Supramolecular Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713649759

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To cite this Article Slowinska, K. U. , Slowinska, K. , Pietraszkiewicz, M. and Bilewicz, R.(1999) 'Hexaazamacrocyclic Ligands with Long Alkyl Chains as Functional Units in Monomolecular Langmuir - Blodgett Films', Supramolecular Chemistry, 10: 3, 201 — 211

To link to this Article: DOI: 10.1080/10610279908559286

URL: http://dx.doi.org/10.1080/10610279908559286

SUPRAMOLECULAR CHEMISTRY, Vol. 10, pp. 201–211
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Hexaazamacrocyclic Ligands with Long Alkyl Chains as Functional Units in Monomolecular Langmuir–Blodgett Films

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(Received 4 August 1998)

Properties of three macrocyclic hexaamine derivatives were studied in monolayers as the anion binding or ion channel units. In monolayers at the air-solution interfaces the protonated molecules were found to interact with perchlorate anions in the solution by simple ion-pairing. Interactions with $Fe(CN)_6^{4-}$ were stronger due to supercomplex formation. In case of hexaamine modified with amide groups additional interactions of $Fe(CN)_6^{4-}$ with amides induced changes in the structure of the macrocyclic molecule at the air–water interface. The hexaaza macrocyclic ligands studied did not form on their own stable monolayers on electrodes, therefore, two-component monolayers containing α,ω-hydroxythiol and the polyazamacrocyclic ligand were prepared at the air–water interface and transferred onto gold electrode using the monolayer lifting procedure. This approach allowed to obtain stable coverage of the electrode with the composite monolayer anchored to the gold surface through the thiol groups of hydroxythiol, and with the hydrophilic parts of the hexaazamacrocyclic molecules facing directly the solution, therefore free to interact with the ions present in the solution.

Keywords: Monolayer, Langmuir–Blodgett films, voltammetry

INTRODUCTION

Molecular recognition is one of the most important subjects of supramolecular chemistry. It has been initially associated with inorganic cation recognition, and further development in this area resulted in recognition phenomena related to organic and inorganic cations, anions and polyanions, neutral species, and chiral molecules/ions [1].

There are numerous methods providing the insight to the quantitative measures of molecular recognition phenomena. To mention a few: spectroscopic (NMR, UV-vis, fluorescence spectroscopy), electrochemical, and thermochemical. More recently, there has been another tool developing rapidly associated with Langmuir and Langmuir–Blodgett methodologies. In fact, there have been many papers dealing with molecular recognition at water–air interface where the subphase contained the molecules, or ions to be recognized by Langmuir films [2].

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Anion recognition phenomena have been the focus of intense research, due to their relevance to biological systems, and also to practical sensing of various anions present in environment as pollutants. There have been many structural types of ligands designed to form the complexes with anions: protonated macrocyclic polyamines [3], macrocyclic polyguanidines [4], neutral ligands based on urea, or thiourea units [5], macrocyclic and macropolycyclic quaternary polyammonium salts [6]. The driving forces between anions and anion molecular receptors have been of electrostatic, hydrogen bonding, and π-donor-π-acceptor nature.

We have been interested in lipophilic, macrocyclic hexaamines in their protonated forms as potential hosts for anions. Due to repulsive interactions between positively charged nitrogen atoms, the macrocyclic polyamines of our interest have remarkable cavity capable of accommodating various anions [7]. Their amphiphilic derivatives were prepared in order to use them as functional units for ion recognition and channeling at interfaces. It turned out that the compounds formed stable monolayers on water, however, on their own did not produce monolayers of satisfying stability on gold electrodes.

In our previous work we have demonstrated that multicomponent monolayers containing *n*-octadecanethiol as the matrix component could be transferred onto gold electrodes by withdrawing the substrate through the monolayer at the air–water interface and stable electrode coatings were obtained using this procedure [8]. This approach forces the molecules to have their hydrophilic part oriented towards the hydrophilic electrode surface. However, there are now numerous molecules tailored for the use in sensor devices which interact with analytes in the solution through their hydrophilic part. Using our former approach the access to this group is made difficult since it is buried deep in the monolayer and isolated from the solution species by the hydrophobic chains. It is also usually involved in some interactions (electrostatic or chemical) with the electrode. This limits the utility of the above approach for the construction of new sensors based on binding or channeling by the macrocyclic molecule in the monolayer. Therefore, we employed the modified lifting procedure described in detail elsewhere [9] and α,ω-hydroxythiol as the main component of the monolayer assembly. This approach lead to the required molecular orientation with the hydrophilic parts facing the solution and at the same time retained the high stability of the monolayer at the electrode surface due to binding of the thiol terminal group of hydroxythiol to the gold substrate.

EXPERIMENTAL

General

All chemicals were purchased from Fluka, Aldrich or Merck, and used without purification, except for THF and triethylamine, which were distilled over $LiAlH_4$, and CaH_2, respectively. The α,ω-hydroxythiol, $HO—(CH_2)_{22}—SH$ was obtained from R.V. Chamberlain, University of California, Berkeley.

