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Izabella Zawisza[a]; Renata Bilewicz[a]; Elzbieta Luboch[b]; Jan F. Biernat[b]
[a] Department of Chemistry, University of Warsaw, Warsaw, Poland [b] Department of Chemical Technology, Technical University of Gdańsk, Gdańsk, Poland

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Electrochemistry of Azocrown Ethers in Langmuir-Blodgett Monolayers

IZABELLA ZAWISZA[a], RENATA BILEWICZ[a]*, ELŻBIETA LUBOCH[b] and JAN F. BIERNAT[b]

[a]*Department of Chemistry, University of Warsaw, ul. Pasteura 1, 02093 Warsaw, Poland and* [b]*Department of Chemical Technology, Technical University of Gdańsk, 80952 Gdańsk, Poland*

(In final form March 13, 2000)

Monomolecular films of amphiphilic derivatives of crown ethers bearing an azo group in the macrocycle were prepared on surfaces of pure water and transferred onto electrodes using the Langmuir-Blodgett technique. The azocompounds studied were separated into *Z* and *E* stereoisomers. Monolayers of both isomers of azocrowns were transferred onto the surfaces of hydrophilic (thin mercury film electrode, TMFE) and hydrophobic (indium-tin oxide, ITO) electrodes. The electrode processes showed more reversible cyclic voltammetry profiles when mercury was used instead of ITO as the electrode substrate. This difference was ascribed to the different orientation of the molecules on the electrode surface.

Azocompounds are used as photo- or redox active components of films deposited on solid substrates by the self-assembly or Langmuir-Blodgett methods [1–14]. The basis of application of these compounds in molecular switching, sensors and image storage devices is the photoinduced cis-trans isomerization [1–3,14–18]. In the solid phase the simplest azocompound – azobenzene exists in two isomeric forms: *Z* and *E*.

The compounds discussed in the present study are the amphiphilic azocrown ethers shown in Fig. 1., further called L13 and L16.

The crown ethers bearing an azo group as a part of the macrocycle may exist in two stereomeric forms: *Z* (cis) and *E* (trans) [19–21]. The amphiphilic derivatives of these azocrowns were synthesized and used as components of ordered monolayer assemblies at the air-water and electrode-solution interfaces [19,22–24].

Both isomers of the amphiphilic azocrowns, L13 and L16 were found to form stable Langmuir's monolayers at air-water interface. Fig.2.

For the more stable *E* isomer the area per molecule in the monolayer is 114 Å^2 for the bigger L16 azocrown, whereas for the smaller L13 azocrown it is 97.4 Å^2. For the *Z* isomer, the values of area per molecule are smaller, which exhibits the different space requirements of this isomer: for *Z*-L13 the A_0 is 79.1 Å^2 and for *Z*-L16 it is 105.0 Å^2.

The parameters characterizing the compression isotherms for the two isomers i.e. compressibility modulus, $K_c = A \cdot d\pi/dA$, collapse pressure, π_{coll}, and the limiting area per molecule, A_0, are also lower for the *Z* isomer than for the *E*-form [25]. Hence, the *E* isomer forms a more condensed and less compressible monolayer. The K_c for *E*-L13 is 162 mN/m while for

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* Author for correspondence.

