Reversed Micellar Extraction of Methylene Blue by using Di(2-ethylhexyl) Phosphoric Acid

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The development of efficient methods for the removal of organic dyes, which are considered to be toxic to the aquatic biota and therefore destroy the ecosystem, is required. In this study, the extraction of methylene blue (MB) from aqueous solution into DEHPA/isooctane solution was investigated. MB was hardly extracted at all from the aqueous to the organic phase at pH values below 5, and the extraction ratio of MB greatly increased with increasing pH in the range of 5-6 by the electrostatic attraction between dissociated DEHPA and MB. MB was not extracted to the organic phase at pH values above 6, since DEHPA leaked from the organic to the aqueous phase. The addition of 2-ethyl-1-hexanol suppressed the DEHPA leakage, and then MB was successfully extracted to the organic phase at pH values above 6. It was found that MB was solubilized as an MB-DEHPA complex in the organic phase in the pH range of 5-5.5, whereas MB would be entrapped in the waterpool of the reversed micelle at pH values above 5.5. The back extraction ratio of MB from the organic to the aqueous phase was about 100 % at pH values below 5 because of the destruction of the reversed micelles and the disappearance of the electrostatic attraction between DEHPA and MB.

1. Introduction

The wastewater from many industrial plants, such as dye works, textiles, leathers, pulp and paper manufacturing, food processing, contains synthetic organic dyes which are considered to be toxic to the aquatic biota and therefore destroy the ecosystem because of eutrophication and reduced photosynthetic activity. Therefore, the development of efficient methods for the removal of such dyes from wastewater is required. There are many conventional processes available for dye removal [1-2], such as adsorption [3], coagulation/flocculation, chemical oxidation, photodegradation [4-5] and biodegradation [6]. However, in these conventional processes, it is impossible to reuse the dyes removed from the effluents.

Recently, the removal of dyes from effluents has been reported by solvent extraction. Solvent extraction is one of the most popular separation techniques in the chemical industry, and has some advantages, such as low energy consumption, simple and economical equipment, continuous operation, ease of scale-up, and high performance by the addition of an extraction reagent. Dye in aqueous solution is transferred to the organic solution containing an extractant, and the dye recovered from the organic phase by back extraction would be able to be reused. Ionic liquid has been used for the extraction of acidic dyes.
The removal of acidic azo dyes by using a pyrrolidinium-based ionic liquid was carried out and the extraction repeated with fresh ionic liquid three times yielded 95% removal of the dyes [7]. In an imidazolium-based ionic liquid system, acidic dyes were extracted quantitatively [8]. Calix[n]arenes and their derivatives were investigated as extractants for azo dyes [9-10]. It was reported that a calix[4]arene crown oligomer and carboxylic derivatives of calix[8]arene acted as host compounds available for the extraction of azo dyes, because of the fit between the cavity of the cyclic ligand and the guest dye.

Some investigators have reported dye removal by reversed micellar extraction [11-15]. Reversed micellar extraction which is the solvent extraction method that uses reversed micelles (W/O microemulsions) as extractants has been mainly applied to the separation of bioproducts, such as proteins, enzymes, amino acids, and nucleic acids [16-19]. Reversed micelles are associated colloids of amphiphilic surfactants in an organic solvent and nanometer-sized waterpools are formed in their hydrophilic cores. Since water soluble substances are entrapped into the waterpool, it was expected that reversed micellar extraction could be utilized for dye removal. Pandit and Basu used the anionic and cationic surfactants, sodium dodecylbenzenesulfonate and hexadecyltrimethylammonium bromide, to extract the basic dye, methylene blue, and the acidic dye, methyl orange, respectively [11]. In their study, back extraction of the dyes from the reversed micellar solution was carried out by using an aqueous strip solution containing a counterionic surfactant [12]. The dyes recovered into the aqueous solution were strongly bound to the counterionic surfactants and a process of surfactant removal is required for reuse of the dyes. They also carried out the removal of different ionic dyes from aqueous solution in the presence of different surfactants in different solvents, and then explained the dye extraction mechanism by a theoretical model based on the ion-exchange reaction between dyes and surfactants [13]. Noritomi et al. attempted the extraction of methylene blue and methyl orange with reversed micelles formed by the nonionic surfactant, dodecyl glucoside, which is biodegradable and biocompatible [14]. It was found that the extraction ratio of the dyes was strongly dependent on pH and temperature, but the back extraction of the dyes from the reversed micellar solution was not studied. Kinugasa et al. investigated the extraction of methylene blue by using sodium bis(2-ethylhexyl) sulfosuccinate (AOT) reversed micellar solution [15]. Methylene blue was shown to be extracted from an aqueous dye solution of low salt concentration and to be recovered to a fresh aqueous solution of high salt concentration. However, the use of a strip solution with a high salt concentration was required.