All solutions for the monolayer studies were prepared daily by dissolving the compounds in pure chloroform. Water for the subphase was distilled and passed through Milli-Q water purification system. The final resistivity of water was 18.3 $M\Omega\,cm^{-1}$. Temperature was 20–22°C. Experiments were carried out on KSV Langmuir troughs LB 2000 or LB 5000 equipped with two hydrophobic barriers, a Wilhelmy balance as a surface – pressure sensor, and 5000SP surface potential meter (vibrating capacitor method). Software version KSV-5000 or 2000 were used to control the experiments. To protect the experimental setup from dust it was placed in the laminar flow hood. The procedures of cleaning the trough and monolayer spreading have been described earlier [8, 10] .

Electrochemical experiments were performed in three electrode arrangement with saturated calomel electrode (SCE) as the reference electrode, platinum foil as counter electrode and the glassy carbon electrode (GCE, Bioanalytical Systems Inc.) or Au electrodes used as the working electrodes. The Au working electrodes ($A = 0.2\ \mathrm{cm}^2$) were 70 - 100 nm thick films of gold (99.95%, Lawrence Berkeley Laboratory) vapor-deposited in vacuum onto glass microscope slides (Corning Plain Micro Slides). Before depositing gold, the glass slides were precoated with 1 - 5 nm thick layers of chromium to induce a desired adhesion of gold to glass. Carbimet Paper Discs and Gamma Micropolish II Alumina, 0.05 m, (Buehler Ltd) were used for the GCE electrode polishing. Voltammograms were recorded using a EG&G PARC Model 273 potentiostat or BAS-100 Electrochemical Analyser (Bioanalytical Systems Inc.) with a HIPLOT DMP-40 plotter (Houston Instruments).

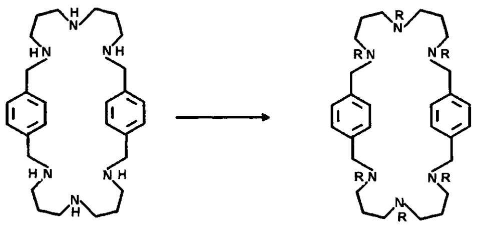
The H-1 NMR spectra were recorded on Varian-Gemini 200 and Varian Unity Plus 200 MHz, with TMS as standard, in $CDCl_3$ solution. The mass spectra were recorded on Intectra AMD-604 spectrometer. Elemental analyses were performed at the Institute of Organic Chemistry, Polish Academy of Sciences, Warsaw.

SYNTHESIS OF COMPOUNDS

Hexaamine 1 was synthesized according to the procedure given by Gasiorowski and Pietraszkiewicz [11].

Preparation of 2

The starting hexaamine **1** (Fig. 1) (0.932 g, 2 mmol) and *n*-hexadecylbromide (3.965 g, 13 mmol) were dissolved in dry THF (70 mL) under Ar and finely ground and calcined anhydrous K_2CO_3 (7 g, 50 mmol) was added with vigorous stirring. Stirring was continued for 24 h at reflux, the solution was filtered off while hot, washed with THF, and evaporated. The yield of the crude product 92%. Further purification by crystallization from ethanol.



synthetic pathways from macrocyclic hexaamine **1** to target ligands **2**, **3**, **6**

i: *n*-$C_{16}H_{33}Br$, K_2CO_3, THF, refl.
ii: $ClCH_2CONHC_{10}H_{21}$, K_2CO_3, THF, refl.
iii: $CH_2{=}CH(CH_2)_8COCl$, Et_3N, THF, 0°C
iv: **4**, *n*-$C_8H_{17}SH$, 9-BBN, THF, 0°C
v: **5**, $LiAlH_4$, THF, r.t., 2 days

2: R = *n*-$C_{16}H_{33}$-
3: R = $CH_2CONHC_{10}H_{21}$-*n*
4: R = $CH_2{=}CH(CH_2)_8CO$-
5: R = $CH_3(CH_2)_7S(CH_2)_{10}CO$-
6: R = $CH_3(CH_2)_7S(CH_2)_{11}$-

FIGURE 1 General scheme of the synthesis of the compounds studied.

H-1 NMR ($CDCl_3$, TMS, δ ppm): 0.89 (t, 6 × CH_3, 18H), 1.28 (m, 6 × — $(CH_2)_{14}$ —, 168H), 1.60 (m, 4 × NC—CH_2—CN , 8H), 2.34 (m, 14 × CH_2N, 28 H), 3.10 (s, 4 × $ArCH_2N$, 8H), 7.20 (m, Ar, 8H).

Elemental analysis calcd for: $C_{124}H_{238}N_6$: C 82.14, H 13.23, N 4.63 found: C 81.97, H 12.98, N 4.57.

