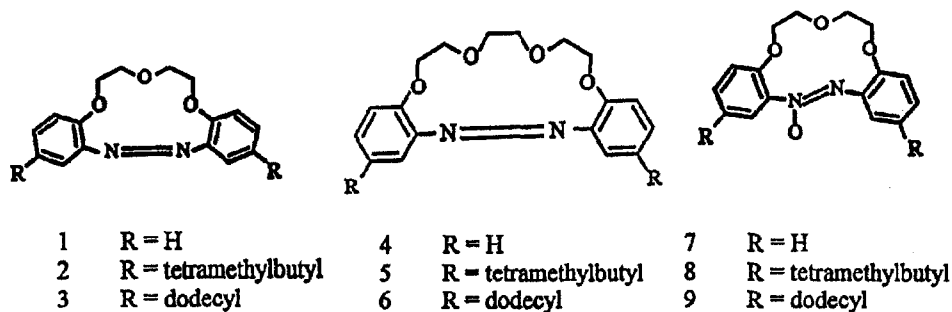


Fig. 1. The structures of the azo and azoxy compounds studied.

previous publications we investigated the electrochemical properties of a series of azo and azoxy crown dimethylformamide solutions and the observed differences were explained in comparison to simple azo and azoxybenzene [6,8]. In general, insertion of the electroactive group into the macrocycle made the reduction of the group more difficult and led to the stabilization of a protonated radical [6,8]. In aqueous solutions the solubility of these compounds is limited. The solubilities were determined using stripping voltammetry with adsorptive accumulation from highly dilute solutions of the azocrowns [9].

In the present work our aim was to prepare monolayers of the azocrowns shown in Figure 1, to check whether such molecular assemblies retain ion recognition abilities known for crown ethers with an azo group from studies in solution [4,5]. Liquid-liquid extraction data concerning compound 4 (Figure 1) reported by Shiga *et al.* [4] revealed that  $\text{Na}^+$  is extracted by this ligand much better [ $\log K_{\text{ex}} = 4.1(8)$ ] than  $\text{K}^+$  [ $\log K_{\text{ex}} = 2.7(7)$ ]. In the next paper [5] the authors reversed this order, reporting that  $\text{K}^+$  is extracted better while  $\text{Li}^+$  is not extracted at all.

Ion binding properties of ionophores assembled in monolayers have been reported by several authors [10–14]. In our study two methods are used to produce the monolayers.

Adsorptive accumulation from the diluted solutions of more soluble azocrowns is used for monolayer formation on mercury electrodes and voltammetry is employed to monitor both the redox properties of the layer and its response towards different cations in the solution.

Amphiphilic derivatives of the azocrowns were synthesized and used as the components of the monolayers on the water-air interface. The monolayer properties were characterized by recording the surface pressure-area per molecule isotherms on subphases containing various cations. The Langmuir-Blodgett approach was employed to transfer the monolayers from the air-water interface onto the electrode substrate. A silver based mercury film electrode was for the first time, to our knowledge, used as a substrate for the Langmuir-Blodgett deposition and proved to be better than evaporated gold electrodes in terms of stability of the azocrown monolayer modified electrodes.

## 2. Experimental

Voltammetric experiments were performed in a three electrode arrangement with a saturated calomel reference electrode, a platinum foil counter electrode and a static mercury drop electrode, SMDE 1 (Laboratorni Pistroje) of 0.015 cm<sup>2</sup> drop area, used in the hanging drop mode. When the Langmuir–Blodgett method of transfer of a monolayer onto the electrode was used, the electrode substrates were a thin layer of evaporated gold on the Ti underlayer on glass slides or a thin mercury film on Ag. Voltammograms were recorded either with the BAS-100 Electrochemical Analyzer (Bioanalytical Systems Inc.) and the HILOT DMP-40 Plotter (Houston Instrument) or with an electrochemical analyzer, PA4 and an XY recorder (Laboratorni Pistroje). All electrochemical experiments were done at 25 °C, in solutions deaerated with argon.

Surface pressure vs. area per molecule isotherms were recorded using the KSV-Minitrough with a Wilhelmy plate type microbalance placed in a laminar-flow hood. The instrument was controlled by a PC AT computer. Software version KSV 5000 was used to control the experiment. The procedures of cleaning the trough and monolayer spreading have been described earlier [15–17].