Here, we investigated the extraction behavior of methylene blue (MB) by using di(2-ethylhexyl) phosphoric acid (DEHPA). DEHPA is one of the most popular acidic extractants for heavy metal cations, such as rare earth metals [20-21]. It is known that DEHPA can form reversed micelles in apolar solvents and there has been much research related to the size of the reversed micelles and the microstructure of the solubilized water [22-25]. However, only a few extraction studies using DEHPA reversed micelles have been reported. Hu and Gulari used the reversed micellar solution of the sodium salt of DEHPA (NaDEHP) for the extraction of proteins and antibiotics [26-27]. Gao et al. reported the extraction of thorium(IV) by a NaDEHP reversed micellar solution [28]. In this study, we investigated the effect of operation conditions, such as surfactant and salt concentrations, on the extraction and back extraction of MB by using a DEHPA/isooctane solution.
2. Experimental

Methylene blue (MB) as the dye was purchased from Kanto Chemical. Di(2-ethylhexyl) phosphoric acid (DEHPA) as the surfactant supplied by Daihachi Chemical Ind. Co. was purified by washing three times alternatively with 6 kmol/m$^3$ hydrochloric acid and distilled water. Aqueous solutions were prepared by adding dye into solutions in which pH and KCl concentration, $C_E$, were adjusted. Organic solutions were prepared by dissolving DEHPA in 2,2,4-trimethylpentane (isooctane) of reagent-grade from Wako Pure Chemical.

Equal volumes of aqueous and organic solutions were shaken in a flask immersed in a water bath at a constant temperature of 298 K. In some experiments, the volume ratio of the organic to aqueous solution was changed. After reaching extraction equilibrium, the solution was centrifuged to separate the two phases. The concentration of MB in the aqueous phase was determined by UV/vis spectrophotometry (Hitachi, U-0080D) at 664 nm. The extraction ratio, $E$, was defined and calculated as follows.

$$E = \frac{C_{\text{org},1}V_{\text{org},1}}{C_{\text{aq},0}V_{\text{aq},0}} = \frac{(C_{\text{aq},0}V_{\text{aq},0} - C_{\text{aq},1}V_{\text{aq},1})}{C_{\text{aq},0}V_{\text{aq},0}} (1)$$

where $C$ is the MB concentration, $V$ the volume; subscript aq denotes the aqueous phase, org the organic phase, 0 initial, 1 after the forward extraction, respectively.

The MB extracted in the organic phase was stripped to a fresh aqueous solution by adjusting pH and KCl concentration, and the mixture was also separated by centrifugation. The MB concentration in the aqueous phase was determined by UV/vis spectrophotometry. The back extraction ratio, $E_B$, was defined and calculated as follows.

$$E_B = \frac{C_{\text{aq},2}V_{\text{aq},2}/C_{\text{org},1}V_{\text{org},1} = C_{\text{aq},2}V_{\text{aq},2} / (C_{\text{aq},0}V_{\text{aq},0} - C_{\text{aq},1}V_{\text{aq},1})} (2)$$

where subscript 2 refers to after the back extraction.

The DEHPA concentration in the aqueous phase was determined from the phosphorus concentration measured by ICP-AES (Seiko, SPS7800), and a leakage ratio of DEHPA from the organic to the aqueous phase, $L$, was obtained. The water content in the organic phase was determined by Karl-Fischer titration (Hiranuma, AQV-7). $W_O$ is the molar ratio of water to surfactant in the organic phase and is defined as follows.

$$W_O = \frac{C_W}{C_S}$$

where $C_W$ and $C_S$ are the water and the surfactant concentrations in the organic phase, respectively.

3. Results and Discussion

3.1 Extraction of Methylene Blue

Figure 1 shows the effect of the aqueous pH on the extraction ratio of MB, $E$, from the aqueous solution to the DEHPA/isooctane solution. MB was hardly extracted at all in the range of pH values below 5, and the extraction ratio of MB greatly increased with increasing pH between pH 5 and 6. The MB extraction was enhanced as the DEHPA concentration increased.

![Figure 1. Effect of pH on extraction ratio of methylene blue into DEHPA/isooctane solution. Closed keys show third phase formation.](image-url)
In some cases (closed keys), a third middle phase containing a large amount of water was formed between the aqueous and organic phases. Since the $pK_a$ value of DEHPA is 5.7, the number of dissociated DEHPA molecules increased with pH from 5-6 and then MB was extracted to the organic phase by electrostatic attraction between the negatively charged DEHPA and positive MB.

