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Voltammetric Recognition of *Cis* (*Z*) and *Trans* (*E*) Isomers of Azobenzene and Azocrown Ethers

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An electroanalytical approach allowing the recognition of isomers of azo compounds and the determination of their ratio in the solution is introduced. Adsorptive preaccumulation of the title compounds at the electrode surface retains on the electrode the ratio of isomers present in the solution. Voltammetric reduciton of the adsorbed species allows recognition of the *cis* (*Z*) and *trans* (*E*) forms of the azo-crowns because their reduction potentials in alkaline solutions are different. In the region below pH 10 fast isomerization follows the first electron transfer, hence both forms appear to be reduced at the same potential. At pH>10 interactions of the large crown radical anion with alkali metal cations slow down the isomerization reaction at the electrode surface and a separate reduction peak for each isomer is seen on the voltammogram. The adsorptive voltammetric method provides a simple and useful way of monitoring the progress of isomerization reactions in the solution. Comparison of azobenzenes, azodibenzo- and azotribenzo-crown ethers revealed the largest stability of the latter against *Z*-to-*E* isomerization in aqueous solutions.

Keywords: Monolayers, crown ethers, adsorptive stripping voltammetry

INTRODUCTION

Renewed interest in azo compounds is connected with their applications in molecular switching, sensors and optical memories. Azo compounds are used as photo- or redox-active components of films deposited on solid substrates by the self-assembly or Langmuir-Blodgett methods [1–7].

In the solid phase the simplest azo compound, –azobenzene, exists in two isomeric forms and these two configurations differ in that the *trans* (*E*) form is flat [8] with its dipole moment equal to zero while in the *cis* (*Z*) form the phenyl rings are not coplanar and the dipole moment is 3.0 D [9]. In the solution, the *cis* form is less stable than the *trans* form and under the influence of solvent, visible light and increased temperature is transformed into the *trans* form [10]. The conversion of *cis*- into *trans*- azobenzene is inhibited in alkaline solutions while in slightly acidic solution the conversion is very fast.

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Reversible *cis-trans* isomerization of azo compounds could be useful for the construction of molecular switches and especially the combination of the — N = N — group with the crown ether should lead to materials joining unique functionalities of both molecular sites. Recently, we have been studying the family of azocrowns (Fig. 1) [11–18].

Crown ethers bearing the azo-group as a part of the macrocycle exist in stereometric *Z* (*cis*) and *E* (*trans*) forms. The first separation of Z and *E* isomers was achieved on a 13-membered azocrown ether [18]. A 16-membered azocrown ether may be obtained according to two procedures [17,19,20] and separated into stereoisomers [17]. On interaction with sodium iodide the L13 ligand (Fig. 1) was found to form a sandwich-type

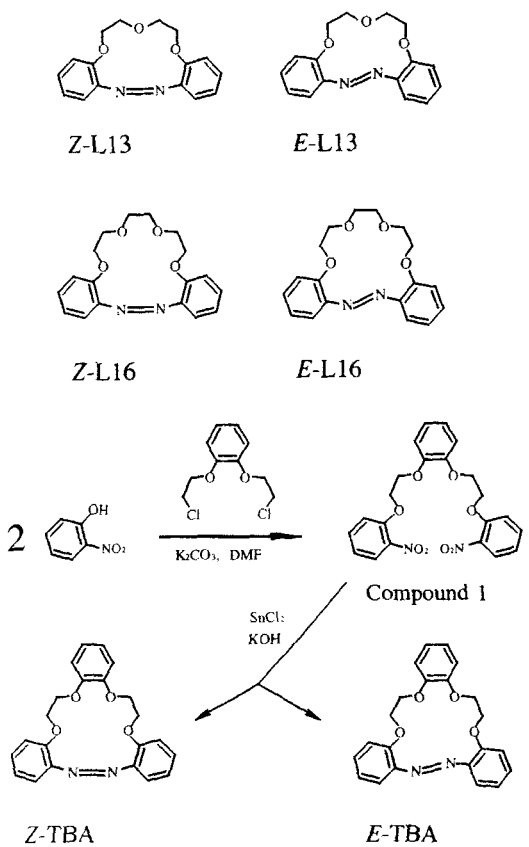


FIGURE 1 Structures of the compounds studied and scheme of synthesis.

complex of formula $Na(L13)_2^+I^-$ with *trans* orientation of benzene residues on the coordinated azo group of the ligand [18]. The bis (tetramethylbutyl) derivative of Z-L13 formed well-packed monolayers at the air-water interfaces [13,15,21] and isomerization under visible light and upon interaction with sodium salts added to the subphase was observed [21–23].