All materials were of analytical grade. The solutions of molecules were prepared daily. Distilled water used as the subphase was passed through a Milli-Q water purification system. Chloroform (Aldrich) was employed as the spreading solvent.

## 3. Results and Discussion

### 3.1. MONOLAYERS ADSORBED ON MERCURY ELECTRODES

Azo and azoxy crowns, like azo and azoxybenzene, undergo adsorption on mercury surfaces [9]. In a stirred solution of the azo or azoxy crown (compound **1** and **7** in Figure 1), a potential of  $-0.2\text{V}$  is applied to the electrode for 1 min and the compound is accumulated at the electrode surface (Figure 2A). As described previously [9] the potential  $-0.1$  to  $-0.2\text{ V}$  was found to be optimal for efficient preaccumulation of the azocrowns. Adsorptive accumulation can be also performed without the potential applied; however, preconcentration in a closed circuit limits the interference caused by adsorption of other compounds. The range of potentials useful for accumulation is limited by onset of mercury oxidation on the one hand and by reduction of the adsorbed azo compound on the other. The amount of the compound accumulated on the electrode surface can be determined from the charge of the voltammetry reduction peak corresponding to the formation of the hydrazo compound (Figure 2C). The azoxy compound **7** is accumulated most efficiently at  $-0.3\text{V}$  (Figure 2B) and also reduced in a 4-electron process to the hydrazo compound. Oxidation of the hydrazo form produces an azo compound that is retained on the electrode surface. It is seen in the scan above in the form of the azo crown reduction peak (Figure 2B – dashed line).

