ABSTRACT

The anion exchange reaction of 4,4'-dialkyldipyridinium dibromide (viologen) was carried out to obtain room temperature viologen melts. After anion exchange, melting point was lowered considerably, and the obtained viologen was quite soluble in many organic solvents including the molten salt, 1,3-diethylimidazolium bis(trifluoromethylsulfonylimide) (diEtImTFSI). With increasing the alkyl chain length of viologen, the melting point lowered and reached minimum, 57.4°C, for an alkyl chain length was 6. Since excellent compatibility with organic solvents, these viologens showed larger peak current than that of bromide salt. High peak current was observed also in diEtImTFSI until high concentration (viologen/diEtImTFSI =1/5 by mol). In addition, these viologens became very fluid at melting state and the ionic conductivity reached to $10^{-3}$ S/cm in bulk above melting point. The redox response of viologen bulk at melting state indicates the long-range electron transfer reaction.

INTRODUCTION

Viologen is one of the most vigorously studied molecules in the field of electrochemistry because it is known to act as an electron mediator in various systems. In a concentrated system, the potential ability to show electron hopping at the reduced state is also expected (1). In addition, the formation of lyotropic and smectic liquid crystalline phases has recently been reported in polymers containing the viologen structure (2).

In order to realize the electron hopping between the viologen molecules, the viologen should be reduced to the radical cation and be condensed enough to allow intermolecular electron hopping. For this, concentrated viologen system is essential. Additionally, electrochemical reduction of viologen needs to the migration of counter
anion because of the charge compensation. Therefore, a certain high mobility of ion was required even in the concentrated media. This was impossible within ordinary solvents because of solubility limit.

Poly(ethylene oxide) (PEO) is a typical polymer electrolyte. Consequently, the combination of PEO and viologen has already been attempted in an effort to make a concentrated viologen system having high ion mobility. Both Murray et. al. and our group have prepared similar systems previously (1,3,4). Our study pointed out some drawbacks in PEO-viologen system. In terms of bulk properties, PEO-viologen became highly viscous liquid or crystal depending on the molecular weight of the PEO part. This led to low ionic conductivity ($10^{-4}$ S/cm) even at temperatures higher than the melting point. Since the PEO part is allowed to dissolve inorganic impurities during reaction, strict purification of PEO-viologen was difficult. As these problems originate from the properties of the PEO part, a good substitute for PEO is desired.

On the other hand, organic room temperature molten salt system, which is constructed from imidazolium salts has recently been collecting attention and as new electrochemical reaction field as well as new solvent for chemicals. Generally, onium salts have low melting point, and sometimes it was obtained as molten salt. Recently, new imidazolium salts were reported to be room temperature melt without AlCl$_3$ (5). The melting point was affected by the anion species and accordingly it became considerably low especially when the counter anion was bis(trifluoromethyl-sulfonylimide) (TFSI$^-$) (6). Since viologen is a kind of onium salt, similar descent of melting point was greatly expected after the anion exchange. In this paper, we report about the effect of anion species on the melting point of viologen and electrochemical response in organic solvent including organic molten salt media.

**EXPERIMENTAL**

**Preparation**

In our laboratory, viologen was obtained as the bromide salt as shown in Scheme 1. The anion exchange reaction from bromide to TFSI$^-$ was carried out as follows. First, LiTFSI aqueous solution was added to viologen bromide $2C_xVBr$ aqueous or alcoholic solution. The amount of LiTFSI was fixed to keep stoichiometric molar ratio to bromide anion in viologen ($2C_xVBr$:LiTFSI = 1:2 in mol). After mixing the solution, the white powder was phase separated from the aqueous phase. In order to enhance the yield, dichloroethane was added to the solution and extracted. This organic phase was then collected and the solvent was removed by evaporation. The anion exchanged viologen, $2C_xVTFSI$, was obtained as white powder, not pale yellow. The obtained viologen is soluble in many kinds of organic solvents but sparingly soluble in water, and it is not hygroscopic.

The exchange of anion from bromide to TFSI was confirmed by the $^1$H-NMR spectrum as shown in Figure 1. All the peaks except for ones attributed to the protons on bipyridinium ring showed no difference in chemical shift. The peaks for protons on
bipyridinium-ring (a and b in Figure 1) shifted to higher magnetic field side after the formation of TFSI salt. Such shift for protons in the hetero-ring was reported in the imidazolium salt (6). For example, in the case of 1-ethyl-3-methyl-imidazolium salt, the protons of H(2) and H(4) on the imidazolium ring shifted from 9.45 and 7.87 ppm to 9.12 and 7.72 ppm in (in acetone), respectively when the anion was exchanged from bromide to TFSI\(^{+}\). The same tendency was observed in the case of viologen, although the peak shift was much smaller than that in imidazolium salts.