The electrochemical behavior of azobenzene and its derivatives has been studied extensively with attention paid to the involvement of proton transport, adsorption–desorption and *cis/trans* isomerization [24–35]. From the beginning of the studies of the electrochemical behavior of azobenzene there have been ongoing discussions on the possibility of electrochemical recognition of the azobenzene isomers. As early as 1953 Hillson and Birnbaum reported that *cis-* and *trans*-azobenzene were reduced in ethanolic solutions at the same potential in acidified medium, while in alkaline solutions their reduction potentials were different [29]. Since the difference in the reduction potentials depends on pH, it cannot be assigned to the difference of free energies of the two forms alone. Later all these early observations were disputed [26, 30,31]. No separate peaks for the separated isomers were seen, even though extreme conditions were applied, such as temperatures equal to −80°C. A small polarographic prewave has been reported by Chuang *et al.* [32] at pH 8–9, and ascribed to the reduction of the Z-form of azobenzene is aqueous – ethanol buffered solutions. The small extent of this effect is understood in view of the results presented in the present paper, since the concentrations of the compounds in the solutions used by the authors were large and did not allow resolution of the reduction of adsorbed forms. Laviron [26] reported different half-wave potentials of the isomers, but only in alkaline ethanol solutions. In water both isomers lead to the formation of the same reduction peak.

The general problem encountered in electrochemical studies of various types of isomers is

that isomerization of the compound diffusing to the electrode is caused by the product of reduction already available in the vicinity of the electrode. In the present paper, we demonstrate that for azo compounds of increased stability against isomerization in the solution, the electrode isomerization can be also hindered by using diluted solutions of isomers and introducing as the initial step the adsorptive preconcentration of the isomers on the electrode surface from alkaline solutions. Under these conditions we get the unique possibility of identifying and determining the isomeric forms of the compounds present in the solution since the reduction of the preadsorbed isomers leads to the formation of well resolved voltammetric signals.

EXPERIMENTAL

All materials were of analytical grade. *E*-azobenzene was commercial, and *Z*-azobenzene was obtained by illumination of the *E* form and separated chromatographically. 16-Membered dibenzoazocrown ethers *Z*-L16 and *E*-L16 (Fig. 1) were obtained as described earlier [17].

Synthesis from compound 1 (Fig. 1) and isomers separation of tribenzoazocrowns *Z*- and *E*-TBA are presented below. Silica gel 60 (FLUKA) was used for column separations of products. Their purity and identity was established by mass spectra taken on a AMD-604 apparatus. ^{1}H-NMR were recorded on a Brucker or Varian (200 MHz) instruments. M.p. are uncorrected.

The solutions of isomers were prepared before each series of experiments. Other compounds were prepared daily by diluting with water stock solutions of compounds dissolved in water or dimethylformamide. Dimethylformamide (Aldrich) was employed to prepare highly concentrated samples of compounds. Water was distilled and then passed through a Milli-Q water purification system.

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 Pristroje) of 0.015 cm^2 drop area, used in the hanging drop mode. Voltammograms were recorded either with the BAS-100 Electrochemical Analyzer (Bioanalytical Systems Inc.) and the HIPLOT DMP-40 Plotter (Houston Instrument) or with an electrochemical analyzer, PA4 and a BAS XY recorder. All electrochemical experiments were done at 25°C, in solutions deaerated with argon.

Syntheses of Compounds

Compound 2

A mixture of *o*-nitrophenol (2.8 g; 20 mmol), *o*-bis[2-chloroethoxy]benzene [36], anhydrous potassium carbonate (2.8 g) and dimethylformamide (4 mL) was refluxed for 5 h. The product was mixed with water to precipitate compound 2 (Fig. 2). The crude material was purified chromatographically by elution with methylene chloride. The product was crystallized from methylene chloride - heptane. Yield 4.2 g (95%), m.p. 128–130°. ^{1}H NMR ($CDCl_3$, δ, ppm): 4.38–4.52 (8H, m); 6.98–7.06 (6H, m); 7.18 (2H, dd, J_1 = 1.1 Hz; J_2 = 8.5 Hz); 7.52 (2H, dt, J_1 = 1.6 Hz; J_2 = 7.2 Hz); 7.81 (2H, dd, J_1 = 1.7 Hz; J_2 = 8.0 Hz).

Tribenzo-16-azocrown ether E-TBA Z-TBA

To a vigorously stirred mixture of compound 2 (1.83 g; 4.1 mmol), stannous chloride dihydrate (4.07 g; 18 mmol) and acetone (21 mL) was added a solution of 7.55 g potassium hydroxide in 21 mL water. The stirred mixture was heated at 60° for 2 hours. Toluene (20 mL) was added and the organic layer was separated, washed with water and the solvents were evaporated. The residue was dissolved in methylene chloride and chromatographed on a silica gel column.