Preparation of 3

The hexaamine **1** (0.932 g, 2 mmol) and *N*-decyl chloroacetamide (3.023 g, 13 mmol) were dissolved in dry THF (70 mL) under Ar and finely ground and calcined anhydrous K_2CO_3 was added with vigorous stirring. Reflux with stirring was maintained for 24 h, the solution was filtered off, washed with THF and evaporated. The yield of the crude product was 89%. Purification by crystallization from ethanol.

H-1 NMR ($CDCl_3$, TMS, δ ppm): 0.91 (t, 6 × CH_3, 18H), 1.27 (m, 6 × — $(CH_2)_8$ —, 96H), 1.59 (m, 4 × NC—CH_2—CN, 8H), 2.34 (m, 8 × CH_2N, 16 H), 2.98 (t, 6 × CH_2NHCO, 12H), 3.48 (s, 6 × CH_2CONH, 12H), 7.20(m, Ar, 8H).

Elemental analysis calcd for $C_{100}H_{184}N_{12}O_6$: C 72.77, H 11.24, N 10.18 found: C 72.59, H 11.00, N 9.96

MS, (LSIMS (+), NBA, 8 kV, z/e): 1650 (M+, 100%), 1453.

Compounds **4** and **5** were half-products for the preparation of compound **6** studied on the air - water interface.

Preparation of 4

The hexaamine **1** (2.33 g, 5 mmol) and triethylamine (4.5 mL, 32 mmol) were dissolved in dry THF (70 mL) under Ar, chilled below − 5°C and undecylenoyl chloride (6.5 mL, 30 mmol) was added with vigorous stirring, and the temperature was maintained below 10°C. Stirring was continued at room temperature for 1 h, water was added (150 mL) and extracted with hexane (150 mL). Organic phase was separated, washed with water (30 mL) and evaporated to dryness. The syrupy oil solidified after several days. Yields 94%. For analytical purposes the product was crystallized twice from ethanol, and dried in vacuum dessicator over P_2O_5.

H-1 NMR (Gemini 200 MHz, $CDCl_3$, TMS, δ ppm): 1.298 (bm, 6 × $-(CH_2)_6-$, 72H), 1.609 (m, 4 × $-NC-CH_2-CN$, 8H), 2.023 (m, 6×$C=C-CH_2$, 12H), 2.342 (m, 8 × CH_2N, 16H), 3.134 (bm, 4 × $ArCH_2N$, 8H), 4.501(m, 6×CH_2 $C=O$, 12H), 4.902-5.027 (m,6×$CH_2=C$, 12H), 5.795 (m, 6 × $CH=C$, 6H), 7.178 (m, Ar, 8H).

Elemental analysis: calcd for $C_{94}H_{154}N_6O_6$: C 77.10, H 10.60, N 5.74 found: C 77.03, H 10.56, N 5.69.

Preparation of 5 [12]

The compound **4** (6.548 g, 4.47 mmol) and *n*-octanethiol (12 mL, 67 mmol) were dissolved in Freshly distilled THF (50 mL) under Ar, cooled in an ice-water bath, and 9-BBN (5 mL, 0.5 M/THF) was added with stirring. The clear solution was left for two days at room temp. THF was evaporated, and the excess of the thiol was removed under reduced pressure (0.05 Torr). The temperature inside the flask should not exceed 80°C. The yield of the crude product was 20 g (93%). The product was dissolved in toluene, washed twice with 5% aq. NaCl (50 mL) and with pure water (100 mL). Organic phase was evaporated to dryness, giving an oil, which solidified after a few days. For analytical purposes the product was twice crystallized from ethanol.

H-1 NMR ($CDCl_3$, TMS, δ ppm): 0.880 (t, 6 × CH_3, 18H), 1.275 (m, 6 × $-(CH_2)_{14}-$, 168H), 1.608(m, 4 × $NC-CH_2-CN$, 8H), 2.356 (m, 8 × CH_2N, 16H), 2.499 (t, 6 × CH_2SCH_2, 24H), 3.139 (m, 4 × $ArCH_2N$, 8H), 4.500 (m, 6 × $CH_2C=O$, 12H), 7.192 (m, Ar, 8H).

Elemental analysis calcd for $C_{142}H_{262}N_6O_6S_6$: C 72.82, H 11.28, N 3.59 found: C 72.75, H 11.19, N 3.51.

Preparation of 6

Lithium aluminium hydride (300 mg) was dissolved in freshly distilled THF (50 mL) under Ar. Compound **5** (987 mg, 0.42 mmol) was dissolved in THF (20 mL) and dropped within 15 min to $LiAlH_4$. Stirring at r.t. was maintained for 4 days. Acetone (3 mL) was added to remove an excess of $LiAlH_4$, and 10% aq. NaOH was added slowly. Inorganics were filtered off, washed with THF, and the solution was evaporated to dryness to give a dense oil, yield 89%. For further purification the product was dissolved in CH_2Cl_2 containing 10% of MeOH (v/v) and filtered through a short layer of silica gel (Merck 60, 230-400 mesh) and evaporated to dryness.

