

Synthesis and Electrochemical Properties of Amphiphilic Crown Ether Langmuir–Blodgett Films [1]

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Abstract. 4'-Octadecanoylbenzo-15-crown-5 (**I**) and four 4'-alkylbenzo-15-crown-5 ligands [4'-XB15C5 where X = *n*-C₁₈H₃₇ (**II**), X = *n*-C₁₆H₃₃ (**III**), X = *n*-C₁₄H₂₉ (**IV**), and X = *n*-C₁₂H₂₅ (**V**)] have been synthesized. The π -A isotherms of **I** and **II** were systematically investigated. The results indicated that the Langmuir–Blodgett (LB) films have high stability where the ratios of **I**/SA and **II**/SA were 1:1 and 1:10, respectively, with a 6.2 pH subphase. The LB films of the crown ethers were deposited onto graphite electrodes pretreated by immersing them in liquid wax. The peak current reached the maximum value when the electrode surface was modified with five layers of the amphiphilic crown ethers.

Key words. Amphiphilic crown ethers, Langmuir–Blodgett films, chemical modified electrodes, cyclic voltammetry.

1. Introduction

Crown ethers have wide applications in phase-transfer catalysis, extractions, in ion-selective electrodes [2, 3], in biological membranes and as chemical sensors [4]. A series of alkylbenzo-crown ethers have been synthesized [5, 6]. The biological activity of membranes containing these alkylated crown ethers increases with the increase of the alkyl chain length [6, 7]. The study of Langmuir–Blodgett (LB) films is a new area for crown ethers. The high selectivity of crown ethers for certain metal cations, combined with the Langmuir–Blodgett (LB) film technique [8], which yields a highly ordered assembly of amphiphilic molecules on a solid electrode, makes this crown ether–LB process promising for the fabrication of ion sensitive devices. Yoshida and co-workers [9] recently deposited LB films of octadecyloxymethyl-18-crown-6 and 6-[bis(tetradecyloxymethyl)methoxyethanoylamino] hexanoylamino-methyl-18-crown-6 onto the SnO₂ electrode to give depletion-mode field-effect semiconductor sensors based on the surface conductance change upon ionic incorporation. This result demonstrates that the crown ether LB film can be used to prepare chemical sensors responsive to particular ions.

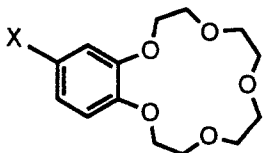
In this paper, we would like to report the synthesis of five new amphiphilic crown ethers, 4'-octadecanoyl-, 4'-octadecyl-, 4'-hexadecyl-, 4'-tetradecyl- and 4'-dodecylbenzo-15-crown-5 (**I–V**), and the π -A isotherms and electrical properties of the LB films based on crown ethers **I** and **III**.

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2. Experimental

2.1. SYNTHESIS OF THE AMPHIPHILIC CROWN ETHERS

Benzo-15-crown-5 (X = H) was prepared by an improved method [5b, 10].



I, X = *n*-C₁₇H₃₅CO; II, X = *n*-C₁₈H₃₇; III, X = *n*-C₁₆H₃₃;

IV, X = *n*-C₁₄H₂₉; V, X = *n*-C₁₂H₂₅.

4'-Octadecanoylbenzo-15-crown-5 (I) was synthesized as follows [7]: 4.5 g (16 mmole) of stearic acid was added to a mixture of 4 g (15 mmole) of benzo-15-crown-5 and 40 g of hot PPA(50–60°C). The resulting mixture was rapidly heated to 70–75°C and then vigorously stirred for 3.5 h at that temperature. The red reaction mixture was hydrolyzed with water and extracted with chloroform. The chloroform extract was dried over anhydrous magnesium sulfate and the solvent was evaporated under reduced pressure. The yellow residue was purified by chromatography on neutral alumina using *n*-hexane/chloroform/acetone: 6/2/1 as the eluent. After evaporating the solvent, the white solid was recrystallized from *n*-hexane containing a small amount of acetone to give 3 g (37.4%) of white needles, m.p. 80.5–81°C; *Anal. Calcd.* for C₃₂H₅₄O₆: C, 71.87; H, 10.18. *Found*: C, 71.75; H, 10.27.