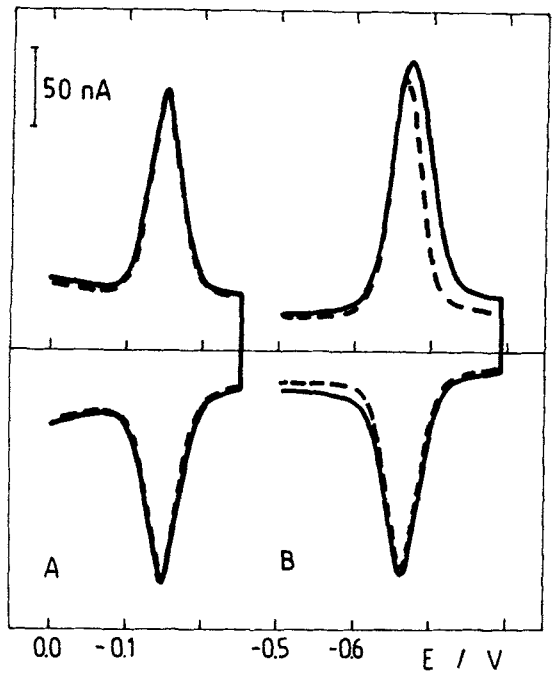


FIGURE 2 Voltammograms for 5×10^{-7} mol/dm^3 *cis*- and *trans*-azobenzene following 1 min preconcentration at (A) −0.0 in solution of pH 4.52 (citrate buffer) and at (B) −0.5 V in solution of pH12 (citrate/LiOH), $v = 100$ mV/s, (—) *cis* form.

The red product was eluted with methylene chloride to obtain 0.6 g (38%). Azocrown ether freshly eluted from the column recrystallized at once from ethyl acetate (or ethyl acetate–heptane) afforded red *E* form (m.p. 128–129°), whereas product obtained during slow crystallization from the same solvent represents orange *Z* form (m.p. 142–143°).

Z-TBA H^1 NMR, 200 MHz ($CDCl_3$, δ ppm): 4.17–4.25 (4H, m); 4.34–4.44 (4H, m); 6.76–6.89 (6H, m); 7.01 (4H, s); 7.07–7.17 (2H, m). MS: calculated m/e for *Z* azocompound $C_{22}H_{20}O_4N_2 = (3.76.41)$; found 376.

E-TBA H^1 NMR, 200 MHz ($CDCl_3$, δ ppm): 4.35–4.50 (8H, m); 6.85–6.97 (4H, m); 7.01–7.12 (4H, m); 7.32 (2H, dt, $J_1 = 1.8$ Hz, $J_2 = 7.8$ Hz); 7.58 (2H, dd, $J_1 = 1.9$ Hz, $J_2 = 7.9$ Hz). MS: calculated m/e for *E* azocompound $C_{22}H_{20}O_4N_2 = (376.41)$; found 376.

RESULTS

Voltammetry with Adsorptive Accumulation of *Cis* and *Trans* Azobenzenes

Figure 2 presents the voltammograms for *cis*- and *trans*-azobenzene recorded in solutions of pH 4.52 and 12, following adsorptive accumulation at −0.0 and −0.5 V, respectively.

At pH 4.52 the *cis*- and *trans*-forms give identical signals and the peak separation is almost zero. The characteristics of the cathodic and anodic signals are given in Table I. The *Z* and *E* forms are hence not recognized by voltammetry. The stereomers are therefore not recognized. Below pH 8 the dependence of the peak potential on pH of the solution is linear with slope equal to 60 mV/pH unit for the cathodic and anodic signals, respectively, pointing to the reversible 2e/2H process (Fig. 3).

The reactions in the electrochemical reduction of azobenzene in the presence of protons are [37]:

$$R - N = N - R + H^+ + e \Rightarrow R - NH - N - R \quad (1)$$

TABLE I Characteristics of the voltammograms for the *Z* and *E* forms of the compounds studied, $C = 5 \times 10^{-7}$ mol/dm^3, citrate/LiOH solution of pH 12

Compound	isomer	E_{pc} V	E_{pa} V	$E_{pc}-E_{pa}$ V	$b_{1/2pc}$ mV
azobenzene	*cis*	−0.665	−0.660	−0.005	45
azobenzene	*trans*	−0.680	−0.660	−0.020	60
L13	*Z**	−0.610	−0.565	−0.045	70
L13	*E**	−0.750	−0.565	−0.185	75
L16	*Z*	−0.720	−0.575	−0.145	110[a]
L16	*E*	−0.755	−0.570	−0.175	75
TBA	*Z*	−0.595	−0.490	−0.105	60
TBA	*E*	−0.735	−0.490	−0.245	75
	*E***	−0.775	−0.495	−0.285	75

* Citrate/NaOH solution.
** Citrate/KOH solution.
[a] Two overlapping signals.

