Redox Potential of N-Hexadecyl-N'-Methyl Viologen$^{(2+/+)}$ Solubilized in Cetyltrimethylammonium Chloride Micelle

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N-alkyl-N'-methyl viologen cations (C_nMV^{2+}) are of recent interest because of their unique chemical and electrochemical properties[1,2]. For example, N-hexadecyl-N'-methyl viologen cations ($C_{16}MV^{2+}$) and N-docosyl-N'-methyl viologen cations ($C_{22}MV^{2+}$) were shown to form Langmuir monolayers at the air/water interface and their Langmuir-Blodgett molecular films produce the double voltammetric peaks for the first redox process, which are very different from the electrochemical behaviors of methyl viologen (MV^{2+}) or other symmetric viologens ($C_nC_nV^{2+}$) in aqueous solutions[3,4]. It is also known that C_nMV^{2+} could be solubilized in the organized molecular assemblies of micelles[5,6] and vesicles[2]. The redox behaviors of $C_nMV^{2+/+}$ are, however, not fully examined in such organized molecular assemblies. Thus Gratzel *et al.* had to assume that the redox potentials of $C_nMV^{2+/+}$ ($n=12$, 14, 16, 18) comicellized in cetyltrimethylammonium chloride (CTAC) micelle are the same as the redox potential of $MV^{2+/+}$ when they successfully empolyed the electron relays to design an efficient photochemical energy conversion system[5]. Since a recent finding concluded that micelles, which have been regarded as a pseudophase, exhibited the properties of a distinct thermodynamic phase with unique critical micelle concentration[7], we thought that the redox properties of $C_nMV^{2+/+}$ comicellized in CTAC micelle would be different from those of $MV^{2+/+}$ or similar viologens dissolved in aqueous phase. In the present work we wish to report some preliminary electrochemical results on $C_{16}MV^{2+/+}$ comicellized in CTAC micelle together with those in Triton X-100 and sodium dodecyl sulfate (SDS) micelles.

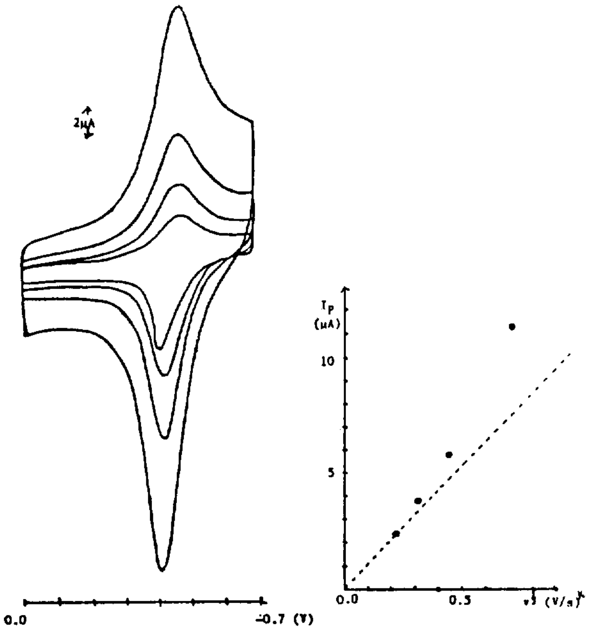

Figure 1. Cyclic voltammograms obtained at glassy carbon electrode (0.071 cm^2) for 0.1 mM $C_{16}MV^{2+}$ in water. Scan rate (mV/s); 50, 100, 200, 500. A; 50 mM NaCl, B; Plot of cathodic peak current versus square root of scan rate.

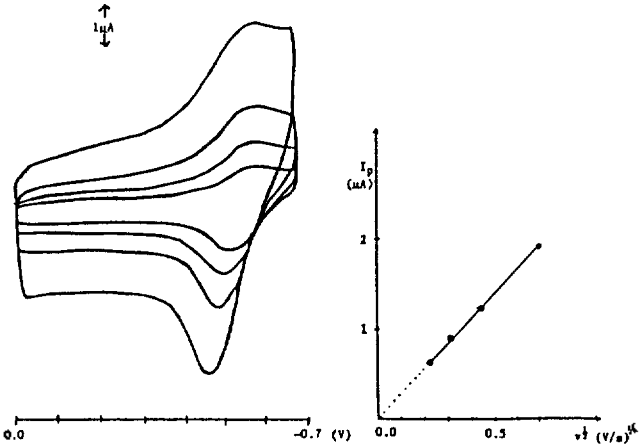

Figure 2. Cyclic voltammograms obtained in the presence of 50 mM CTAC (A) and plot of cathodic peak current versus square root of scan rate (B). Experimental conditions are the same as in Figure 1.