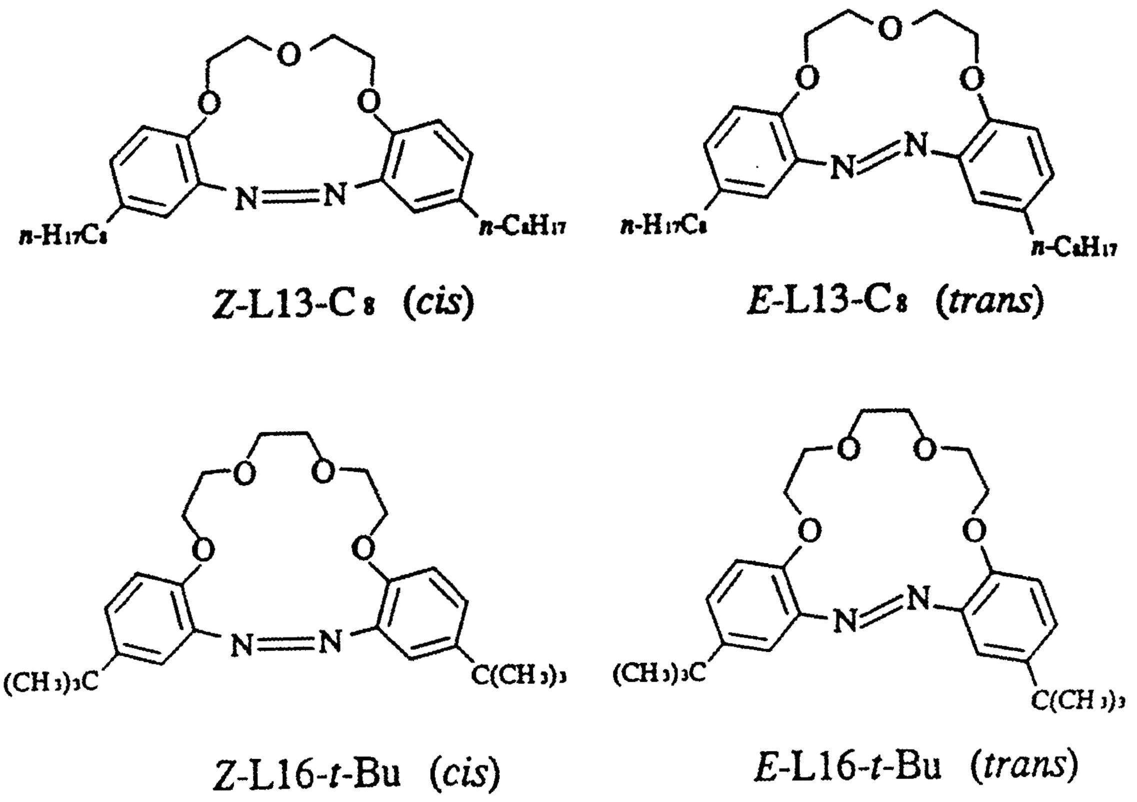

FIGURE 1 Structures of the compounds studied: Z-L13, *E*-L13, *E*-L16 and Z-L16

Z-L13 it is 112mN/m. For *E*-L16 K_c is 94.0 mN/m and for Z-L16 it is only 74 mN/m. The monolayer of the Z-form is also destroyed under lower surface pressure than that of the *E* form for both azo macrocycles.

The shape of the surface pressure – area per molecule isotherms depends on the size of the azocrown ether and on the nature of hydrophobic substituents. When a bulky substituent, such as tetramethylbutyl is used (for L16) the monolayers are more liquid and A_0 is larger compared to monolayers formed by molecules with normal alkyl chains.

The dipole moment for both conformers was calculated from the change of surface potential brought about by the formation of monolayer. [19,26–28]

The values of dipole moments in the Langmuir monolayers are: 1.17D, 0.90D 0.85D and 0.73D for *E*-L16 *E*-L13, Z-L13 and Z-L16, respectively. Higher values of dipole moments for the *E* forms indicate that the interactions of the head group with water are stronger in case of the *E* isomers.

Azocrown ethers are known to interact with alkaline metal cations. L13 has been found to bind Na^+ ions [21] and L16 – K^+ ions [20]. In solutions of alkali metal hydroxides monolayers of both isomers are more stable. In the presence of ions in the subphase the values of parameters characterizing the compression isotherms increase. This reveals simple electrostatic interactions with the Li^+, Na^+, K^+ and OH^- ions in the subphase as the predominant mode of interaction.