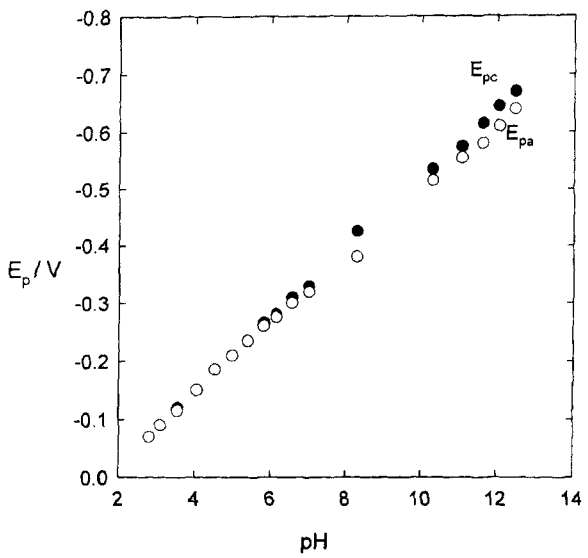


FIGURE 3 Dependence of *trans*-azobenzene peak potentials on pH (citrate buffer, LiOH). Other conditions as Figure 2.

$$R-NH-N-R+e+H^+ \Rightarrow R-NH-NH-R \quad (2)$$

These results are in agreement with the literature data [26] and indicate that the stability of the less stable *cis*-form in the acidic and neutral solutions is low and the *trans*-isomer is predominating. In highly alkaline solutions the procedure of Laviron (1% ethanol added) allows switching off of the isomerization in the solution, however, the peaks for both isomers appear at similar potentials, pointing to involvement of the above mentioned electrode surface isomerization. However, careful inspection of the curves allows detection of small differences in the electrode behavior of the *cis*- and *trans*-form in alkaline solutions. They are exhibited by the slightly larger separation of the cathodic and anodic peak (20 mV for *trans*-compared to 5 mV for the *cis*-form), and 15 mV larger width at half-height in case of the *trans*-isomer (Tab. I). Interestingly, in ethanolic medium and at very high pH the cathodic peaks corresponding to the reduction of isomers attain constant potentials different from those in purely aqueous solutions. The *trans*-form is always reduced at more negative potentials.

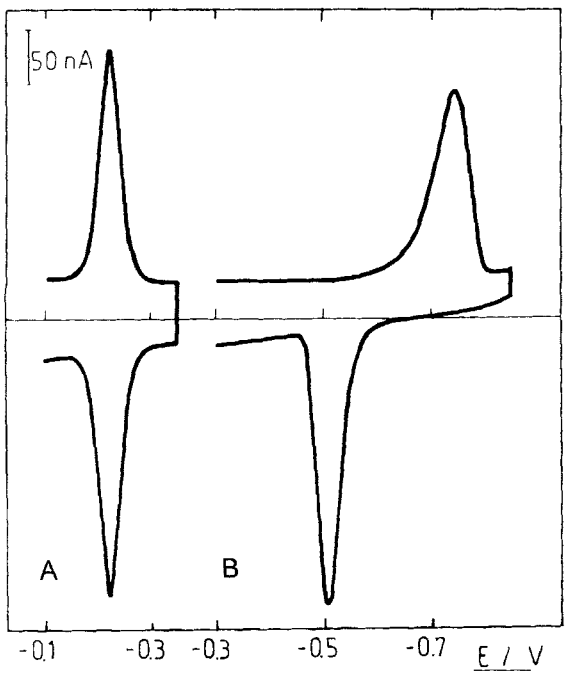
Figure 4 shows the voltammograms for the pure *E* (*trans*) form of TBA in solutions of pH 6.16 and 12.

In acidified solutions the shape of the voltammogram resembles that of azobenzene. The shapes of cathodic and anodic peaks and potentials are very similar. The $b_{1/2}$ is 0.45 mV. The system is close to reversible. There is a large decrease in the reversibility of the system in alkaline solution, exhibited by the large anodic to cathodic peak separation increasing with the increase of scan rate (Fig. 4C) and large shift of the cathodic signal towards negative potentials, exceeding that of the anodic signal. It should be noted that for azobenzene the splitting of cathodic and anodic peak is only recognized at highest pH (Fig. 2). The dependence of peak potentials for the azocrown ethers TBA and L16 on pH is clearly different from that of azobenzene (Fig. 5).

Below pH 8 the slope of cathodic and anodic peak potentials is described by the following equations:

Ep [V] = −0.059 pH +0.142 for TBA, and
Ep [V] = −0.060 pH + 0.116 for L16.

In solutions of pH lower than 8 the peaks for azocrown reduction appear at more positive potentials than for azobenzene. This shows easier reduction of the azo unit incorporated into a crown ether. Above pH 8 the anodic peaks are still shifted towards negative potentials with increasing pH which gives plots ressembling those of azobenzene. The reduction peak for azocrowns behaves in a completely different manner compared to azobenzene. It is first shifted faster towards negative potentials with increasing pH and above pH ca. 10 the peak potential attains constant value. This behavior points to increased irreversibility of the process at pH above 8 and independence of pH in highly alkaline solutions. Figure 6 exhibits voltammograms for a mixture of isomers of the TBA azocrown in solutions of pH 4.18 and 11.56 and 12.33.



