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Photo-Induced Reduction Reaction of Methylene Blue in an Ionic Liquid

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Abstract

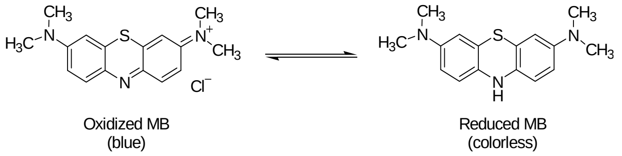
Reduction of methylene blue (MB) occurred by photo irradiation at 280 - 370 nm wavelengths to a solution of MB in an ionic liquid, 1-butyl-3-methylimidazolium chloride (BMIMCl), which was confirmed by color change and UV-Vis measurement of the solution. Furthermore, the reduced MB was oxidized again by standing the solution under the conditions of light shielding at 50˚C. The fluorescence spectra of the solution excited at 350 nm suggested that the photo-induced reduction probably took place via electron-transfer from BMIMCl to MB.

Keywords: Methylene Blue, Ionic Liquid, Reduction, Photo Irradiation

1. Introduction

Redox dyes where color depends on oxidation state have been useful in studies in conjugation with electrochemical applications such as a redox indicator [1]. It can be expected that development of new redox system using redox dyes leads to further application of the dyes. Methylene blue (MB) is one of the representative redox dyes, which possesses good electrochemical properties via its redox reactions [2-6]. Therefore, it has been widely used for basic electrochemical studies and applications, for example, electrocatalysis, solar cells, and biosensors [2,7,8]. Redox reactions of MB reversibly occurred according to **Scheme 1**. An oxidized MB exhibits blue color, whereas a reduced MB (leucomethylene blue) has colorless nature.

On the other hand, ionic liquids, which are low-melting salts and form liquids at the temperature below the boiling point of water, have continued to receive a great deal of attention for a wide variety of possible applications, such as the solvent system for a large number of organic and inorganic reactions, gel components, catalysis, separation, and electrochemical studies [9-17]. The utility of the ionic liquids as media for various photophysical and photochemical studies has also been explored [18-20]. For example, photo-induced electron-transfer reactions in ionic liquids have been reported [21-23]. In this paper, we report photo-induced reduction reaction of MB in an imidazolium-type ionic liquid, 1-butyl-3-methylimidazolium chloride (BMIMCl) in the absence of additional reductant. Furthermore, the reduced MB could be oxidized again by molecular oxygen under the conditions of light shielding. Previously, redox reactions of some substrates by pulse radiolysis in ionic liquids have also been reported [24,25].



Scheme 1. Redox reactions of MB.

2. Results and Discussion

When the photo irradiation at 280 - 370 nm wavelengths to a solution of MB in BMIMCl (0.125 μmol/g) was performed at room temperature for 12 h, decolorization of the solution occurred. We assumed that this decolorization was owing to the reduction of MB, because it has been well-known that the similar decolorization happens by the general reduction reaction of MB in the presence of some reductants such as glucose. To confirm occurrence of the reduction of MB in BMIMCl by the photo irradiation, the UV-Vis measurement of the resulting solution after the irradiation for 12 h was conducted. In **Figure 1**, the UV-Vis spectra of the solution of MB in BMIMCl before and after the photo irradiation are shown.

The absorption at around 660 nm due to MB obviously decreased by the photo irradiation to largely disappear after 12 h. When the decolorized solution was left standing under the conditions of light shielding at 50˚C with stirring, the solution was colorized to exhibit blue again. Indeed, the absorptions due to MB in the UV-Vis spectra gradually increased as shown in **Figure 1**, but the intensity was lower than that in the initial solution even after light shielding for 6 h. The colorization was reasonably explained by the oxidation of MB caused by molecular oxygen. Furthermore, we confirmed that the change of the UV-Vis absorptions in the above experiments was similar as that observed in well-known redox reactions of MB by glucose and molecular oxygen in alkaline aqueous solution, which we had carried out as the comparative experiment according to the literature procedure [26].