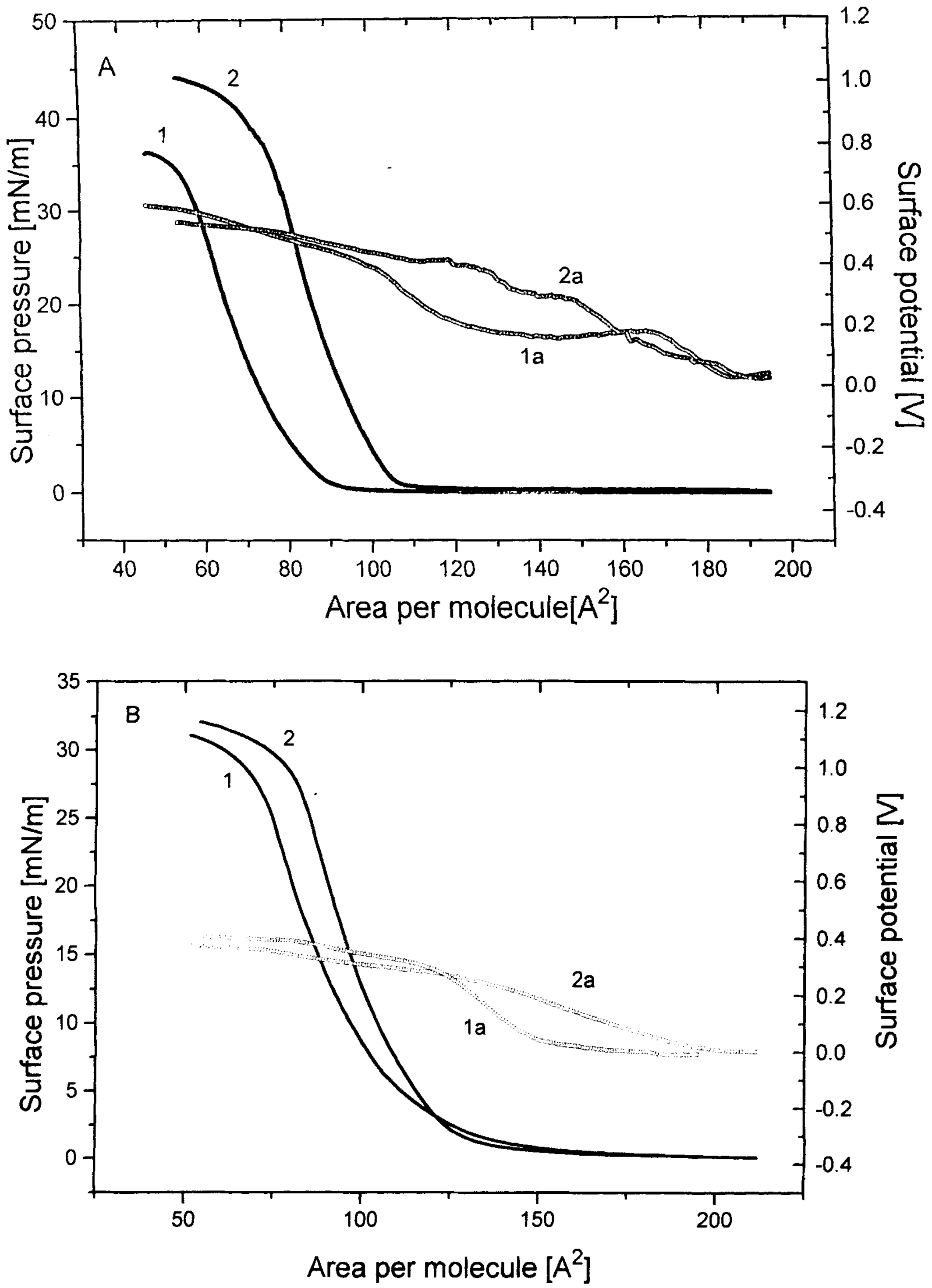

FIGURE 2 Surface pressure – area (1, 2) and surface potential – area (1a, 2a) isotherm of the azocrown at the air-water interface, isomers: *Z* (1,1a), *E* (2,2a). (A) L13, (B) L16

When monolayers were already densely packed and well organized, and still far from the monolayer collapse value i.e. at surface pressure 20 mN/m the films of azocompounds were transferred by immersion of the hydrophobic TMFE and withdrawing of hydrophilic ITO electrode through the monolayer covered air/water interface.