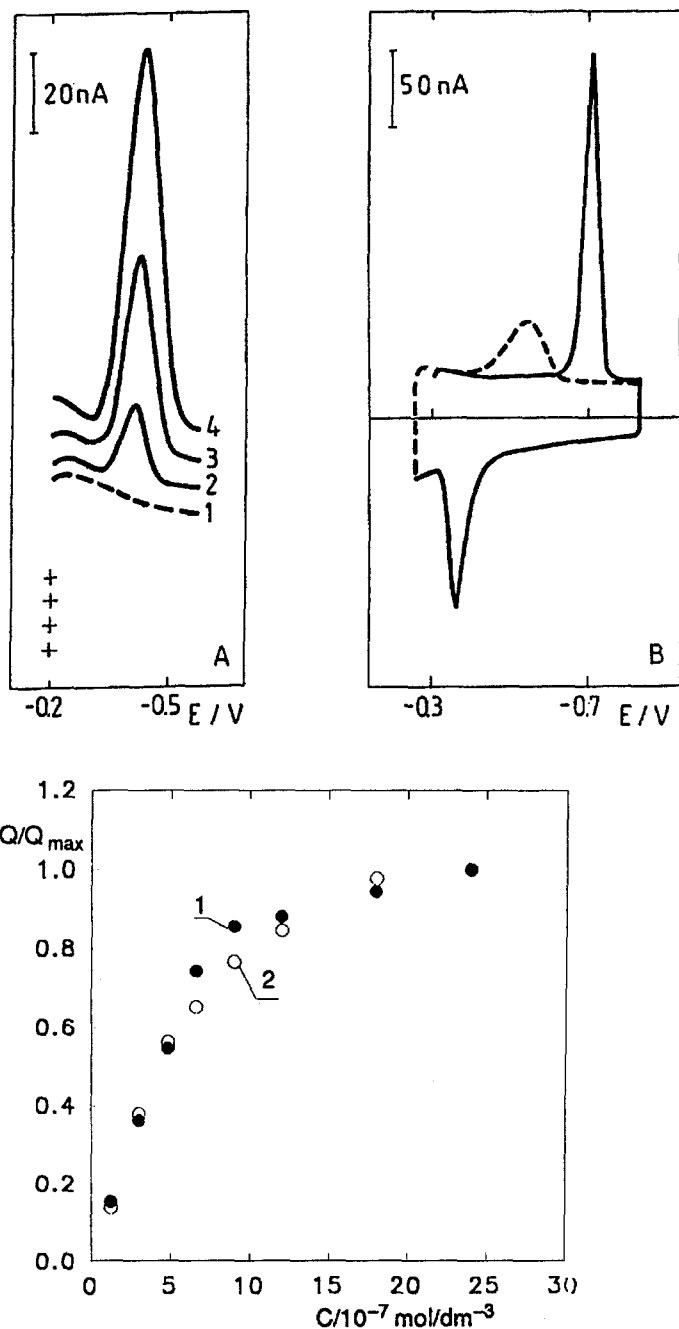


Fig. 2. Stripping voltammetry with adsorptive accumulation of compounds 1 (A) and 7 (B). Stripping curves recorded after 3 min preaccumulation at (A)  $-0.2$  V and (B)  $-0.3$  V in solution of  $0.1 \text{ mol dm}^{-3}$   $\text{CaCl}_2$  containing: (A) 1) 1; 2) 3; 3)  $7 \times 10^{-8} \text{ mol dm}^{-3}$  compound 1 and (B)  $1 \times 10^{-7} \text{ mol m}^{-3}$  compound 7. (C) Charge of reduction peak vs. concentration of compound 1 (1) and azobenzene (2). Scan rate:  $100 \text{ mV/s}$ .

The reduction signal increases both with the increase of preconcentration time and concentration of the macrocycle in the solution. At longer times deviations from linearity are seen even at very low concentrations in the solution, although the equilibrium value of surface excess is probably not attained yet. It may be an indication of coadsorption of contaminants from the solution. To eliminate this, the preaccumulation time was never longer than 3 min. As seen in Figure 2C, at a certain concentration the reduction peak attains a constant charge, which corresponds to a full coverage of the electrode surface by a monolayer of azocrown. The surface-coverage-concentration plot can be approximated by a Langmuir type isotherm similar to that of azobenzene. From the charge corresponding to the monolayer coverage the area occupied by a single molecule of compound **1** is  $72 \text{ \AA}^2$  which, based on the structure of the compound [6], points to a flat conformation (calculated to be  $70\text{--}100 \text{ \AA}^2$ ) rather than one perpendicular to the electrode surface (predicted to be  $40\text{--}50 \text{ \AA}^2$ ). Figure 3 exhibits the stripping voltammograms for the 13-membered azocrown (compound **1**) recorded in a neutral and an alkaline medium.

As shown, in NaOH solution the cathodic peak is located at more negative potentials and its half-width is narrower than in the NaClO<sub>4</sub> solution. In alkaline medium the process is a 2e reduction of the adsorbed species to an azo dianion, while in neutral solution a 2e, 2H<sup>+</sup> process prevails [18].

### 3.2. RECOGNITION OF CATION BY THE AZOCROWN MONOLAYER ADSORBED ON A MERCURY ELECTRODE

Figure 4 presents the cyclic voltammogram recorded for  $2 \times 10^{-7} \text{ mol dm}^{-3}$  13-membered azocrown accumulated for 1 min at  $-0.1\text{V}$ . in a solution containing  $0.1 \text{ mol dm}^{-3}$  calcium, lithium and sodium chloride, respectively.

The most positive value of the peak potential and narrowest peak width indicates zero or very weak interactions of the macrocycle with the calcium ion. In this medium the surface coverage vs. adsorbate concentration plot (see Figure 2C) can be approximated by the Langmuir type of adsorption isotherm [18]. The peak width is similar to that of adsorbed simple azobenzene. However, in solutions containing Na<sup>+</sup> ions the reduction peak is shifted towards negative potentials (Figure 4). The difference in the peak potentials and changes of the peak width indicate interactions of the macrocycle with the sodium ion. The negative potential shifts can be explained by stronger interaction with the neutral, initial form of azocrown than with the reduced form. Similar shifts of the voltammetric peak were observed by Bernardo *et al.* [19] in the case of binding of neurotransmitters from the solution by macrocyclic receptors incorporated in Nafion films on electrodes.

For azocrowns interacting with supporting electrolyte cation the peak width is larger and the isotherm steeper, which indicates interactions within the layer. Larger half-widths are expected for repulsion between molecules forming the layer [18]. In solutions containing Na<sup>+</sup> (for 13-membered macrocycle) and K<sup>+</sup> ions (for the 16-membered macrocycle) as opposed to those with Ca<sup>2+</sup>, tetramethylammonium