H-1 NMR ($CDCl_3$, TMS, δ ppm): 0.906 (t, 6 × CH_3, 18H), 1.266 (m, 6 × $-(CH_2)_{15}-$, 180-H), 1.576 (m, 4 × $NC-CH_2-CN$, 8H), 2.364 (t, 8 × CH_2N, 16H), 2.495 (t, 6 × CH_2SCH_2, 24H), 3.499 (s, 4 × $ArCH_2N$, 8H), 7.209 (s, Ar, 8H).

Elemental analysis calcd for $C_{142}H_{274}N_6O_6$: C 75.53, H 12.23, N 3.72 found: C 75.47, H 12.14, N 3.68 MS: (LSIMS (+) NPOE, 8kV, z/e): 2259 (M^+), 2114 (100%), 1140.

RESULTS AND DISCUSSION

Studies of Hexaamine Derivatives (Compound 2, 3 and 6) in Monolayer Assemblies at the Air-water Interface

Figure 2 presents isotherms for the formation of monolayers of the three compounds **2**, **3** and **6** on the air-pure water interface.

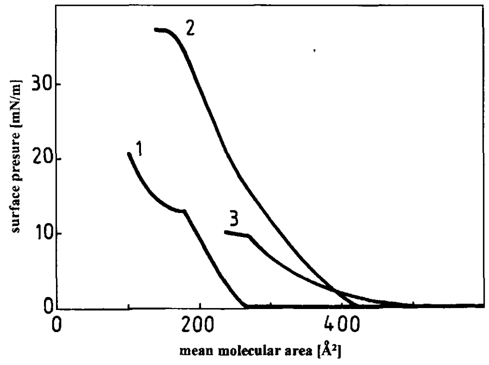


FIGURE 2 Isotherms of the compounds studied on the water subphase. 1-compound **2**; 2-compound **3**; 3-compound **6**. Compression rate: 10 mm/min.

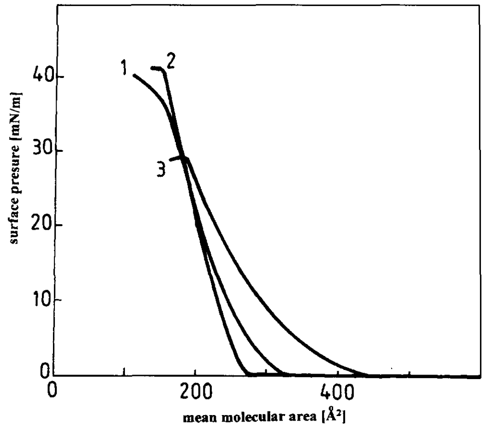


FIGURE 3 Isotherms recorded for the three compounds studied on perchloric acid subphase, pH-2.3, 1-compound **2**; 2-compound **3**; 3 -compound **6**. Compression rate: 10 mm/min.

Highest collapse pressure is seen for the amide derivative **3** [Figure 2 -curve 2]. The surface pressure increases to almost 40 mN/m and the limiting area per molecule is much larger than the area of the hexaamine macrocyclic ring (250 Å^2). This suggests that the monolayer of the amide derivative retains the amide oxygens at the interface, hence in direct contact with water. Further compression leads to reorganization of the monolayer to pack in a similar way to the alkyl derivative (compound **2** -curve 1 in Figure 2), so that the oxygens are now removed from the interface. The area per molecule at this point decreases to ca. 260 Å^2, hence similar to the limiting area for the alkyl derivative. The latter gives a well developed isotherm, however, the small slope of the isotherm is typical for a liquid-like not a solid monolayer. The compressibility factor K_S is only 46.3 mN/m, and the collapse pressure is 12.6 mN/m. The 260 A^2 area is similar to the predictions for a flat orientation of the hexaaza ring on the air–water interface. In contrary to the former compounds the thioether derivative **6** has poor compression abilities probably because the chains bend in the region of sulfur atoms which does not help in packing of the molecules into an organized monolayer.

When pure water subphase is changed for 0.01 mol/dm^3 perchloric acid solution (Fig. 3) the isotherms clearly improve in that the collapse pressures increase even for the thioether derivative [Tab. I].

The compressibility factor for the monolayer of the alkyl derivative (compound **2**) increases from 46.3 to 98.1 mN/m, hence a more condensed phase is formed at the air-acid solution interface. In case of the amide derivative the limiting area decreases to 250 A^2 which is similar to that of the alkyl derivative [Tab. I]. Under these conditions the amide groups probably leave the air–water interface and immerse into the subphase. The compressibility factor, K_S, also increases from 58.5 mN/m on water to 119.2 mN/m on perchloric acid, similarly to the behavior observed for the alkyl derivative.

