Regulated Electrochemistry of Viologen-containing Langmuir–Blodgett Film Prepared by Polyion Complex Technique

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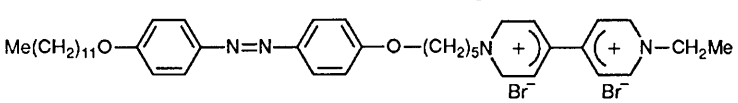
A polyion-complexed monolayer of a water-soluble viologen amphiphile and poly(acrylic acid) was immobilized as a Langmuir–Blodgett (LB) film on an indium–tin oxide (ITO) electrode; electrochemical reduction of the viologen was found in the LB film and the redox potential was affected by pH.

Well organized two-dimensional molecular assemblies, *e.g.* bilayer membranes or Langmuir–Blodgett (LB) films, are suitable candidates for constructing designed molecular assemblies in the field of biomimetic chemistry and molecular engineering. Shimomura and Kunitake succeeded in immobilizing bilayer membranes as LB multilayers by the polyion complex technique.[1] As the result of the electrostatic interaction at the air–water interface, a stable monolayer of the bilayer-forming charged amphiphile was prepared on an aqueous solution of the counter-charged polyelectrolyte. The polyion-complexed monolayers could be transferred onto solid substrates as multilayer films by the normal LB technique. Recently, Kimizuka and Kunitake found that the molecular orientation in the polyion-complexed monolayers was strongly affected by the chemical structure of the polyelectrolytes.[2]

Azobenzene amphiphiles having a viologen group as a hydrophilic head form the bilayer assemblies in water. A large bathochromic shift in the absorption spectrum attributed to the J-aggregate of the azobenzene chromophore[3] was observed in the aqueous bilayer solution. Owing to its high solubility in water, however, amphiphile **1** could not form a stable monolayer on a pure water subphase at 20 °C. A similar result in the surface chemistry of a single-chain derivative, *N*-methyl-*N*′-hexadecylviologen, on a pure water subphase was found by Lee and Bard.[4] They reported that the stable monolayer could be formed on concentrated aqueous sodium perchlorate (above 60 mmol dm^{-3}) and be transferred on an indium–tin oxide (ITO) electrode as an LB film.

Addition of an anionic polyelectrolyte into the water subphase could stabilize the monolayer of **1**. A condensed monolayer with a limiting molecular area of *ca.* 0.6 nm^2 $molecule^{-1}$ was formed on a dilute solution (*ca.* 6×10^{-5} mol dm^{-3}) of potassium poly(vinyl sulphate). Carboxymethylcellulose (degree of substitution; $d = 1.41$, where d means average substitution numbers of carboxymethyl group per one glucose unit) in the subphase caused the monolayer to expand. The shape of the pressure–area isotherms (π-A curves) on the



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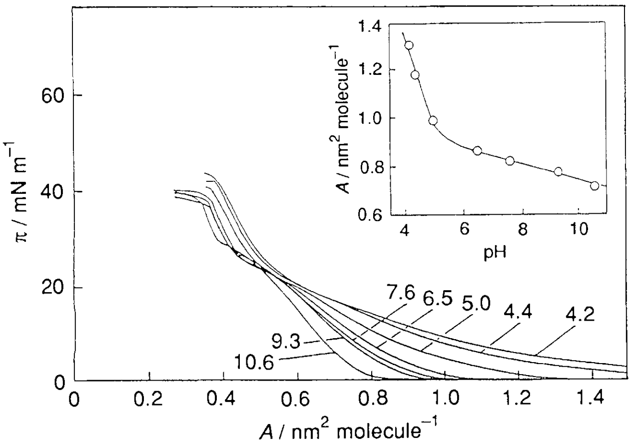

Fig. 1 The pH-dependence of the pressure–area isotherm (π–A) of amphiphile **1** on the aqueous poly(acrylic acid) solution. The molecular area at 5 mN m^{-1} is plotted against the pH value of the subphase; pH value of the subphase was adjusted by hydrochloric acid and sodium hydroxide.

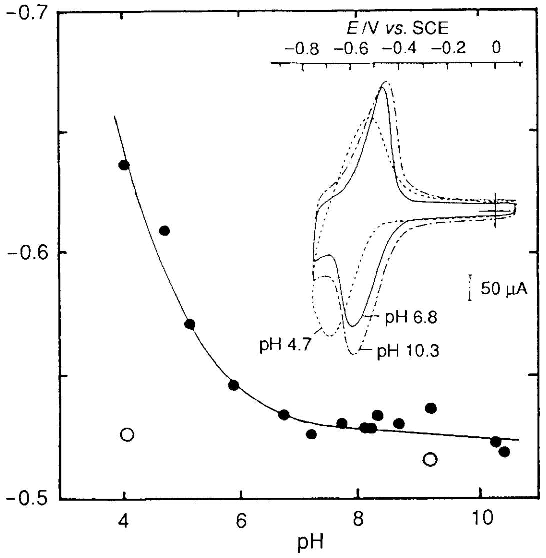

Fig. 2 The pH-dependence of the formal redox potential for the first reduction–oxidation reaction of the polyion complexed LB films deposited at pH 4(●) and pH 10(○). Typical cyclic voltammograms of the LB film deposited at pH 4 in 0.1 mol dm^{-3} potassium chloride are also shown; pH of the electrolyte solution was adjusted by hydrochloric acid and sodium hydroxide. Scan rate: 500 mV s^{-1}.

aqueous carboxymethylcellulose was strongly dependent on the degree of substitution. A condensed monolayer was found on the solution of a higher substituted carboxymethylcellulose (d = 2.81). Molecular orientation in the polyion-complexed monolayer is strongly affected by the charge density of the polyelectrolyte.