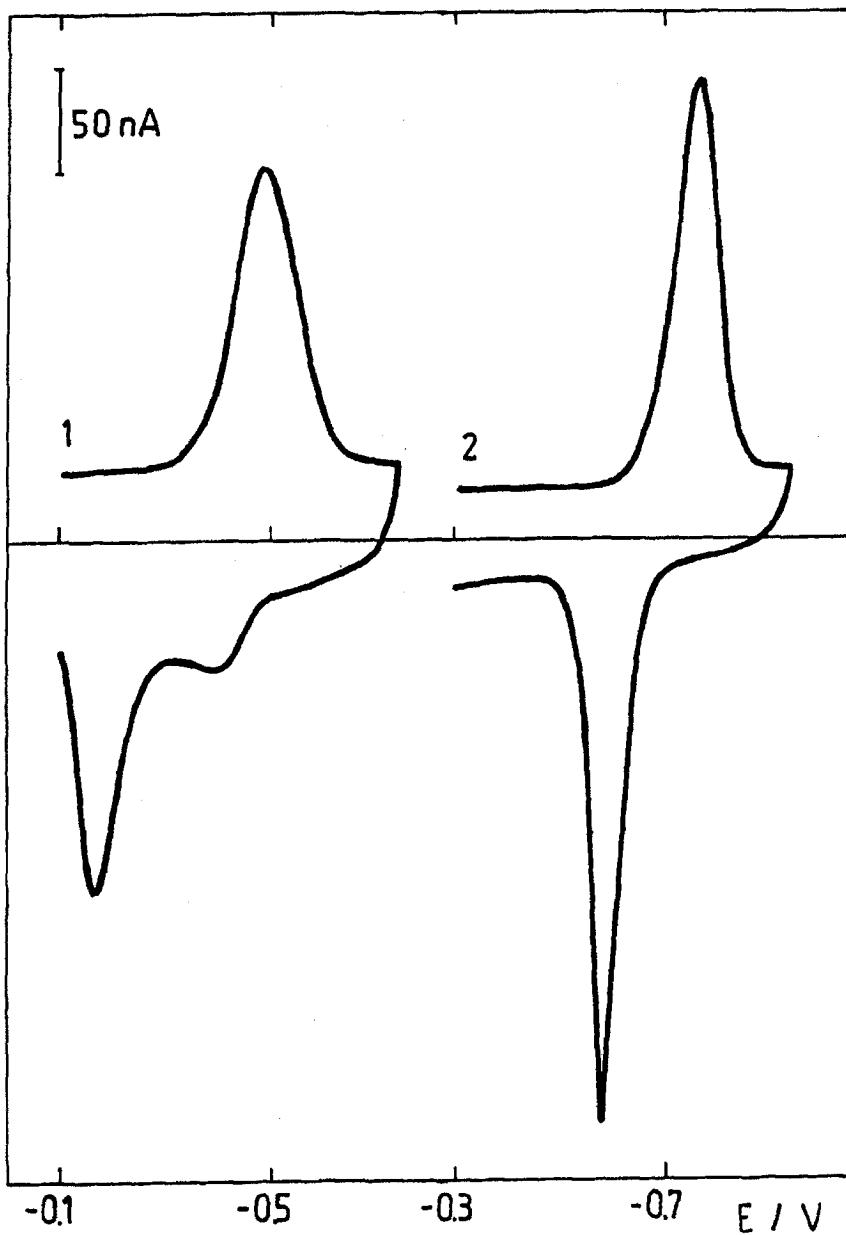


Fig. 3. Voltammetric curves for  $5 \times 10^{-7}$  mol dm $^{-3}$  compound 1 following 1 min accumulation at the SMDE at potentials: (1)  $-0.1$ ; (2)  $-0.3$  V in  $0.1$  mol dm $^{-3}$  solutions of: (1) NaClO $_4$  and (2) NaOH. Scan rate: 100mV/s.