4'-Octadecylbenzo-15-crown-5 (II) was synthesized by an improved method [5b,7] as follows. A suspension of palladium hydroxide on carbon catalyst (0.2 g) in 10 mL of glacial acetic acid was shaken under 2–3 kg/cm² hydrogen gas pressure at 30°C for 1 h. A solution of 1.7 g (3.18 mmole) of I in 20 mL of glacial acetic acid was added and the resulting mixture was shaken under 3–4 kg/cm² hydrogen gas pressure at 50–60°C for 3.5 h. The catalyst was filtered from the cooled reaction mixture. The solvent was evaporated under reduced pressure and the yellow solid was chromatographed on neutral alumina using petroleum ether/chloroform/acetone: 10/2/1 as the eluent. The solvent was removed and the residue was recrystallized from *n*-hexane to give 4.1 g (85%) of white crystals, m.p. 63.5–64°C; *Anal. Calcd.* for C₃₂H₅₆O₅: C, 73.80; H, 10.84. *Found*, C, 73.78; H, 11.09.

4'-Hexadecylbenzo-15-crown-5 (III) was synthesized by the same reduction procedure from 4'-hexadecanoylbenzo-15-crown-5 [7, 11] in a yield of 89%, m.p. 59.5–60°C; *Anal. Calcd.* for C₃₀H₅₂O₅: C, 73.13; H, 10.64. *Found*, C, 73.05; H, 10.81.

4-Tetradecylbenzo-15-crown-5 (IV) was synthesized by the same reduction procedure from 4'-tetradecanoylbenzo-15-crown-5 [7, 11] in a yield of 84%, m.p. 53.5–54°C; *Anal. Calcd.* for C₂₈H₄₈O₅: C, 72.37; H, 10.41. *Found*, C, 72.17; H, 10.61.

4'-Dodecylbenzo-15-crown-5 (V) was obtained by the same reduction procedure from 4'-dodecanoylbenzo-15-crown-5 [7, 11] in a yield of 95%, m.p. 42.5–43.5°C; *Anal. Calcd.* for C₂₆H₄₄O₅: C, 71.56; H, 10.09. *Found*, C, 72.03; H, 10.34.

2.2. PREPARATION OF LANGMUIR-BLODGETT (LB) FILMS

A known amount of crown ether **I** or **II** and stearic acid (molar ratios of **I** and **II** to stearic acid were varied from 0 : 1 to 1 : 0 and 1 : 10 to 1 : 0, respectively) was dissolved in chloroform. The total concentration of stearic acid and crown ether was $1.0 \times 10^{-3} \text{ mol L}^{-1}$. This solution ($600 \mu\text{L}$) was spread on the subphase containing 5 mmol/L of TICl (pH 6.2). The film was treated on an Atemeta Langmuir machine. After complete evaporation of the solvent, the monolayer film was compressed by a mobile Teflon barrier at a speed of 4.5 mm/min. The LB films of crown ethers **I** and **II** were kept under a surface pressure of 40 mN/m and 35 mN/m, respectively, for 30 min in order to make sure that the films were stable. The film was transferred onto the substrate (graphite or glass carbon electrodes) at a substrate up-down speed of 4 mm/min. The prepared glass carbon and graphite electrodes were polished with #05 sandpaper, followed by treatment with freshly-distilled water under an ultrasonic wave for 10 min. The electrodes were dried in a flow of nitrogen gas and used immediately.