As was expected, the π-A curve on poly(acrylic acid) (M 2000, Aldrich Chemical Co., *ca.* 1.4 × 10^{-4} mol dm^{-3}) solution showed a large pH-dependence. On lowering the pH of the subphase, the π-A curve of the monolayer showed greater expansion with pressure (Fig. 1). The pH-dependence of the surface area at 5 mN m^{-1} is also shown in Fig. 1. A drastic expansion of the surface area found below pH 6 suggests that the pH-dependence of the π-A curve may be ascribed to the dissociation equilibrium of poly(acrylic acid); the pK_a value of poly(acrylic acid) is reported to be 5.6.[5]

The monolayer complexed with poly(acrylic acid) was transferred onto an ITO electrode by the vertical dipping method. The electrode was immersed in and pulled up from the water subphase for several times. Y-type deposition was found at pH 4. The monolayer was deposited during both down and up strokes of the electrode, whereas at pH 10, the monolayer was deposited only during the up stroke. Cyclic voltammograms (CV) of the LB films deposited at 25 mN m^{-1} (5 layers at each pH) were measured at several pH values. As shown in Fig. 2, the CV curve of the LB film deposited at pH 4 was strongly affected by the pH value of the electrolyte solution of the CV measurement. On changing the pH value of the CV solution from 4.1 to 10.4, a large positive shift in the cathodic peak potential for the first reduction reaction was found to be from −720 to −590 mV. A drastic change of the formal redox potential is found around pH 6. However, signficant pH-dependence of the redox potential was not found in the LB film deposited at pH 10. A significant pH-dependence on the redox potential of ethylviologen (−720 mV *vs.* SCE, aqueous solution) also was not found in our CV experiment (SCE = saturated calomel electrode).

Positive shifts in the redox potentials of viologen derivatives have been often found in molecular aggregates, *e.g.* the self-assembling bilayer system,[6] LB film[4] and the immobilized bilayer membranes,[7] where the dimer radicals of the reduced viologens were favourably formed. Viologen–viologen interaction in the densely packed monolayer is reflected in the redox potential of the LB film deposited at pH 10, since the potential value is more positive than that of ethylviologen in the aqueous solution measured under similar pH conditions.

The pH-dependence of the redox potential in the LB film deposited at pH 4 is ascribed to the molecular rearrangement in the LB film regulated by the dissociation equilibrium of the poly(acrylic acid). At low pH, the expanding nature of the monolayer is maintained in the deposited film on the electrode; therefore the viologen–viologen interaction is interrupted by the unionized side groups of the polymer. On the other hand, the unionized carboxy groups could enable flexible molecular motion of the polymer main chain to occur. A molecular arrangement similar to the LB film deposited at pH 10 is assumed to be induced when the pH value of the CV solution is increased above *ca.* 6. Owing to the reduced mobility in the densely packed film deposited at pH 10, the molecular interaction is fixed and the redox potential is not so affected by the pH change. Conformational change of the polymer main chain should be more restricted because the polymer is tightly fixed as counter anions of the LB film deposited at pH 10.

In conclusion, we demonstrated for the first time that the polyion complex technique is very effective for preparing stable monolayers and LB films of a water-soluble viologen amphiphile and thereby show that the electrochemistry of the viologen was regulated by the controlled molecular interaction based on the well organized polyion-complexed monolayer. Detailed investigations of the effect of the chemical structure of the polyelectrolytes on the electrochemistry will be described elsewhere.

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References

1 M. Shimomura and T. Kunitake, *Thin Solid Films*, 1985, **132**, 243.
2 N. Kimizuka and T. Kunitake, *J. Am. Chem. Soc.*, 1989, **111**, 3758.
3 M. Shimomura, R. Ando and T. Kunitake, *Ber. Bunsenges. Phys. Chem.*, 1983, **87**, 1134.
4 C. Lee and A. J. Bard, *J. Electroanal. Chem.*, 1988, **239**, 441.
5 T. Ikawa, K. Abe, K. Honda and E. Tsuchida, *J. Polym. Sci. Polym. Chem. Ed.*, 1975, **13**, 1505.
6 C. J. Miller, C. A. Widrig, D. H. Charych and M. Majda, *J. Phys. Chem.*, 1988, **92**, 1928.
7 M. Shimomura, K. Utsugi, J. Horikoshi, K. Okuyama, O. Hatozaki and N. Oyama, *Langmuir*, 1991, **7**, 760.