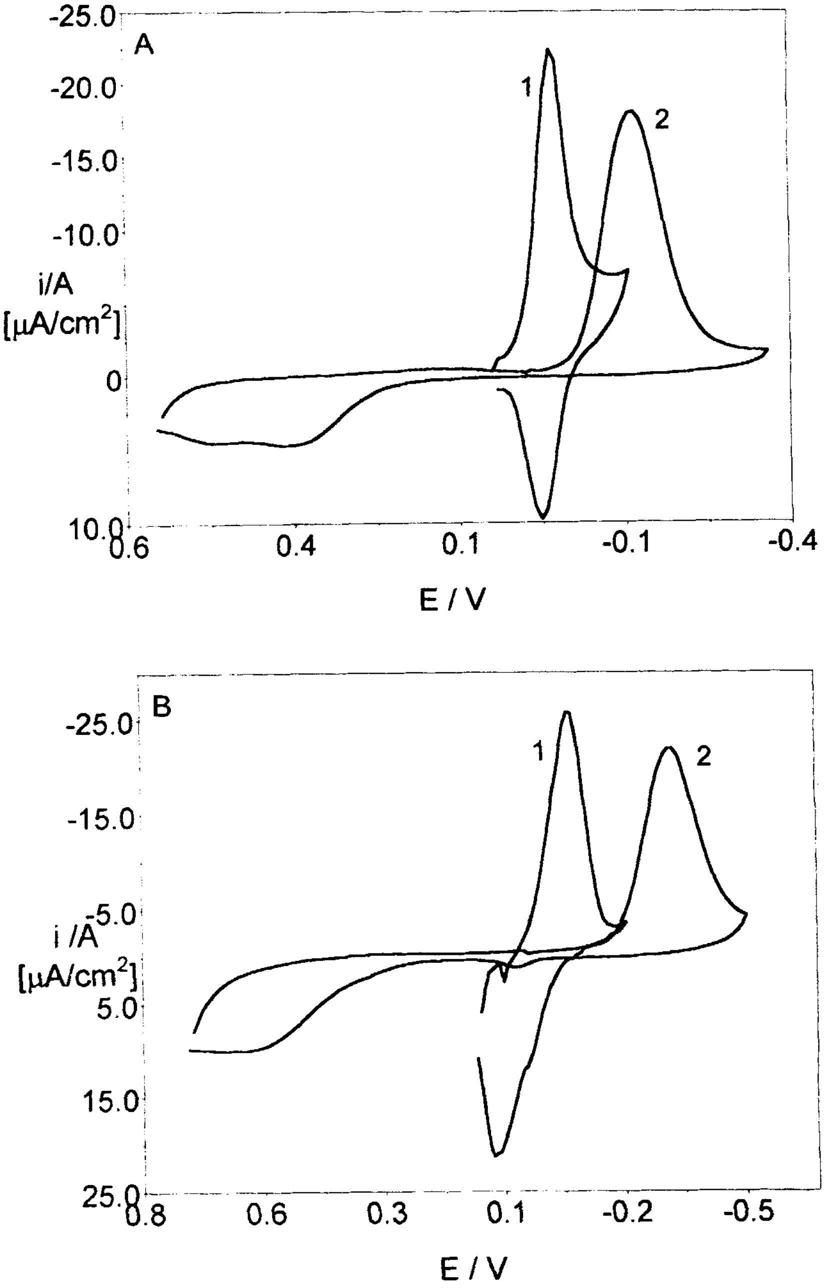

FIGURE 3 Cyclic voltammograms recorded on 1 (TMFE) and 2 (ITO) electrodes covered by L-B monolayer of (A) E-L13 and (B) *E*-L16 in 0.025 M citrate buffer solution, pH = 2.5, v = 0.1 V/s

For a single layer of the azocompound the electroreduction process is far more reversible on mercury electrode then on ITO electrode. Fig.3. shows the voltammograms recorded using TMFE and ITO electrodes as the electrode substrates and solutions of pH=2.5.

On mercury electrode monolayer of L13 is reduced with the formation of a peak at potential Epc= −0.034V and L16 is reduced at −0.065V. On ITO electrode the potentials of the reduction peak are more negative: for L13, Epc= −0.175V, and for L16 Epc = −0.300V. The system of peaks observed for the smaller azocrown, L13 on both electrodes is more reversible than the bigger one, L16.