2.3. MEASUREMENT

Electrochemical studies were carried out in a conventional three-electrode cell. The multilayer LB film of the amphiphilic crown ether was deposited on a graphite or

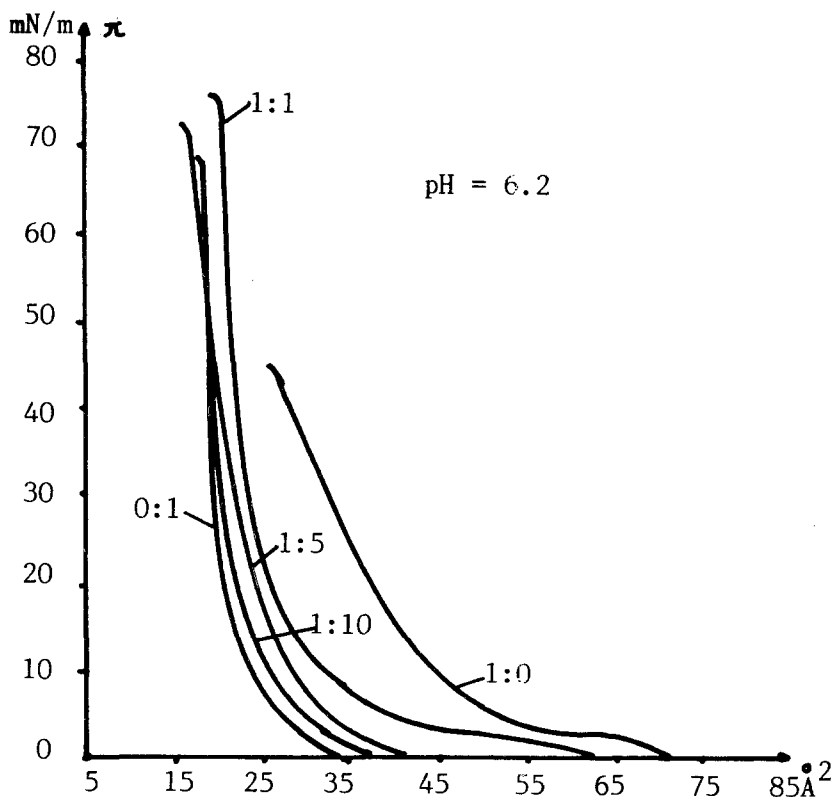


Fig. 1. π -A Isotherms for different ratios of crown ether **I** to SA.

glass carbon working electrode. A 232 model saturated calomel electrode was used as reference electrode and a platinum electrode was used as the counter electrode.

3. Results and Discussion

The amphiphilic crown ethers (I–V) were first synthesized in high yields and were all characterized by elemental analyses and IR spectroscopy.

Figure 1 shows the π -A isotherms of the LB film obtained from amphiphilic crown ether I for four different ratios of I to stearic acid (SA). The monolayer film of I alone was stable up to 45 mN/m and its limiting molecular area was about 26 Å², which shows that the macrocyclic polyether ring of the crown ether is partly immersed in water in this case. When the ratio of I/SA was 1:1, the monolayer film was stable up to 77 mN/m and the limiting molecular area was about 20 Å² which shows the effect of the aliphatic chain of the crown ether. The π -A isotherms of the LB film obtained from the mixture of amphiphilic crown ether II and SA are shown in Figure 2. The collapse pressure for the monolayer film of II alone was 38–40 mN/m and its limiting molecular area was 37 Å² with a low slope of the π -A curve. However, the π -A curve slope increased with increasing II/SA ratios. The π -A curve has the highest slope when the ratio was increased to 1:10.