Figure 1A shows the cyclic voltammograms obtained at glassy carbon electrode in an aqueous solution of 0.1 mM $C_{16}MV^{2+}$ and 50 mM NaCl under nitrogen atmosphere. The plot of the cathodic peak current versus square root of scan rate (Figure 1B) shows a positive deviation at larger scan rates, indicating that adsorption of the reactant is involved in the electrode process. The strong adsorption at glassy carbon surfaces was previously illustrated at the low concentration of 10^{-6} M by Bard[3]. The adsorptive nature of the voltammetric signal faded out as CTAC was added to the sample solution because $C_{16}MV^{2+/+}$ comicellized into CTAC micelle[5]. Figure 2A shows the cyclic voltammograms observed in 50 mM CTAC solutions. Figure 2B shows a zero intercept with a linear plot of the peak current versus square root of scan rate, indicating that the electrode process is diffusion-controlled at the scan rates used. The cyclic voltammograms at lower scan rates revealed that the electrode reaction was nearly nernstian, from which the redox potential was determined to be -0.54 V *vs.* SCE. This value is different from either of the redox potentials of $C_{16}MV^{2+/+}$ adsorbed at glassy carbon electrodes (-0.58 V) or of $MV^{2+/+}$ in aqueous solutions (-0.69 V)[3]. The similar measurements were made in Triton X-100 and SDS micellar solutions. In Table 1 the voltammetric data are summarized for $C_{16}MV^{2+/+}$ redox process in different solution conditions. Bard has measured the redox potentials of $MV^{2+/+}$ in CTAC, Triton X-100 and SDS micelles as -0.69, -0.68, and -0.65 V (*vs.* SCE), respectively. The present results object that the redox properties of the asymmetric viologens solubilized in different functional assemblies are the same as those of $MV^{2+/+}$[5], and strongly suggest that the redox potentials of $C_nMV^{2+/+}$ could be controlled by "hydriphobic fine tuning" with the length of alkyl chain and in addition that the redox dynamics

Table 1. Cyclic Voltammetric Data for the First Reduction-Oxidation Process of $C_{16}MV^{2+}$ in Several Aqueous Media[a]

Medium	Reduction peak potentials (V)	Oxidation peak potentials (V)	Redox potentials (V)
(A) 50 mM NaCl	−0.47	−0.42	−0.45
(B) (A)+50 mM CTAC	−0.57	−0.50	−0.54
(C) (A)+5% Triton X-100	−0.51	−0.45	−0.48
(D) (A)+50 mM SDS	−0.72	−0.58	−0.65

[a] All potentials were measured in 0.1 mM $C_{16}MV^{2+}$ against SCE at 25℃. Scan rate; 500 mV/s.

should be carefully scrutnized in organized molecular assemblies to apply for useful chemical reactions such as energy conversion systems[5]. Further electrochemical investigations of $CnMV^{2+}$ systems are in progress in this laboratory.

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Resolution of Racemic α-Amino Acids on a Dynamic Chiral Stationary Phase by Ligand-Exchange Chromatography

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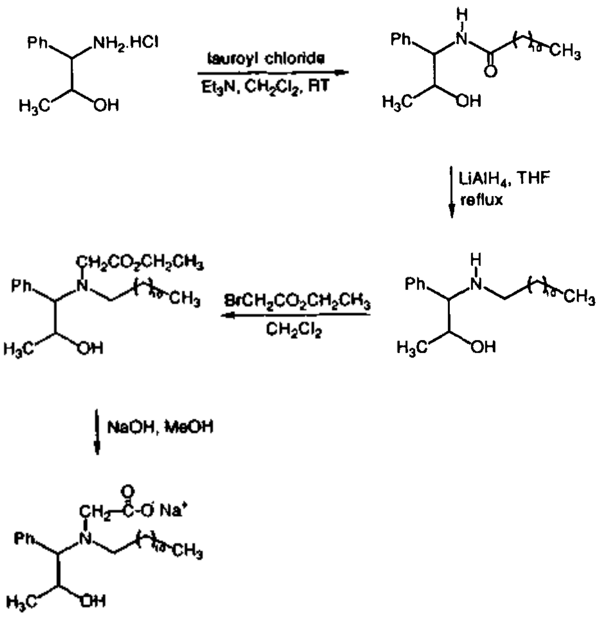
Chiral ligand-exchange chromatography has been extensively studied and used for the resolution of racemic α-amino acids since Davankov's pioneering work in the late 1960s.[1] In chiral ligand-exchange chromatography, chiral selectors are usually copper (II) complexes of optically pure α-amino acids which are used as chiral mobile phase additives or as chiral stationary phases after being bonded to solid column support such as polymer or silica gel.[1] Very few of other optically active materials have been used as chiral selectors in chiral ligand-exchange chromatography.[2]



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Scheme 1

In recent years, we have been interested in the use of optically active norephedrine as a chiral selector for chiral liquid chromatography and, previously, we reported the preparation of π-π complex forming chiral stationary phases, N-(3,5-dinitrobenzoyl)-(1S, 2R)-norephedrine bound to silica gel.[3] From ongoing efforts to use norephedrine derivatives as chiral selectors, we have been able to resolve various unmodified α-amino acids by using the copper(II) complex of a (1S, 2R)-norephedrine derivative tentatively adsorbed onto a commercial octadecyl-silica gel column. We, herein, report preliminary results of this study.

Norephedrine derivative **1**, which is used as a chiral selector in this study, was prepared from (1S, 2R)-norephedrine hydrochloride as shown in Scheme 1.[4] The hydrophobic loading of **1** onto a commercial reverse phase octadecyl-silica gel column (Waters μ $10C_{18}$, 4.6×250 mm) was accomplished by eluting 15 m*l* of a solution of **1** (1.3 g) in methanol/water (1 : 1, v/v) through the reverse phase octadecyl-silica gel column (flow rate: 0.5 m*l*/min) followed by washing with 150 m*l* of methanol/water (1 : 1, v/v, flow rate: 0.3 m*l*/min).[5,6] After use, chiral selector can be easily removed form the column and recovered by washing the column with organic solvent such as methanol.

To resolve racemic α-amino acids on the dynamic chiral stationary phase thus prepared, 10% acetonitrile solution in water containing $CuSO_4$ (2×10^{-4} M) was eluted through the column until the baseline (UV monitor, 254 nm) became stable and then, a methanolic solution of a racemic α-amino acid was injected. The rapid and reversible formation of energetically different diastereomeric ternary complexes by the