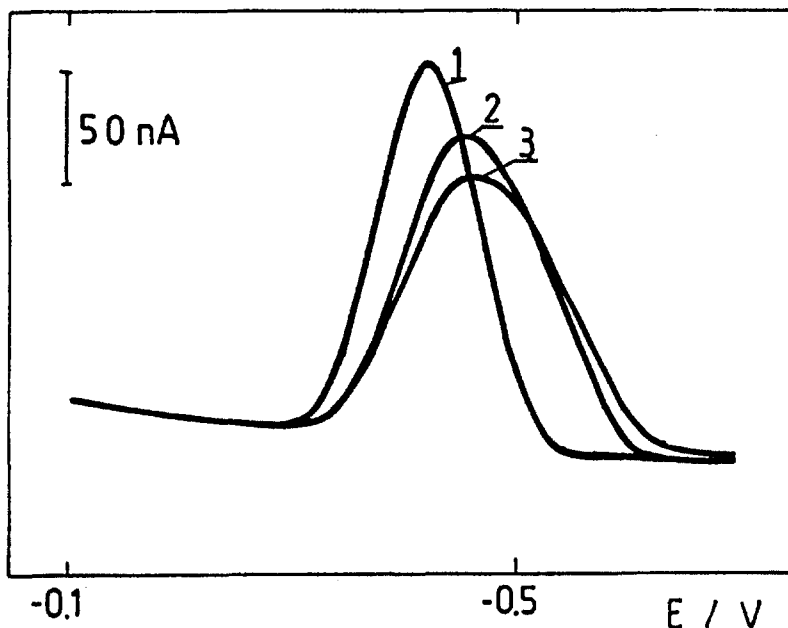


Fig. 4. Voltammetric curves following 1 min accumulation at  $-0.1$  V of  $2 \times 10^{-7}$  mol dm $^{-3}$  compound **1** at the SMDE in  $0.1$  mol dm $^{-3}$  solutions of (1) CaCl $_2$ , (2) LiCl, (3) NaCl. Scan rate:  $100$  mV/s.

Table I. Parameters of the cathodic voltammetric peak for 16-membered azocrown (I) and azobenzene (II) in  $0.1$  mol dm $^{-3}$  solutions of different bases

Parameter	KOH		NaOH		LiOH	
	I	II	I	II	I	II
$E_{pc}$ , mV	-780	-710	-760	-705	-760	-705
$i_{pc}$ , nA	68	88	69	90	79	95
$b_{1/2c}$ , mV	90	60	76	60	78	60
$b_{1/2a}$ , mV	60	60	60	60	60	60

ion and Li $^+$  the surface excess-concentration isotherm is better described by the Frumkin type isotherm [18]. Table I depicts the characteristic parameters of the voltammetric peaks recorded in  $0.1$  M KOH, NaOH and LiOH for the larger, 16-membered azocrown (compound **4**) and for azobenzene, for comparison.

The specific interaction of the 16-membered macrocycle with potassium ion leads to a shift of the reduction peak to more negative potentials and to an increase of the peak half-width; hence the features of the cathodic signal in cases of binding are similar to those observed for the smaller azocrown. On the other hand, interaction of the cation of the supporting electrolyte with the anionic, reduced form of the azo compound, like ion-pairing for example, would shift the reduction peak in the

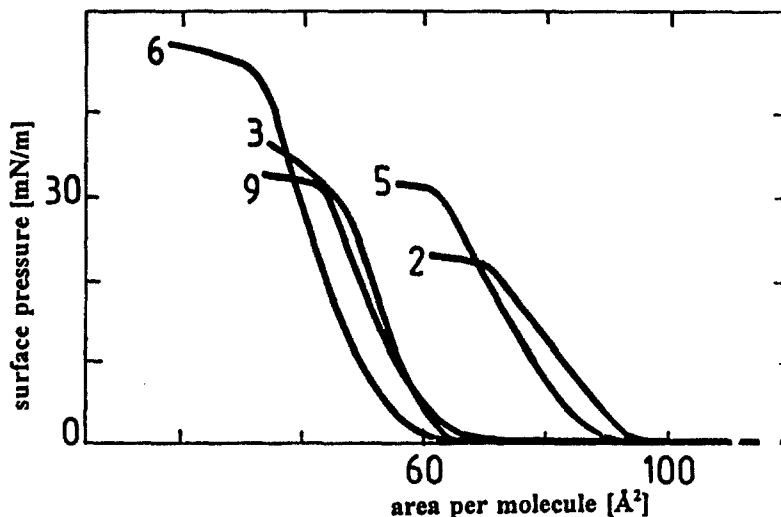


Fig. 5. Surface pressure-area isotherms for the compounds studied on a pure aqueous subphase. Numbers on the curves denote numbers of compounds from Figure 1.

opposite direction – towards positive potentials. This effect is seen in the case of azobenzene (Table I). Lack of changes in the peak width for different supporting electrolyte cations observed for azobenzene as opposed to the crown ether confirm that this parameter, together with the shifts of the reduction signal, provide a sensitive probe of binding of the cation by the macrocycle.

### 3.3. MONOLAYERS ON THE AIR–WATER INTERFACE

Monomolecular layers of amphiphilic azo and azoxy crowns with tetramethylbutyl or dodecyl alkyl chain substituents (Figure 1) were prepared initially on a pure water subphase (Figure 5).