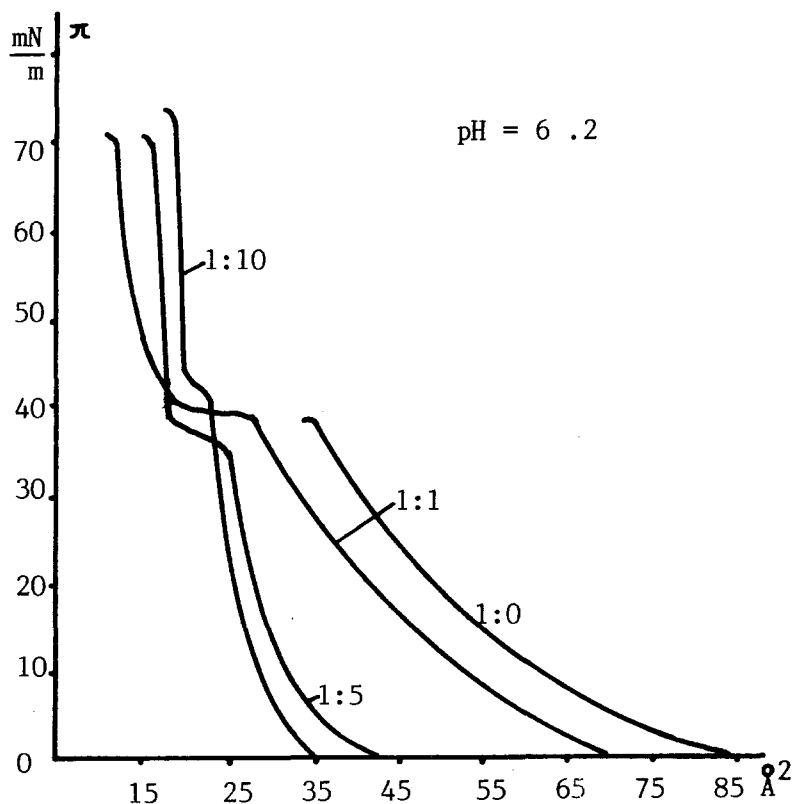


Fig. 2. π -A Isotherms for different ratios of crown ether II to SA.

The influence of pH values in the subphase on the stability of the crown ether LB films was also investigated. The result indicates that the stability was good at a pH value of about 6.2. However, the collapse pressure decreases rapidly when the pH value was smaller than 4.6.

The cyclic voltammetric study of LB films obtained from pure crown ethers revealed that several potential sweeps were needed in order to make the films fully electro-active. Figure 3 shows the cyclic voltammograms of crown ether I. From Figure 3 we can conclude that the oxidation-reduction peak current of the LB film is greater than that of the coated film. Also it is evident that the sensitivity of the LB film system was better than that of the coated film system. The electrode modified by the LB film has better repeatability than that of the coated electrode at a given concentration.

Figure 4 shows the peak current of the electrode whose surface was modified by amphiphilic crown ether II with a different number of layers. When the electrode surface was modified with five layers of the amphiphilic crown ether, the peak current was maximum. This indicates that the number of LB film layers modified on the electrode greatly influences the sensitivity of the electrode. The electrochemical properties of the electrode modified by the crown ether I were similar to those obtained from the electrode modified by the crown ether II.

The experimental results indicate that the LB films with long-chain amphiphilic crown ethers have high stability. The monolayer film can be maintained on the