The molten salt, 1,3-diethylimidazolium TFSI (diEtImTFSI) was prepared by the anion exchange reaction from 1,3-diethylimidazolium bromide salt (diEtImBr). This diEtImBr was obtained by the reaction of 1-ethylimidazole and ethylbromide in N,N'-dimethylformamide (DMF) in ice bath for 48 h at least. The obtained solution was evaporated at 120°C and the residual viscous solution was added dropwise to the excess of diethylether. DiEtImBr was obtained as slightly yellowish liquid even in diethylether, it was collected and dried in vacuo at 65°C. Anion exchange reaction was carried out in water by mixing with LiTFSI. To collect the anion-exchanged imidazolium salt, dichloroethane was added, and the organic phase was collected. The solvent was removed by the evaporation, and diEtImTFSI was obtained as colorless liquid.

**Thermal Properties (DSC)**

The melting point of viologens was measured with the differential scanning calorimeter (Seiko Instruments Inc., DSC-6 200). Cooling rate was controlled by the automatically from -150 °C to 120 °C at -10°C/min. Measurement was carried out during the heating process. Scanning rate was fixed +10°C/min.

**Cyclic Voltammetry**

The redox reaction for the obtained viologen was analyzed with a function generator (Nikko-keisoku, NFG-3) and potential galvanostat (Nikko-keisoku, NPGS 2501 10nA). The working electrode used was plastic formed carbon with diameter of 0.5mm. Platinum and silver wire was used as counter and reference electrode, respectively. All the electrodes were polished just before the measurement and sonicated in ion-exchanged water. Since the radical cation, which was produced when the viologen was reduced is very sensitive against oxygen, all the cyclic voltammetry measurements were carried out under nitrogen flow. The viologen concentration was 50 mM in diEtImTFSI, and no supporting electrolyte was added.

First, the cyclic voltammogram was taken in acetonitrile (AN). The viologen concentration was 1mM because of the solubility limit of 2C\(_x\)VBr. As a supporting electrolyte LiBr or LiTFSI was added (0.1M) to 2C\(_x\)VBr or 2C\(_x\)VTFSI AN-solution, respectively. The dissolution of viologen was taken place when diEtImTFSI was used, because diEtImTFSI worked as solvent as well. The mixed solution was dried in vacuo at 65°C at least for 48 hours and the measurement was carried out immediately after the sample solution was taken out from vacuum oven.
Ionic Conductivity Measurements

Conductivity measurement was carried out by the complex impedance method with an impedance phase-gain analyzer (Schulumberger, Solartron 1260). Frequency range was from 10 to 10 MHz. A pair of comb-shaped electrodes made of gold, of which the distance between adjacent comb is 0.3 mm and the gap was approximately 1 µm, respectively, was employed. The cell constant was calibrated with KCl aqueous solution. The sample (viologen) was put on the electrodes and covered with a piece of clean glass. The sandwiched sample was inserted to a rolled heating tape. Scan rate was well controlled to be 3°C/min. Measurement was carried out under air, because the anion-exchanged viologen was very stable against moisture.

RESULTS AND DISCUSSION

Thermal properties

Anion exchange from bromide to TFSI⁻ was revealed to be very effective to lower the melting point (Tm) of viologen as shown in Figure 2. In the case of the number of alkyl chain unit was 6, the melting point was lowered from 142.5°C (dotted line in Figure 2) to 57.4°C (n=6: 2C₆VTFSI). In addition, Tm decreased with increasing the alkyl chain length up to n=6. In the case of n=4 and 8, relatively large peaks were observed at the lower temperature, however, these were confirmed not to be the isotropization temperature by microscopic observation of heated samples. In the case of n=4, it was estimated to be solid-solid transition. The large peak of n=8 is still lowest unknown, however, the reason of this increased Tm should be the increase of van der Waals force attributed to the increase of molecular weight of the viologen. At this point, the melting point was 57.4°C for 2C₆VTFSI.

Redox reactions

The redox response of anion-exchanged viologen was analyzed in organic solvent at first. Distinctive two-step redox reactions were observed in acetonitrile (AN) as shown in Figure 3. Although the obtained viologens (2CₓVTFSI) itself and the solution was colorless on the contrary to the yellowish color of 2CₓVBBr, the formation of dark blue compounds attributed to the radical cation was observed around the working electrodes when the viologen was reduced around at -400 mV vs. Ag wire. The redox potentials of 2CₓVTFSI were much lower than that of 2CₓVBBr as shown in Figure 3. it was common tendency for other viologens with different alkyl chain length. In such diffusion-controlled system, the diffusion of counter anion should be the dominant factor for the redox reaction.