A chloroform solution of an amphiphilic derivative of the azocrown was syringed on the water–air interface and compressed to form the monolayer. The area per molecule in the monolayer are 94; 62; 85; 52; 105 and 61 Å<sup>2</sup> for the 13-membered azocrowns 2 and 3, the 16-membered azocrowns 5 and 6, and the 13-membered azoxycrowns 8 and 9, respectively. The shape of the surface–pressure isotherm depends on the size of the crown and the nature of its hydrophobic substituent. When a bulky substituent such as tetramethylbutyl is used, the area per molecule is larger than for a normal alkyl chain substituent, indicating that the bulky substituent controls the area occupied by the molecule on the air–water interface. On the other hand, the stability of the monolayer measured by its collapse pressure value is larger when the normal 12-carbon alkyl chain is attached to the molecule.



### 3.4. RECOGNITION OF CATIONS BY THE LANGMUIR MONOLAYER OF AZOCROWN

Since the stripping curves indicated that the monolayer of azocrown **1** distinguishes  $\text{Na}^+$  from  $\text{K}^+$ ,  $\text{Ca}^{2+}$  and  $\text{Li}^+$ , and the oxidized form of the ligand participates in the binding process we decided to check whether amphiphilic forms of the ligand can be assembled in Langmuir monolayers that are responsive to cations.

The limiting pressure and slope of the isotherm increases in the presence of selected alkali cations in the subphase indicating interactions of the crown with certain ions. Correlation between the size of ring and size of cation can be shown, namely stronger interactions exist between the 13-membered azocrown (compound **2**) and  $\text{Na}^+$  (Figure 6A), and between the 16-membered azocrown (compound **5**) with  $\text{K}^+$  than with other cations (Figure 6B). In the cases shown in Figure 6 the area per molecule does not change since both azocrowns possess the bulky tetramethylbutyl substituent. The effect of cation in the subphase can be seen even better if surface potential is monitored, rather than surface pressure [20].

As demonstrated in Figure 7 the increase of the concentration of the noninteracting cation ( $\text{Li}^+$ ) does not affect the shape of the isotherm, while for the cation that binds to the macrocycle ( $\text{K}^+$ ) increase of the cation concentration by orders of magnitude in the range  $1 \times 10^{-3}$ – $1 \text{ mol dm}^{-3}$  leads to a proportional increase of the collapse pressure value.

Cation binding to the azocrown increases the interactions of neighboring molecules and improves the organization and stability of the layer. Our recent X-ray structures of the complexes of 13-membered azocrowns with NaI indicate that sandwich-like complexes are formed. This would mean that one  $\text{Na}^+$  ion may also keep two ligand molecules tightly together in the monolayer at the interface, which would explain the improvement of the stability of the layer upon complexation of the cation from the solution.

The monolayer formed on the water subphase can be transferred onto various substrates, in our experiments usually gold films on glass slides or thin mercury films on silver electrodes (TMFAg). The monolayer modified electrodes are then placed in supporting electrolyte solution and cyclic voltammograms recorded (Figure 8).

In  $0.1 \text{ mol dm}^{-3}$  LiOH the peak potentials and peak shapes for the cathodic and anodic signals are very similar. From the charge of the peak the surface concentration of the compound was calculated and compared to the surface concentration in the monolayer on the water–air substrate. Similar values were obtained using the mercury film electrode. In the case of an evaporated gold electrode loss of the molecules takes place in the supporting electrolyte solution. This shows that the monolayer is not firmly attached to the electrode surface.

Cyclic voltammetric curves recorded on these monolayer modified electrodes also depend on the kind of supporting electrolyte cation (Figure 8A, B, C). In the presence of potassium ions, as opposed to lithium ions, the cathodic peak is much wider and the anodic peak becomes split, showing that additional interactions