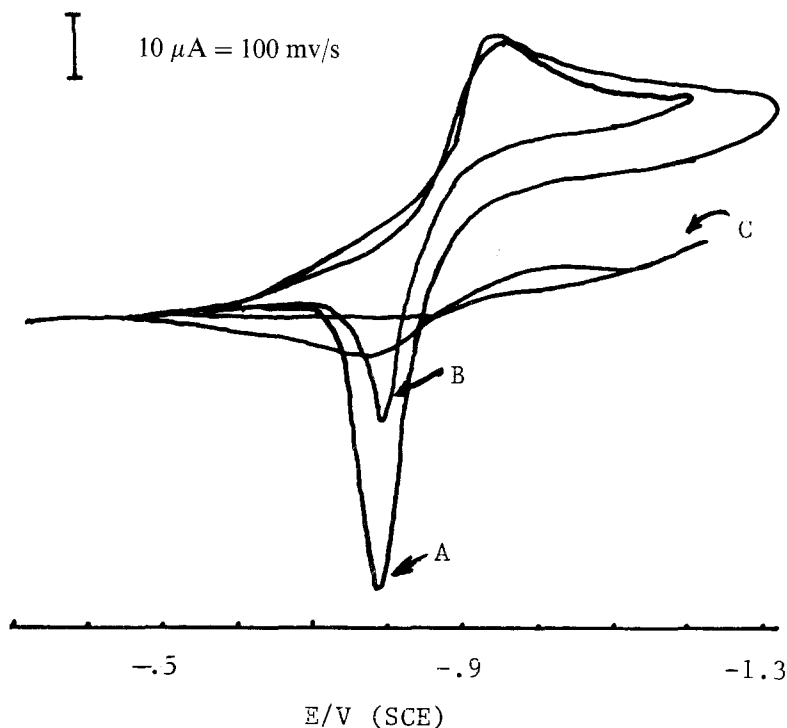


Fig. 3. C-V curves of wax-immersed graphite electrode: (A) before modification; (B) modified by 5 layers of LB film; (C) modified by coated film.

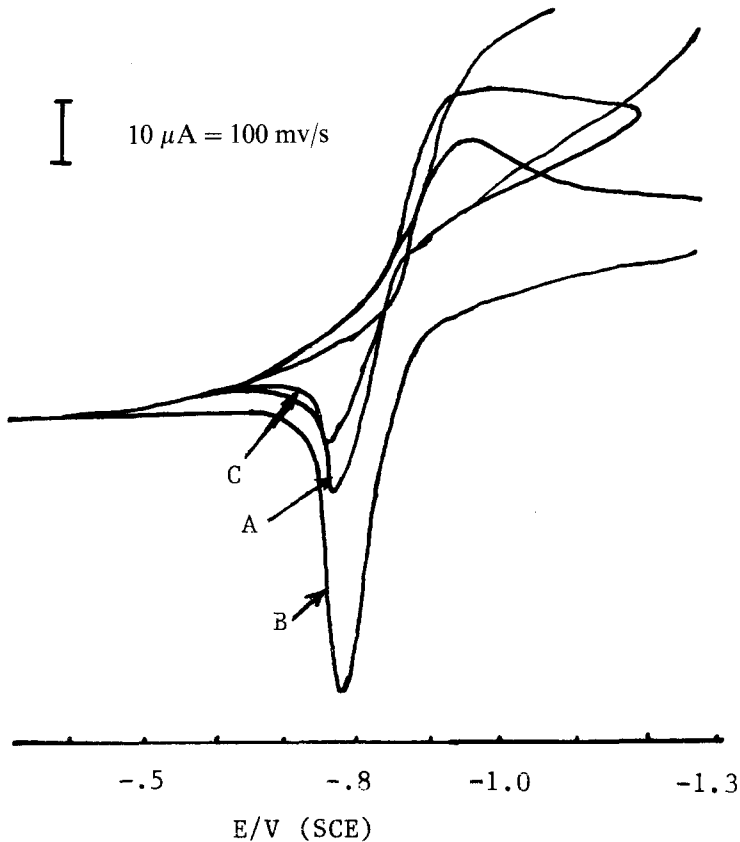


Fig. 4. C-V curves of wax-immersed graphite electrode modified by LB films. (A) 1 layer; (B) 5 layers; (C) 10 layers.

surface of water for 24 h after compression. The transfer ratio of the film is 1.0 ± 0.1 which indicates that the monolayer film is compact and stable. Further transfer studies indicated that reproducible results can be obtained for about a week. When the prepared LB films were used to modify graphite or glass carbon electrodes, the response of the electrode to Tl^+ increased about 4 fold as compared to that of the coated film.

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