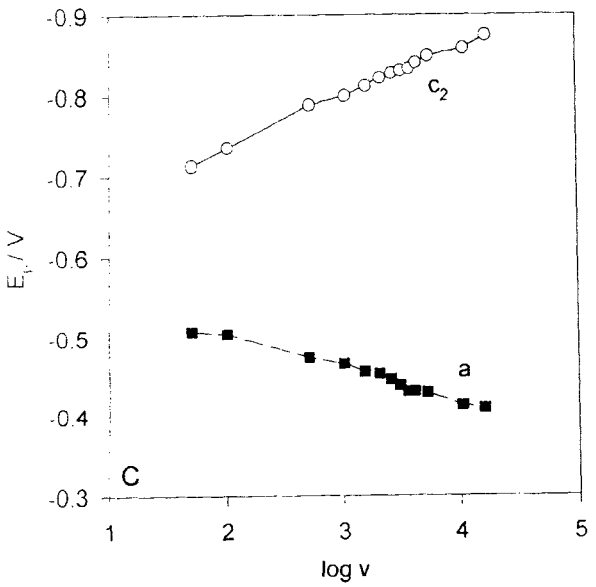


FIGURE 4 Voltammograms for 5×10^{-7} mol/dm^3 *E*-TBA following 1 min preconcentration at (A) −0.0 in solution of pH 6.16 (citrate buffer) and at (B) −0.3 V in solution of pH12 (citrate/LiOH), $v = 100$ mV/s. (C) Dependence of peak potentials on log scan rate.

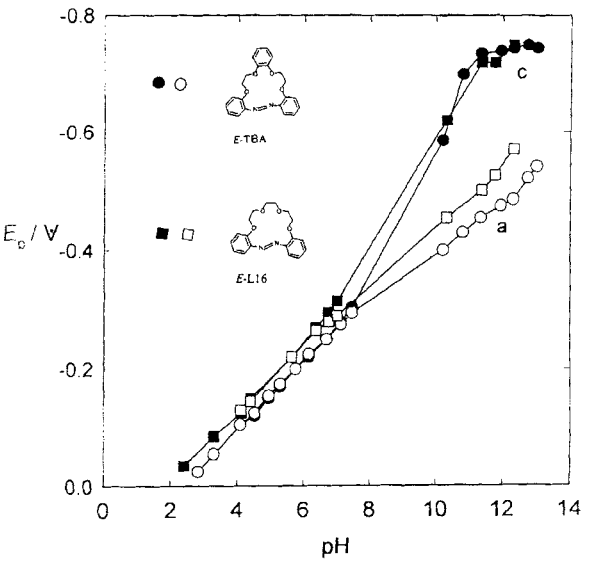


FIGURE 5 Plot of dependence of peak potentials on pH for (A) *E*-TBA and (B) *E*-16L in citrate/LiOH buffer. Other conditions as Figure 4.

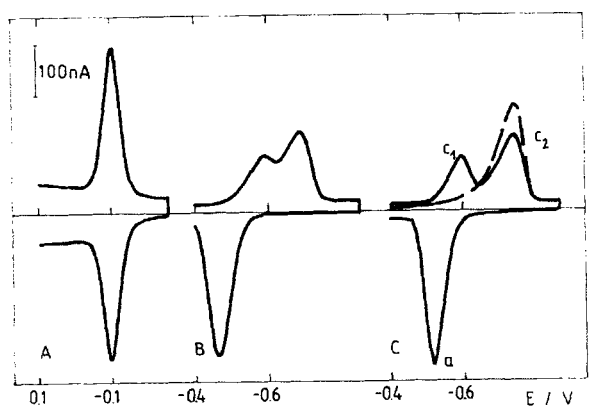


FIGURE 6 Voltammograms for 5×10^{-7} mol/dm^3 TBA mixture of isomers following 1 min preconcentration in Li citrate buffer solution of pH: (A) 4.18; (B) 11.56; (C) 12.33. $v = 100$ mV/s; (—) third half-cycle.

The total concentration of the TBA compound is 5×10^{-7} mol/dm^3. Up to pH 10 a single couple of peaks is observed which is shifted to more negative potentials with increasing pH. At pH 4.18 (Fig. 6A) the peak potentials are −0.100 and −0.095 V for the cathodic and anodic peaks, respectively, hence in practice there is no splitting of peaks in this system. The width of the peak at half-height, $b_{1/2}$ is ca. 45.5 mV which indicates almost ideal 2e electrode process in the