In acidified and neutral solutions the potential of reduction of the azocompounds is changing linearly with pH [22,29]. The slope of the plot on the mercury electrode is 58mV/decade and on ITO electrode it is 62 mV/decade for L13. The reduction proceeds similarly to the reduction of azobenzene in the presence of protons [30]:

$$-R-N + N-R- + 2H^+ + 2e^- \rightarrow -R-NH-NH-R- \quad (1)$$

In alkaline solutions, the mechanism of the process of reduction is different [30]:

$$-R-N = N-R- + 2e^- \rightarrow [-R-N-N-R-]^{-2} \quad (2)$$

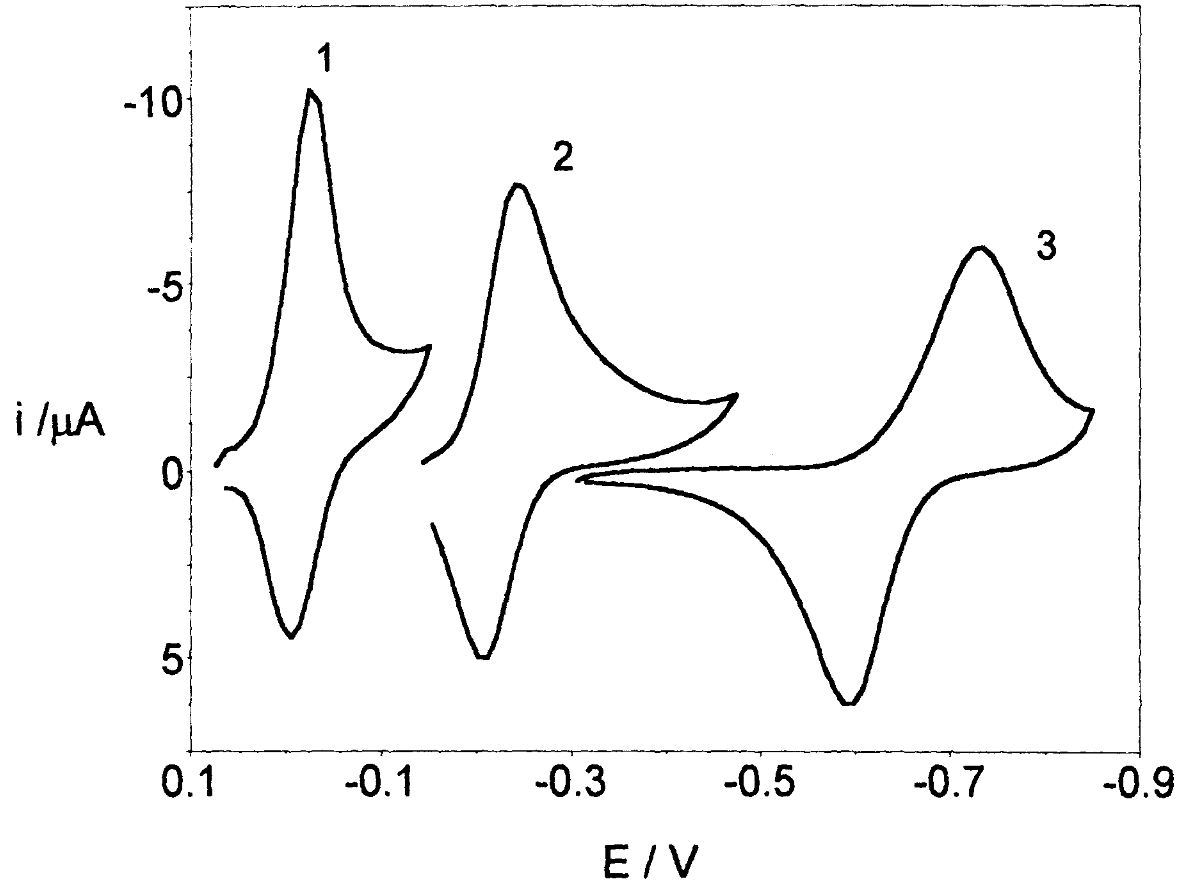

FIGURE 4 Cyclic voltammograms on TMFE modified with a monolayer of *E*-L13, v = 0.1 V/s, in solutions of pH: (1) 2.50, (2) 5.76 (3) 12.24

Reversibility of the process and kinetic parameters depend on the pH of the solution. Fig.4 presents voltammograms recorded in solutions of different pH for a TMFE modified with a monolayer of E-L13