Because it had been considered that the aforementioned reduction of MB in BMIMCl was probably owing to electron-transfer from BMIMCl to MB by the photo irradiation, evidence for occurrence of the electron-transfer was attempted to be provided by the fluorescence measurement of the solution of MB in BMIMCl. **Figure 2** shows the fluorescence spectra of the solutions of MB in BMIMCl in various concentrations excited at 350 nm, which is in the wavelength areas of the photo irradiation for the aforementioned reduction of MB. The emissions at around 450 nm due to BMIMCl decreased with increasing the concentrations of MB. The similar decrease of the emissions in the fluorescence spectra excited at other wavelengths such as 280, 300, and 330 nm was also observed with increasing the concentra- tions of MB in BMIMCl. Because MB had not exhibited the absorption at around 450 nm as shown in **Figure 1**, where the emission of BMIMCl was observed, however, it was evaluated that the decrease of the emissions in **Figure 2** was not attributed to energy-transfer from BMIMCl to MB by fluorescence resonance. Therefore, the result of the fluorescence measurement in **Figure 2** can be taken to suggest that the electron-transfer has happened in the solution of MB in BMIMCl by the photo irradiation to cause the reduction of MB [27]. The similar excited state of an imidazolium-type ionic liquid was previously reported for the mechanism of photo-induced polymerization of aniline [28]. The aforementioned redox reactions of MB could be repeated by the cycle of the photo irradiation and light shielding experiments although the intensity of absorption at around 660 nm due to the oxidized state of MB in the UV-Vis spectra decreased according to the repeated numbers.

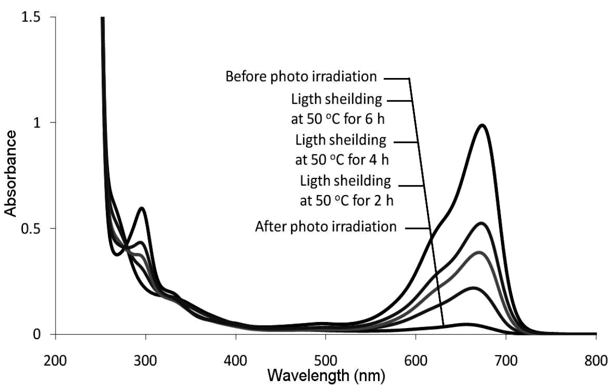


Figure 1. UV-Vis spectra of a solution of MB in BMIMCl before and after photo irradiation (12 h), and spectra of the solution which was left further standing under the conditions of light shielding at 50˚C for 2, 4, and 6 h.

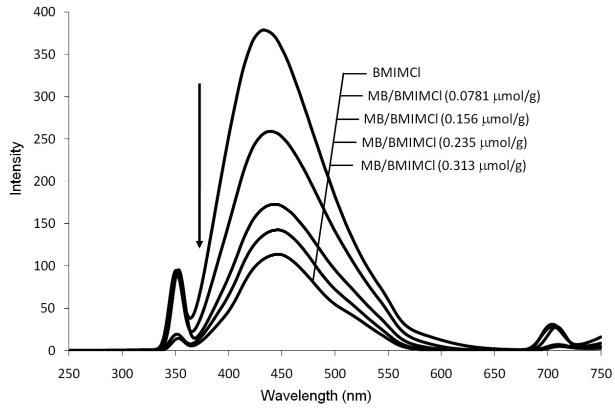


Figure 2. Fluorescence spectra of solutions of MB in BMIMCl in various concentrations excited at 350 nm.

3. Conclusions

In this paper, we reported the photo-induced reduction of MB in BMIMCl. When photo irradiation at 280 - 370 nm wavelengths to the solution of MB in BMIMCl was carried out, decolorization of the solution occurred. The UV-Vis analysis of the solution suggested occurrence of the reduction of MB by the photo irradiation. Furthermore, the oxidation of MB by molecular oxygen took place by standing the solution under the conditions of light shielding at 50˚C. The fluorescence measurement of the solution excited at 350 nm indicated that the photo-induced reduction of MB probably happened via the electron-transfer from BMIMCl to MB. The detailed studies on the mechanism of the present reduction as well as the photo-induced reductions using other redox dyes in the ionic liquid are now in progress in our research group.

4. Experimental

All reagents were commercially available and used as received. Redox reaction of MB by glucose and molecular oxygen in alkaline aqueous solution was conducted according to the literature procedure [26].

As a typical procedure for redox reactions of MB in BMIMCl, a solution of MB in BMIMCl (0.125 μmol/g) was placed in a quartz cuvette (thickness 1 cm). After photo irradiation at 280 - 370 nm wavelengths (USHIO SX-UI 250HQ with 250W Hg lamp and UG11 filter) to the cuvette was performed at room temperature for 12 h for progress of the reduction, it was subjected to the UV-Vis measurement. Then, oxidation of MB was carried out by standing the solution under the conditions of light shielding at 50˚C for 6 h with stirring, which was analyzed by the UV-Vis measurement. The UV-Vis and fluorescence spectra were recorded on Jasco V-650 spectrometer and FP-6300 fluorometer, respectively.

5. References

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