All these changes are not unexpected since the hexaazamacrocycles become protonated at the amine nitrogen atoms. The charged head groups become much more hydrophilic and the ammonium ions are known to form strong ion pairs with perchlorates in the solution. Strong ion-pair formation stabilizes the monolayer, hence higher surface pressures can be attained.

Ferricyanates differentiate the behavior of the compounds studied at the air–water interface (Fig. 4)

TABLE I Characteristics of the monolayers of the compounds studied

Compound	subphase	H_2O	$H_2O + HClO_4$ pH 2.3	$H_2O + HClO_4$ pH 2.3 + 1 mM $Fe(CN)_6^{4-}$
2	collapse pressure mN/m.	12 ± 1	38 ± 2	53 ± 2
2	area per molecule Å^2	250 ± 2	260 ± 2	220 ± 5
3	collapse pressure mN/m.	37 ± 4	41 ± 2	49 ± 5
3	area per molecule Å^2	330 ± 2	250 ± 5	260 ± 2 ($350^* \pm 5$)
6	collapse pressure mN/m.	9 ± 2	29 ± 5	47 ± 5
6	area per molecule, Å^2	380 ± 8	320 ± 5	230 ± 4

*Limiting area from the extrapolation of the initial part of the isotherm (see text).

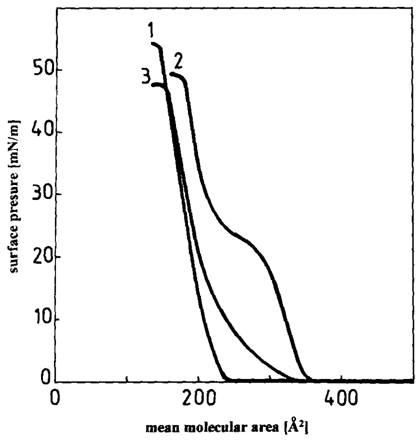


FIGURE 4 Isotherms received for compounds **2**, **3** and **6** on the perchloric acid subphase with 0.001 mol/cm^2 $Fe(CN)_6^{4-}$. 1-compound **2**; 2-compound **3**; 3 -compound **6**. Compression rate: 10 mm/min.

The slope of the isotherm for the alkyl derivative increases, and the compressibility factor is 235.6 mN/m which means that the monolayer obtained under these conditions is solid. The collapse pressure also increases from 38 to 54.4 mN/m). This indicates that the alkyl derivative interacts stronger with the $Fe(CN)_6^{4-}$ than with perchlorate ions [Tab. I]. Distinctly different is the behavior of the amide derivative in the presence of $Fe(CN)_6^{4-}$. The isotherm consists now of two parts with similar slope: one starting at 350 Å^2/ molecule and the next at 260 Å^2. This can be interpreted in terms of specific ferricyanate incorporation into the layer of compound **3** followed by squeezing it out at pressures higher than 20 mN/m. At this point the molecules reorganize again into a layer similar to that of the simple alkyl derivative on the acidified subphase containing $Fe(CN)_6^{4-}$. The compressibility factor is nearly identical, 235.7 mN/m. The existence of these two regions in the isotherm indicates that the amide groups occupying place on the water–air interface induce a specific interaction of the macrocycle with $Fe(CN)_6^{4-}$. It leads to a different organization of the monolayer compared to that of the alkyl derivative. In the region above 20 mN/m the amides are squeezed into the subphase and the $Fe(CN)_6^{4-}$ binding is then similar to that of the alkyl derivative **2**. The behavior of the thioether derivative, compound **6**, towards $Fe(CN)_6^{4-}$ anion resembles that of compound **2**- the slope of the isotherm is higher and area per molecule is decreased from 320 to 230 A^2/molecule compared to the acidified subphase [Fig. 4 and Tab. I].

Addition of 0.001 mol/dm^3 KCl or $CuCl_2$ leads only to the increase of collapse pressure for all compounds studied. For the simple alkyl derivative the collapse pressure is increased from 14 mN/m (water) to nearly 40 mM/m (on KCl subphase). This indicates that metal cation interacts with the nitrogen atoms of the macrocycle making the head-group more polar which in turn leads to higher stability of the monolayer [Fig. 5].

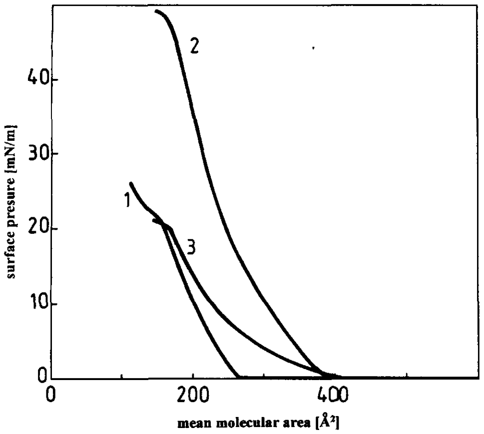


FIGURE 5 Isotherms of compounds **2**, **3** and **6** on the subphase containing 0.001 mol/cm^2 $CuCl_2$ 1-compound **2**; 2 - compound **3**; 3 - compound **6**. Compression rate: 10 mm/min.