The rate constants were calculated for monolayers of azocrown ethers, L13 and L16 on TMFE and ITO electrodes using equations [31]:

$$E_c = E^{0'} - (RT/\alpha nF)\ln(\alpha nFv/RTk_s)$$
$$E_a = E^{0'} + [RT/(1\text{-}\alpha)nF \ln[(1\text{-}\alpha)nFv/RTk_s]$$

where $E^{0'}$, v and α are formal potential, scan rate and transfer coefficient, respectively. On mercury electrodes the k_s values are $26.4.s^{-1}$ and 2.7 and on ITO electrode the $k_s$are $1.9x10^{-2}$ s^{-1} and $1.5x10^{-2}s^{-1}$ for L13 and L16, respectively.

Differences of the rate constants on the two electrode substrates can be understood in terms of different orientation of the azocompound on the surface of hydrophobic TMFE and hydrophilic ITO electrodes. On the surface of mercury, the molecules of azocompounds are oriented with the hydrophobic chains to the electrode surface. Polar head group which at the same time is the electroactive part of the molecule is directed towards the solution. Since in the process of reduction of the azocompound both electrons and protons are involved their transport may determine the rate constant of whole process. The interaction of the headgroups with protons in the solution is easier in case of hydrophobic electrode surfaces. In case of ITO electrode, polar head group is oriented to the electrode surface and protons have to penetrate to the electroactive azo group through the densely packed hydrocarbon chains attached to the crown ether. This may explain the more negative peak potential observed when ITO is used as the electrode. Thus the ease of counterions approach and not the distance of the electroactive center from the electrode surface seems to be controlling the kinetics of electrode process. The calculated rate constants (k_s), transfer coefficients (α, 1-α) for L13 on mercury electrode are collected in Table I.

TABLE I Kinetic parameters: ks, α,1-α at different values of pH for L13 in monolayers on TMFE

PH	*k [s^{-1}]*	α	*1-α*
2.50	26.4	0.39	0.56
3.28	10.2	0.25	0.77
5.76	6.7	0.24	0.76
6.10	3.9	0.12	0.88
12.24	4.3 [a] 22.6	0.20 [a]0.32	0.79 [a]0.78

a. For isomer Z.

The process of reduction is fastest in strongly acidic solutions and values of rate constant decrease with the increase of pH.

In alkaline solutions, the *Z* and *E*-isomers can be recognized by voltammetry [21,30], because of the difference in kinetics of reduction. The *Z*-form is reduced more reversibly than the *E*-form. Values of rate constant for the Z-form is 22.6 s^{-1} and is almost as high as in acidic medium, whereas for the *E*-form it is much lower – almost equal to the value of rate constant in neutral medium, 4.3 s^{-1}.

These experiments were performed in solutions containing Li^+ cations. Azocrown ethers were found to interact with Na^+ and K^+ cations [20,21]. When Na^+ and K^+ cations were added to the solutions, potentials of the reduction peaks were more negative [22,24]. This indicates that azocrowns in the monolayer form complexes with the alkali metal cations. Upon interaction of the macrocycle with Na^+or K^+ ions the reduction process is made more difficult since protons during reduction have to bind now to the positively charged complexed form of the azocrown. This is believed to provide explanation for the negative shift of the reduction potential of the azocrown ethers in the monolayer.

In monolayers of azocrown ethers both at the air-water interface and on surface of electrode the *Z* and *E* isomers are recognizable. The values of parameters characterizing the Langmuir monolayers are higher for *E* isomer. Also voltammetry is a convenient method for the recognition of both isomers, because the *Z*-form is reduced in alkaline solutions at more positive potentials than the *E* form. The kinetic parameters of the reduction of azogroup in the macrocycle depend on the orientation of the molecules on the electrode surface. On hydrophobic surfaces the process of reduction is more reversible than on hydrophobic ones, although the electroactive centers might be located further from the electrode surface. This conclusion is in line with the observations of Kaifer at al. [32], who indicated that quinone redox centers immobilized on the external surface of the monolayer exhibit more reversible cyclic voltammetry behavior, even though the quinones are located further from the gold surface. Orientation of the molecules in the monolayer seems, therefore, to be an important factor for the kinetics of the process of electroreduction.

Acknowledgements

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