adsorbed state. The peak current becomes smaller above pH 8, difference in the cathodic and anodic peak potentials increases (compared to simple azobenzenes), and the half-widths of the peaks increase. Finally at pH 11 the cathodic peak splits into two separate signals (Figs. 6B and 6C). For TBA in solution of pH 12.33 the peak potentials are −0.595 and −0.735 V for the two resolved cathodic peaks c_1 and c_2. The third half - cycle of the recorded voltammogram (Fig. 6C) demonstrates that upon oxidation only one isomer is produced at the electrode, and its peak area (proportional to the amount of compound undergoing reduction) is equal to the sum of peaks areas c_1 and c_2 of the initial scan. It is also equal to the oxidation peak area. This means that nothing is lost from the electrode but the final product is the same hydrazo compound for both isomers and its oxidation leads exclusively to the *E* form of the azomacrocycle. Thus, adsorption retains or freezes the isomer ratio from the solution and makes the reduction more difficult especially for the *E* isomer while upon 2e reduction the adsorbed layer is transformed into only one form. Since clean *E*-TBA and *E*-L16 of the compounds are obtained, we can assign the c_2 signal in the mixtures to the surface reduction of the *trans*-form. In a sample containing two isomers, we can therefore ascribe peak c_1 to the *Z* isomer and determine the content of the *Z* form in the mixture. Figure 7 depicts the plots E_p *vs.* pH for the mixture of isomers and for pure sample of the *E*-TBA isomer.

Splitting of the cathodic signal means that, first, both peak potentials are shifted towards more negative potentials faster than predicted by the 2H/2e dependence with increasing pH but the *Z* form is reduced easier than *E*, and finally, when the potentials stabilize at pH over 11 the potential of the *Z* form (c_1 peak) is −0.595 V and that of the *trans*-form is 140 mV more negative (Fig. 7). Figure 8A shows that the ratio of peaks for a given mixture of isomers remains constant when the time of adsorptive preconcentration is increased which proves that

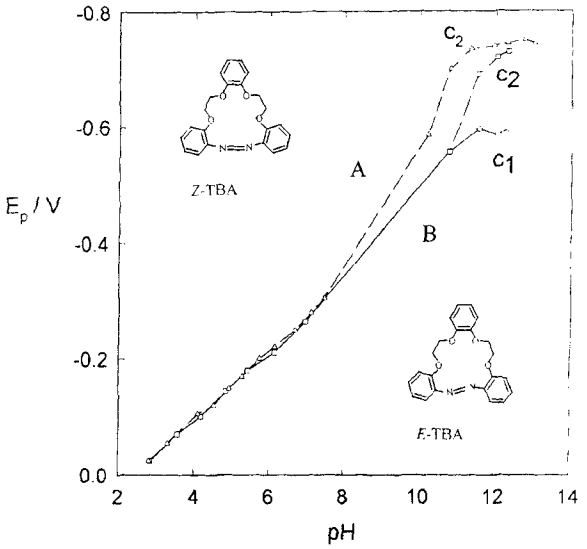


FIGURE 7 Plot of dependence of peak potentials on pH for (A) *E*-TBA and (B) TBA sample containing a mixture of isomers in citrate buffer. Other conditions as Figure 6.

none of these isomers is favored on the electrode surface. Of course, one should keep in mind that a too negative adsorption potential will favor the deposition of the compound reduced at more negative potential; hence, the optimal deposition potential has to be carefully selected especially when the content of the *Z* isomer is small (Fig. 8B).

In our case the deposition potential of choice would be −0.05 to −0.1 V.

The Influence of Metal Cations on the Separation of Voltammetric Signals of the Reduction of Isomers

The best conditions for the recognition of isomers are obtained in highly alkaline solutions where the cathodic peak positions become pH independent. The resolution of the c_1 and c_2 signals can be still improved by appropriate choice of the hydroxide used to get the required high pH in the solution. Alkali metal cations are known to interact with the selected azocrown ethers to form sandwich-type complexes [15–18]. Binding of the alkali metal cation was demonstrated