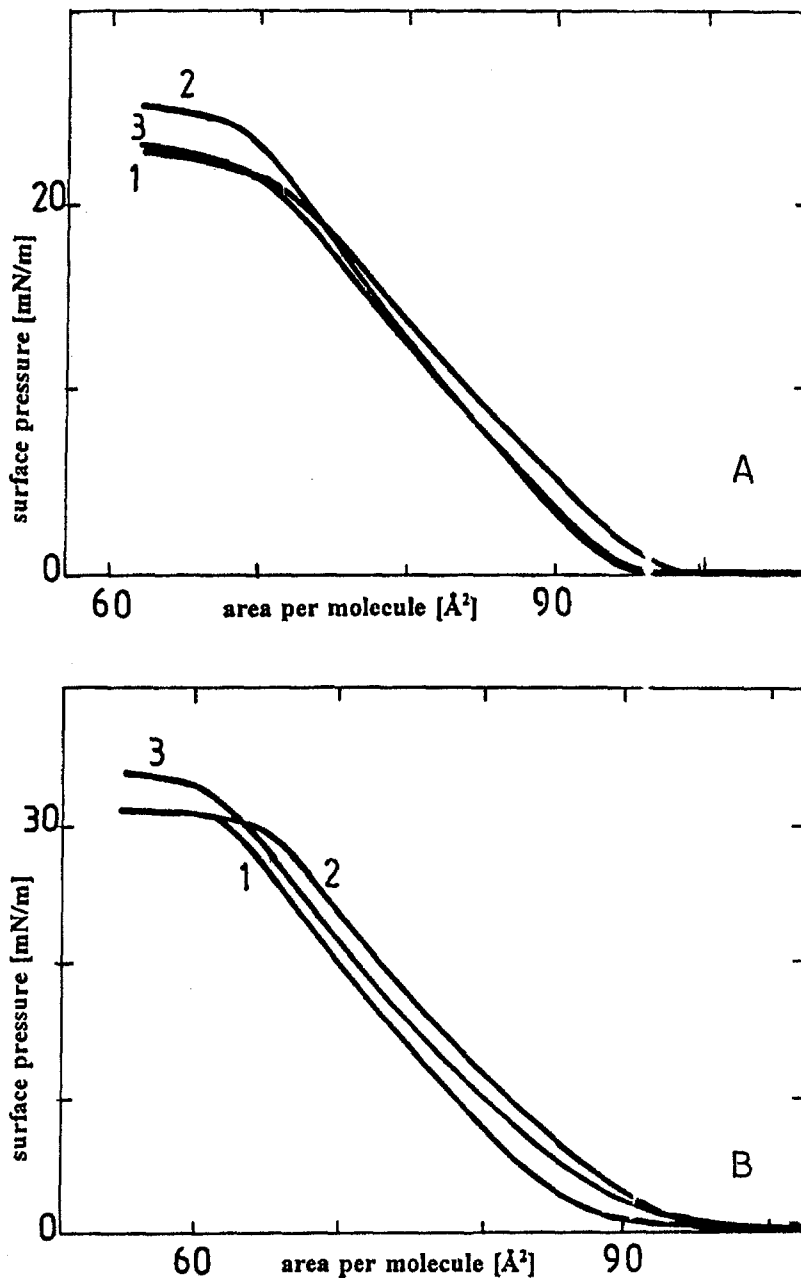


Fig. 6. Langmuir isotherms recorded for (A) the 13-membered azocrown with tetramethylbutyl substituent (compound 2) and (B) the 16-membered azocrown with tetramethylbutyl substituent (compound 5) on: (1) pure water, (2)  $0.1 \text{ mol dm}^{-3}$  NaCl, and (3)  $0.1 \text{ mol dm}^{-3}$  KCl subphases.

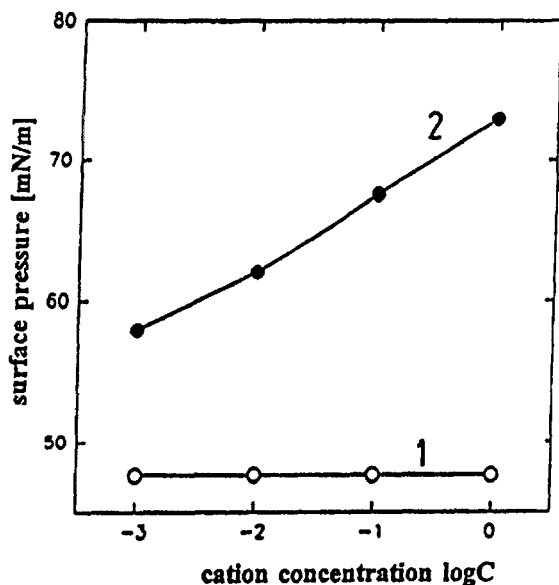


Fig. 7. Dependence of collapse pressure of the monolayer of compound 6, on the concentration of (1) LiOH and (2) KOH in the subphase.