Similar interactions observed in the presence of $CuCl_2$ and KCl point to ion-pairing type rather than inclusion into the macrocycle in the former case, which is unexpected since in the solution phase the complexes of $CuCl_2$ with the unsubstituted hexaamine are readily formed and are stable as described in our earlier papers [13]. If, however Cu(II) trifluoromethanesulfonate is used instead of the chloride salt the interactions with the monolayer become more specific and resemble the interactions with $Fe(CN)_6^{4-}$, especially in case of the amide derivative [Fig. 6 -curve 2].

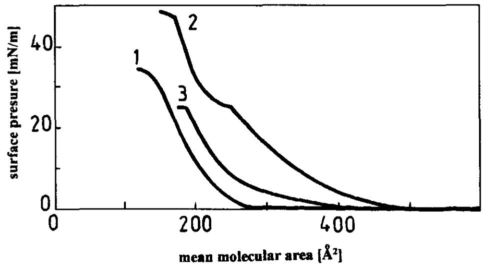


FIGURE 6 Isotherms of compounds **2**, **3**, and **6** on the subphase containing 0.001 mol/cm^2 Cu(II) trifluoromethanesulfonate 1 - compound **2**; 2 - compound **3**; 3 - compound **6**. Compression rate: 10 mm/min.

Monolayers at the Electrode-solution Interface

The hexaazamacrocyclic ligands modified with alkyl chains form stable monolayers at the air-water interface, however, the monolayers prepared on gold surfaces by self-assembly or Langmuir-Blodgett transfer were not stable and detached from the electrode upon immersion to the electrolyte solution. Also, attempts to use the ligand modified by substituting thioether groups have been so far unsuccessful since the transfer ratio of the monolayer from the air-water interface onto the electrode was always low. Therefore, we used our former approach of mixing the compound studied with one containing a thiol group to anchor the whole monolayer to the electrode surface [9].

Isotherms for varying ratio of the hexaazamacrocyclic ligand and hydroxythiol in the spreading solution are depicted in Figure 7.

With the increase of the ligand to hydroxythiol ratio the isotherms are shifted towards higher molecular areas [Fig. 7]. The plot of area per molecule *vs.* mole fraction of the ligand in the monolayer [Fig. 7 -inset] exhibits linearity. Moreover, the collapse pressure does not change when the mole fraction of ligand is decreased and in the region of the first plateau it is always equal to that of the collapse pressure of the monolayer of

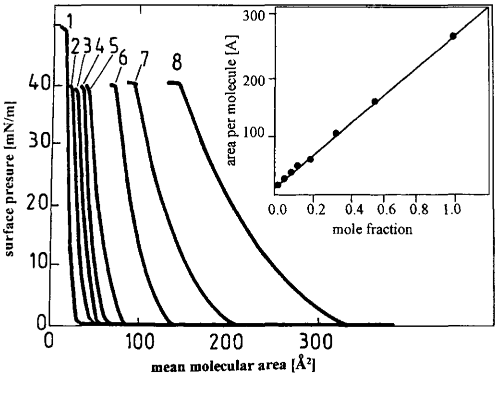


FIGURE 7 Isotherms for mixtures of compound **3** and $HO(CH_2)_{22}SH$ on water subphase, pH 6.0. Compression rate: 10 mm/min. Mole percent of amide (compound **3**) in the mixture : 1) 0; 2) 4.0; 3) 8.5; 4) 11.1; 5) 17.2; 6) 35.7; 7) 55.5; 8) 100%. Inset: Area per molecule *vs.* mole fraction of ligand in the $HO(CH_2)_{22}SH$ monolayer.

hexaazamacrocyclic ligand alone. These results allow to describe the multicomponent monolayer as the ideally nonmixing case, hence separate domains of ligand and hydroxythiol coexist in the monolayer formed at the air–water interface.

When the surface pressure attained 30 mN/m, the gold electrode was lowered towards the water surface inclined 60° *vs.* normal to the interface and a speed of 5 mm/min [Fig. 8].

After removing the compound from the surface of water the electrode is withdrawn, rinsed with water and placed in the solution of 1 mM $Ru(NH_3)_6^{3+}$ or $Fe(CN)_6^{4-}$ in 0.5 M KCl and the cyclic voltammograms are recorded. Figure 9 shows the changes of the voltammograms observed using electrodes modified with monolayers containing different mole ratios of ligand and hydroxythiol in a solution containing $Ru(NH_3)_6^{3+}$.