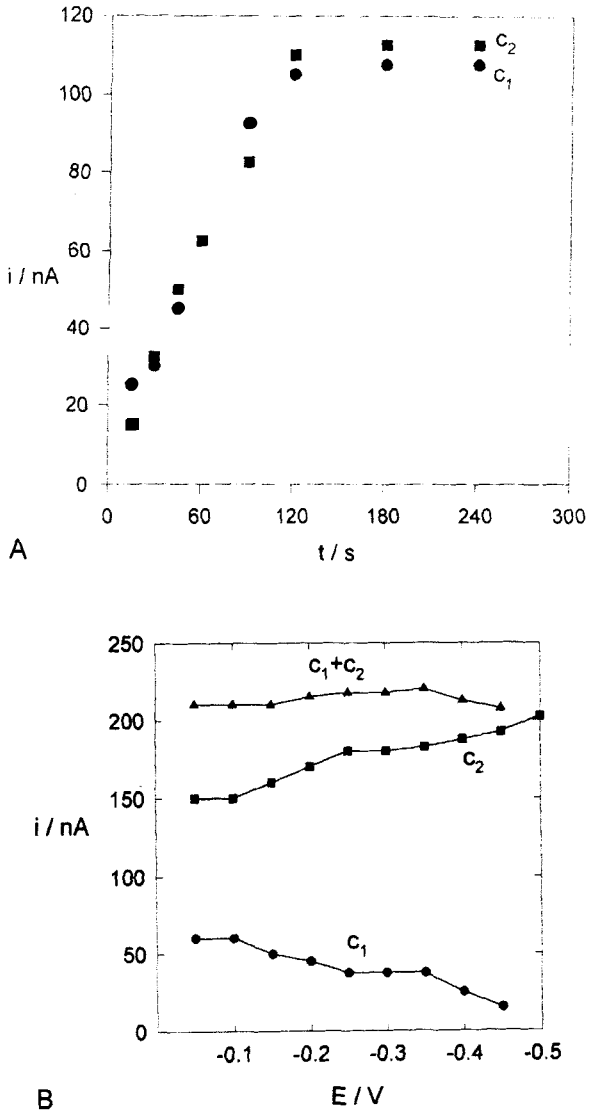


FIGURE 8 Dependence of peak current on deposition (A) time and (B) potential for a mixture of Z and E- TBA isomers. Other conditions as Figure 7.

to lead to increase of the peak width, $b_{1/2}$ of the cathodic peak and to its shift towards more negative potentials [15] without changes of the peak area. In case of TBA and L16, the reduction E-form is shifted towards negative potential and the most negative potential is attained in the presence of K^+ ions in the solutions. This is not unexpected since binding of K^+ to the E form of the 16-membered azorcrowns has been shown earlier and structures of the sandwich potassium iodide complexes in the solid state were determined by X-ray diffraction methods [17]. For the TBA ligand the potentials of peak c_2 were -0.735 and -0.775 V in the presence of LiOH and KOH, respectively. The resolution of c_1 and c_2 peaks (hence resolution of signals of isomers) increased from 140 to 180 mV (Tab. I) when LiOH was substituted for KOH (pH was 12 and ionic strength was kept identical). This mean that the K^+ ion improves the recognition of isomers by binding to the E form preferentially and by shifting its reduction to still more negative potentials. Smaller, but even more important shift of the reduction potential of the E form, was seen for the 13-membered azocrown in solutions of Na^+ ions. In solutions of Li^+ or K^+ ions there is no clear separation of cathodic peaks into c_1 and c_2 signals in the presence of mixtures of isomers, only the single cathodic peak observed is distinctly wider than in the presence of one isomer only. On the other hand, in NaOH/citrate solutions the separation of c_1 and c_2 peak potentials is 140 mV, hence the isomers can be easily determined from the well separated signals (Tab. I).

Monitoring the Ratio of Isomers in the Solution

Peak c_1 corresponds to the Z isomer. Its content in samples received as "Z" is high (95% as found by NMR in $CDCl_3$ for the newly synthetized sample), however, the Z form is not very stable under visible light and in water (Fig. 9), and, therefore, we do not work with the pure Z form in aqueous solutions. Even when the sample is dissolved in the dark in a covered cell at the time of recording the voltammogram the c_2 peak corresponding to the presence of E isomer is seen. At the same time, the sample of the E form is perfectly clean and only one component is observed. Hence, based on the well resolved c_1 and c_2 peaks, and on calibration

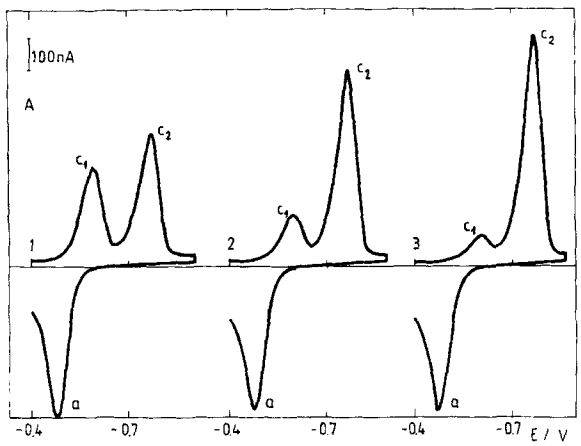


FIGURE 9 (A) Changes of voltammograms for a mixture of isomers of TBA (total concentration 2×10^{-6} mol/dm^3) with time. After (A) 1 min; (B) 5 min and (C) 9 min under visible light.