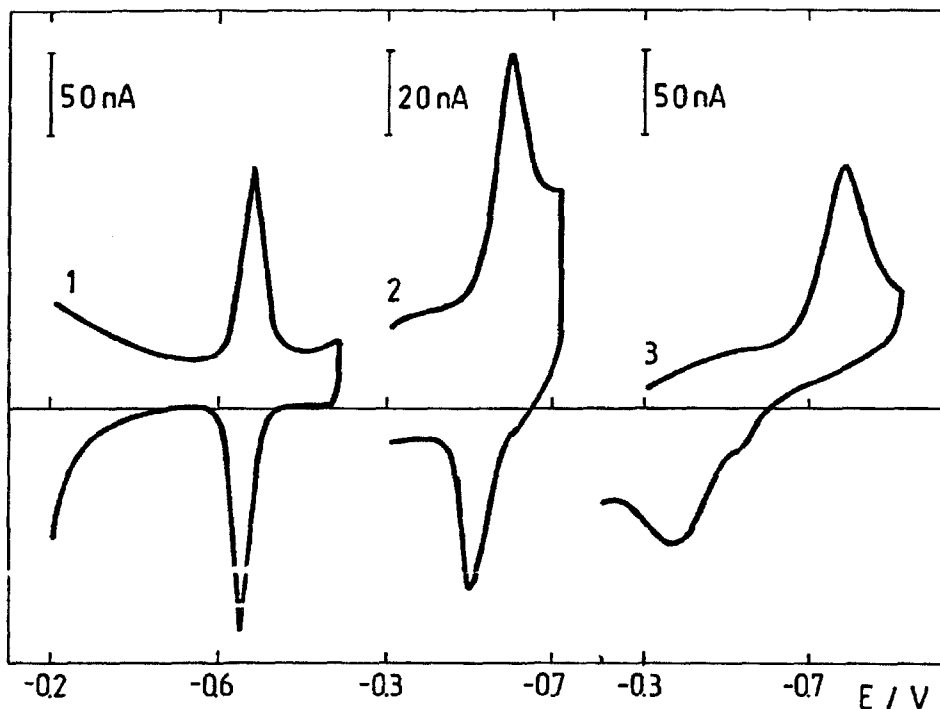


Fig. 8. Cyclic voltammograms recorded on TMFAg electrodes modified with a Langmuir-Blodgett monolayer of compound 6 transferred at a pressure of 20 mN/m. Supporting electrolyte solution, 0.1 mol dm<sup>-3</sup> (1) LiOH, (2) NaOH and (3) KOH. Scan rate : 50 mV/s.

involving the 16-membered azocrown macrocycle occur. More quantitative studies on the nature of these interactions and on the analytical applicability of these Langmuir–Blodgett monolayer modified electrodes remain to be done and work in these directions is now continuing in our laboratory.

## Conclusions

Azo and azoxy crown ethers form an interesting new group of compounds which retains the complexing abilities of simple crowns but in addition exhibits electroactive properties due to the presence of the azo or azoxy units. This allows one to monitor the properties, surface concentration and binding abilities of these crown ethers by voltammetric methods. The shift of the cathodic peak of the azo or azoxy bond reduction together with an increase of the peak half-width may serve as a probe of specific interaction of the cation with the macrocycle since parallel experiments with simple azobenzene show lack of such changes of the voltammogram. Monolayer assemblies can be formed on solid substrates either by adsorptive preconcentration from the diluted solution of the crown or, in the case of insoluble derivatives, by the Langmuir–Blodgett technique. The interactions with alkali metal cation are clearly demonstrated by the changes of surface pressure–area per molecule isotherms recorded on the subphase containing the interacting cation. Namely, the increase of the isotherm slope and collapse pressure value are seen for the 13-membered azocrown on the subphase containing  $\text{Na}^+$  cation and for the 16-membered azocrown on the subphase containing  $\text{K}^+$  cation. In both cases on a  $\text{Li}^+$  containing subphase, the properties of the isotherm are identical to those observed on pure water. The monolayers can be transferred onto the solid substrates with a transfer ratio of 1, however, the layer remains attached to the electrode surface only when a mercury film silver based electrode is employed as the working electrode. On other substrates it is removed from the electrode surface to the solution upon repeating the cyclic voltammograms.

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