Curve *E* was recorded on a pure hydroxythiol modified electrode. Its sigmoidal shape points to well blocked electrode surface with only few remaining defects. The observed limiting current 2.5 mA/cm^2 (curve *E*) is only 1.6% of the diffusion current recorded on the bare gold electrode (curve *A*). The wave indicates stationary state and the current does not change when the scan rate is increased from 20 to 500 mV/s. The slightly increasing limiting current at higher overpotentials can be explained by the participation of electron tunneling through the adsorbed monolayer [14]. If the monolayer covered electrode is additionally immersed in a solution containing 1 mM $CH_3(CH_2)_5SH$ then instead of a wave, only exponentially increasing current is observed (Fig. 9, curve *E*-dashed line). It means that the passivating properties of the layer can be improved by filling the remaining defects with shorter chain thiols.

Curves *B*, *C*, *D* in Figure 9 were obtained at electrodes covered by mixed monolayers. The height of the $Ru(NH_3)_6^{3+}$ reduction wave decreases with decreasing content of hexaazamacrocyclic ligand in the layer. According to the Amatore–Savéant–Tessier theory [15] the wave should be observed when the separate ligand domains act as independent microelectrodes in the otherwise blocking layer. Under such conditions as discussed earlier [8], the voltammetric limiting current becomes proportional to the radius (R_a) of the microelectrode and to the number of electrodes, *N*:

$$i = 4N_n FR_a DC \tag{1}$$

For the conditions of curve C the concentration of ligand in the monolayer can be calculated to be

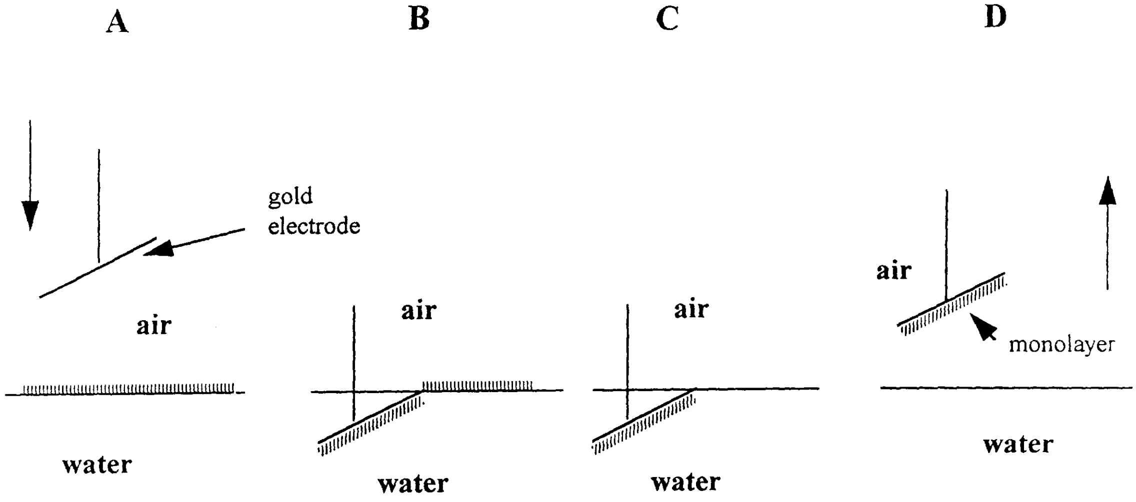


FIGURE 8 Scheme of the Langmuir monolayer transfer procedure onto gold electrodes.

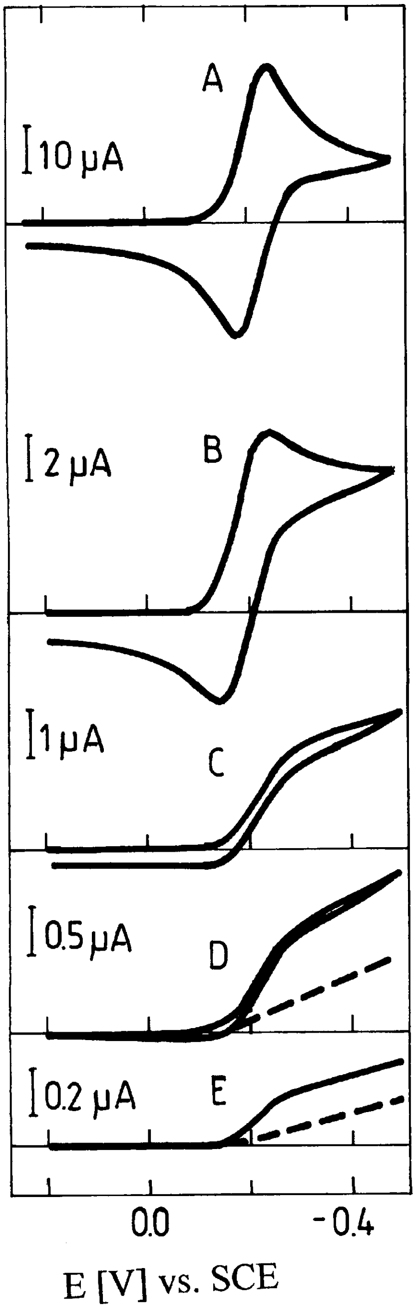


FIGURE 9 Cyclic voltammograms recorded in solution of 1 mmol/dm^3 $Ru(NH_3)_6^{3+}$ in 0.5 mol/dm^3 KCl on (A) bare electrode (B–E) covered by mixed monolayers. Surface concentration of ligand: A, E) 0; B) $1.95 * 10^{-13}$; (C) $1.95 * 10^{-16}$; (D) $7.8 * 10^{-17}$ mol/cm^2 (-----) additionally immersed to 1 mM $CH_3(CH_2)_5$ SH solution for 3 hours.