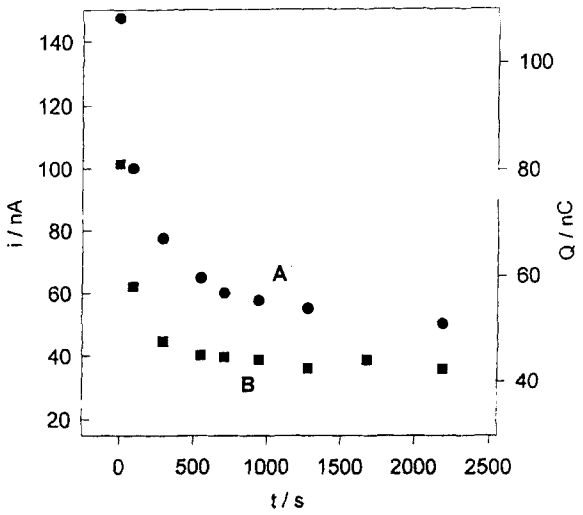


FIGURE 10 Plot of decay of (A) current and (B) charge of peak c_1 on time of isomerization in solution of Li citrate buffer, pH 12, in visible light. Initial concentration of the *Z*-isomer of TBA 2.83×10^{-7} mol/dm^3.

curves for the *E* form, we can distinguish the isomeric forms present in the sample and from the peak currents or charges of these peaks corresponding to the reduction of the adsorbed isomers we can determine the ratio of isomers in the solution phase. The progress of isomerization in solution can be easily monitored by recording changes of the voltammograms with the time as shown in Figure 9 and by measuring the decay of current, or perhaps more correctly, the change of peak c_1 (Fig. 10) at the expense of peak c_2.

CONCLUSIONS

Laviron [26] could not detect any differences in aqueous alkaline solutions for the *cis*- and *trans*-forms of azobenzene. We get similar results for azobenzene adsorptively preconcentrated from diluted solutions, however, careful inspection of the voltammograms recorded in alkaline solution indicates slight differences in the electrode behavior of the isomeric forms. They are visualized by the larger separation of the cathodic and anodic peak, more negative peak potential of the cathodic peak and larger width of the cathodic peak at half-height for the *trans*-isomer. These differences for isomers of azobenzene remain insignificant in contrary to those observed for azocrowns. The difference in the electrode behavior of azobenzene and azocrowns is demonstrated by the dependence of peak potentials on pH. Continuous dependence of the peak potential on pH shows that protons participate in the process of azobenzene reduction up till strongly alkaline solutions. On the contrary, for the azocrowns, the first step of reduction becomes more irreversible in alkaline medium and the peak potential first changes more rapidly with pH, and above pH 12 it finally becomes pH independent. At the highest pH the azocrowns are hence reduced by a different mechanism, although 2e are still involved per molecule of azocrown. It is proposed that this mechanism involves reaction with alkali metal ion and stronger interaction is seen always for the *E* isomer, in agreement with the stronger ability of this isomer to form sandwich type complexes with alkali metal cations, as reported earlier [17, 18].

The observations that the *cis*- and *trans*-*Z* and *E* radical forms interact with some electrophile in a different way appear in the literature especially for the compounds possessing $-C=C-$ bonds [38–40], but usually they concern nonaqueous media. Our observation is important since it reveals that by building an appropriate structure around the double bond we are able to control the lifetime of the isomer both in aqueous solution phase and on the electrode: before and following the first step of its reduction. It simply means that we are able to "freeze" the difference between the isomeric forms of radical anions as well. We ascribe this new property to the interaction in the adsorbed state between the radical anion and alkali metal cation. In a previous paper we discussed the increased stability of radical anion forms of azocrowns compared to azobenzenes in nonaqueous medium [13].

The general problem encountered in electrochemical studies of isomeric forms of compounds is that isomerization of the substrate diffusing to the electrode is caused by the product of reduction available at the electrode. Based on the results obtained we can define the following conditions necessary to recognize the isomers of azocompounds by the method proposed:

- First of all the isomers have to be stable in the solution and this is effected by increasing the pH of the solution above 10.
- Second, the isomerization before and following initial electron transfer should be prevented. This may be done by using the Langmuir–Blodgett deposition [7] for water insoluble compounds, or by adsorptive preconcentration of the water-soluble azocompound from diluted aqueous solutions. Under these conditions the oxidized and reduced forms of the azocompound remain strongly adsorbed on the electrode. Using adsorptive accumulation electrode coverages lower than full monolayer are favorable in order to allow both isomers to occupy independently the sites on the mercury surface. It should be noted that this approach allows detection of traces of isomers, since the adsorptive preconcentration step is introduced. In our earlier paper we discuss in detail the detection limits for the azocrown determination by voltammetry with adsorptive accumulation [14].
- Third, formation of sandwich complexes of two crown ether molecules with one alkali metal cation ensures that isomerization is slower than further reaction at the electrode surface. Since the *E* form is reduced much more irreversibly, the reduction peaks of the two isomers appear at well-separated potentials. Thus, appropriate choice of alkali metal cation can increase the separation of signals corresponding to the *Z* and *E* isomer reduction. Under these conditions we get the possibility of identifying and determining the isomeric forms of the compounds present in the solution, and of monitoring the progress of isomerization in aqueous solution.

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