Since 2CₓVTFSI was freely soluble in organic solvent, the redox reaction was analyzed in molten salt, 1,3-diethyl-imidazolium TFSI (diEtIm-TFSI). Although the two-step redox reaction was observed also in diEtImTFSI, however, the symptom of dimerization or absorption was observed when the viologen was reduced to nonionic state, only the first redox cycle was repeatedly measured to analyze the redox response at
steady-state. Because high affinity to the molten salt media, 2CxVTFSI showed larger redox current than 2CxVBr as shown in Fig. 4. In molten salt media, the most part of anion was TFSI\(^-\), therefore, the anion exchange reaction should occur even when the viologen was bromide salt. If anion exchange from Br\(^-\) to TFSI\(^-\) occurred in the bulk, there should be little difference in the redox response of viologen with Br\(^-\) and TFSI\(^-\). However, apparent difference was observed not only in peak current but also in redox potential. It strongly suggested that the counter anion of Br\(^-\) existed near the viologen molecule and no anion exchange reaction occurred in molten salt media because of less affinity (solubility) of 2C\(_4\)VBr in molten salt.

When high solubility of 2CxVTFSI was confirmed, the effect of viologen concentration on redox response was analyzed. With increasing the viologen concentration, redox current became larger until the 2C\(_4\)VTFSI concentration to diEtImTFSI was 1/10. In more concentrated solution (when 2C\(_4\)VTFSI/diEtImTFSI = 1/5), the redox current seemed to be saturated as shown in Fig. 5, although the peak current was still kept large. We tried to make further concentrated system, however, the phase turned to be crystallized when the viologen (2C\(_4\)VTFSI) concentration of 1/2 to diEtImTFSI. It was difficult to make the concentrated phase which shows the redox response at room temperature even by the use of room temperature melts such as diEtImTFSI.

Since these anion-exchanged viologen formed very fluid liquid at melting state, the bulk ionic conductivity was measured to confirm the fluidity for the analysis of redox response in viologen bulk at melting state. Temperature dependence of the ionic conductivity for 2C\(_4\)VTFSI bulk is shown in Figure 6. Ionic conductivity was considerably low at around room temperature, however, it drastically increased with elevating temperature. 2C\(_4\)VTFSI has melting point at 83.2°C as shown in Figure 2.

The change in ionic conductivity was apparent to originate the phase transition. High ionic conductivity about 10\(^{-3}\) S/cm was observed at melting state because of the high fluidity as expected. This value was much higher when the PEO chain was attached to the viologen molecule (4). The exchange of counter anion should provide the phase likeonium-type molten salts, therefore, such high fluidity was induced.

The fluidity of 2C\(_4\)VTFSI at melting state was enough to obtain redox response with our usual size of electrodes system. Finally, the redox response was observed when the 2C\(_4\)VTFSI was kept at 90°C, and the long-range electron transfer was indicated when the viologen was reduced to the radical cation. However, here still remains the fear of precipitation of viologen suggested from the shape of cyclic voltammogram. On the contrary to this, the steady-state current flow was increased with increasing the distance of working and counter electrodes when the redox potential of −500mV was applied. Very large current flow about 100\(\mu\)A was observed even when the distance of electrode was 6mm. It strongly suggested that the long-range electron transfer occurred in the viologen melts. The details about this phenomenon will be discussed hereafter.
SUMMARY

Viologens having low melting point were obtained by the anion exchange from halide (Br⁻) to TFSI⁻ anion. The lowest melting point was 57.4°C for 2C₆VTFSI. These viologens are little soluble in water and freely soluble in most organic solvents. Therefore, the higher redox current was observed both in AN and diEtImTFSI comapring the viologen with bromide salt because of high affinity with the matrix. The anion-exchanged viologen (2CₓVTFSI) became fluid and showed high ionic conductivity above the melting temperature. The electron transfer occurred when it was reduced to the radical cation.

ACKNOWLEDGEMENT

We appreciated to the experimental assistance of Ms. Miyuki Morikawa and Ms. Michiko Hirao. One of the authors (K. I-A.) appreciated the financial support from Research Fellowship of the Japan Society for the Promotion of Science (JSPS) for Young Scientists. The present study was supported by the Grant-in-Aid for Scientific Research from the Ministry of Education, Science, Sports and Culture, Japan (#11555250)

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Scheme 1  Preparation of 2VCxTFSI
Figure 1. $^1$H-NMR spectra for 2C$_4$VBr (gray line) and 2C$_4$VTFSI (black line).

Figure 2. DSC curves for 2C$_n$VTFSI: dotted line is one for 2C$_6$VBr described to show the effect of anion replacement on melting point.
Figure 3. Cyclic Voltammogram of 2C₄VBr (dotted line) and 2C₄VTFSI (solid line) in AN. Scan rate: 100mV/sec. The concentration of viologen: 1mM, and that of supporting electrolytes (LiBr or LiTFSI): 0.1M to AN, respectively.

Figure 5. Effect of 2C₄VTFSI concentration on redox response in diEtImTFSI. Concentration was shown in the figure.

Figure 4. Cyclic Voltammogram of 2C₄VBr (dotted line) and 2C₄VTFSI (solid line) in diEtImTFSI. Scan rate: 100mV/sec. The concentration of viologen: 50mM (Viologen/diEtImTFSI = 1/50)

Figure 6. Temperature dependence of ionic conductivity for 2C₄VTFSI in bulk.