$7.8 \bullet 10^{-17}$ mol/cm^2 based on the composition of the spreading mixture used for the preparation of the monolayer at the air–water interface. The molecular area of the ligand is 250 Å^2, hence the radius of the molecule can be taken as 9 Å. If we assume that at this high dilution of ligand in the monolayer single ligand molecules act as individual microelectrodes the current expected based on Eq. 1 would be 9.9 mA/cm^2. Mean current obtained for 5 electrodes modified with mixture *D* is 7.0 ± 2.0 mA/cm^2. It is close to the predicted value. For curve C the surface concentration of ligand is $1.95 \bullet 10^{-16}$ mol/cm^2. The predicted value of current would be 23.9 mA/cm^2, and experimental value is 14.7 ± 3.0 mA/cm^2. The increasing difference may be due to agglomeration of the molecules of ligand into bigger domains. For example if 3- molecule domains are assumed, the calculated current would be 13.79 mA/cm^2. For curve *B* in Figure 9 the peaked shaped voltammogram indicates that the diffusion zones to each domain start to overlap, hence for concentrations $1.9 \bullet 10^{-13}$ mol/cm^2 or higher, the domains are too close one to each other and do not behave as individual microchannel electrodes any more. Hence, under conditions of very low population of hexaazamacrocyclic molecules in the blocking monolayer these molecules may function as channels opening access of small ions to the electrode surface. If these ions are electroactive and their electrode processes are sufficiently fast {for $Fe(CN)_6^{4-}$ they are too slow as discussed elsewhere [8]}, and uncomplicated as shown on the example of $Ru(NH_3)_6^{3+}$, their approach to the electrode surface through the channels may be monitored by the voltammetric method, which becomes then a probing technique of the perforated monolayer on the electrode.

CONCLUSIONS

Macrocyclic hexaamine derivatives were found useful as the anion binding units. Three amphiphilic derivatives of the hexaamine- compounds

2, **3**, and **6** form monolayers on the water subphase. Upon protonation of the nitrogens, the Langmuir films become much more stable due to ion-pair interactions with the perchlorate anions in the solution. Monolayers of compound **2** and **6** interact in the solution of pH 2 with the $Fe(CN)_6^{4-}$ anion much stronger than with the simple perchlorate anion as shown by the increase of the collapse pressure. Specific binding of $Fe(CN)_6^{4-}$ to monolayers of compound **3** is due to the presence of amide group. It leads to a new structure at the air – water interface shown by the splitting of the original isotherm into two parts of similar slopes. The limiting area for the first part of the isotherm is 350 Å^2 which is much larger than predicted for the hexaamine ring alone located parallely to the water – air interface. The high value of compressibility factor indicates formation of a solid-like monolayer already at very low surface pressures. These features can be understood assuming that amide groups located on the water surface participate in the formation of a complex with $Fe(CN)_6^{4-}$ anions. Within the second part of the isotherm the area is similar to that of the macrocyclic ring, hence amide groups are removed from the water – air interface, but still the slope of the curve is very high ($K_s = 235.7\,mN/m$) pointing to solid structure of the monolayer as opposed to that observed in the absence of $Fe(CN)_6^{4-}$.

Since the hexaazamacrocyclic molecules alone did not form well organized and stable monolayers on gold we used our former method [8] of preparing stable two- component monolayers on electrodes. In this approach the number of active sites in the otherwise blocking organothiol monolayer is controlled by changing the ratio of components in the spreading solution placed at the air – water interface. The modification employed now is the use of the monolayer lifting [9] procedure at constant surface pressure to modify the electrode surface. This allows most stable coverage of the electrode surface in which the monolayer is anchored to gold through the thiol groups of hydroxythiol. At the same time, the hydrophilic part of the monolayer- the hydroxyl groups of hydroxythiol and the macrocyclic ring of the amphiphilic ligand remain in the outer part of the monolayer directed towards the solution. The importance of such orientation of the molecules at the electrode- solution interface is due to the fact that the macrocyclic ring, hence the functional unit of the monolayer, is free to interact with the analytes in the solution. The transfer method proposed in this approach should also extend the number of molecules that can be used as active sites, channels or receptors in sensing devices based on monolayer assemblies.

Acknowledgements

This work was supported by Grants from Warsaw University BST 562/5 and KBN Grant 3T09A09908, and from Institute of Physical Chemistry, Polish Academy of Sciences.

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