The reason why there are no data for pH values above 6 is because the absorption peak of MB after extraction was higher than that before extraction. In Figure 2, the absorption spectrum of MB in the raffinate after extraction at pH 4.4 (spectrum (b)) corresponded to that of MB in aqueous solution before extraction (spectrum (a)). However, the MB absorption peak near 664 nm in the raffinate at pH 6.4 (spectrum (c)) was higher than that before extraction and the shoulder peak near 610 nm of spectrum (c) disappeared. The spectrum (c) was similar to the absorption spectrum of MB in the DEHPA aqueous solution (spectrum (d)). It is suggested that the MB interaction with DEHPA resulted in spectra (c) and (d). Therefore, the concentration of DEHPA leaked from the organic to the aqueous phase was measured and the leakage ratio of DEHPA is shown in Figure 3. Over 80% of DEHPA leaked to the aqueous phase at pH values above 6. This suggests that dissociated DEHPA is easily distributed to the aqueous phase. Therefore, little dissociated DEHPA would exist in the organic phase and so MB was not extracted. Since the absorption peak of MB near 665 nm was enhanced by bonding of the dissociated DEHPA to MB in the aqueous phase, the extraction ratio was obtained as a negative value at pH values above 6. The extraction ratio corrected by the MB peak height change owing to the DEHPA leakage was almost zero.

### 3.2 Addition of 2-Ethyl-1-hexanol to DEHPA/Isooctane

Hu and Gulari reported that tributyl phosphate (TBP) was added to the organic solution to prevent third phase formation in the protein extraction system from aqueous solution to NaDEHP/isooctane [26]. However, the reason why third phase formation was suppressed by the addition of TBP was not explained. We considered that the leakage of DEHPA from the organic phase would be avoided by an enhancement of the polarity of the organic phase, and therefore the addition of 2-ethyl-1-hexanol as a modifier in the DEHPA/isooctane solution was examined. As shown in Figure 3, the leakage ratio of DEHPA from the organic phase, $L$, was significantly reduced by the addition of 2-ethyl-1-hexanol at pH values above 6 (the 2-ethyl-1-hexanol concentration, $C_{A}$, is 0.05 kmol/m$^3$). Figure 4 shows the effect of the 2-ethyl-1-hexanol concentration on the leakage ratio of DEHPA. The $L$ value suddenly decreased at 0.03 kmol/m$^3$ of 2-ethyl-1-hexanol. The following experiments were performed at a concentration of 0.05 kmol/m$^3$ of 2-ethyl-1-hexanol. In Figure 5, the effect of pH on the extraction ratio of MB to the DEHPA/2-ethyl-1-hexanol/isooctane solution is shown. The extraction ratio of MB at pH values above 6.8 was almost 100% and there

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**Figure 2.** Absorption spectra of MB (a) in aqueous solution, (b) in raffinate at pH = 4.4, (c) in raffinate at pH = 6.4, and (d) in DEHPA aqueous solution ($C_{S,aq} = 0.01$ kmol/m$^3$).
was no third phase formation.

The relationship between the aqueous pH and the water content, \( W_O \), solubilized in the DEHPA/isooctane solution after contact with the aqueous phase is shown in Figure 6. The water content in DEHPA/isooctane without 2-ethyl-1-hexanol was very low. In contrast, the \( W_O \) value in the organic solution containing 2-ethyl-1-hexanol increased with pH beyond 5.5. This suggests that reversed micelles were formed by the dissociated DEHPA. The absorption spectra of MB extracted in the organic phase containing 2-ethyl-1-hexanol are shown in Figure 7. There are two peaks near 610 and 650 nm in the MB spectrum in the organic phase at a \( W_O \) value of 0.6 (spectrum (a)). The spectra of MB extracted from the aqueous
solution at pH 5.8-6 to the organic solution in the absence of 2-ethyl-1-hexanol ($W_O = \text{ca. 0.2}$, spectrum not shown) were similar to spectrum (a). At such a low $W_O$ value, probably reversed micelles were not formed in the organic phase. On the other hand, the spectra of MB in the organic phase at $W_O = 4.7$ (spectrum (b)) and 30.4 (spectrum (c)) were similar to that in the aqueous solution (spectrum (a) in Figure 2). It is considered that MB would be solubilized as a MB-DEHPA complex in the organic solution in the absence of reversed micelles at lower $W_O$ values, whereas MB would be entrapped in waterpool of the reversed micelles at higher $W_O$ values. The absorption spectra of MB extracted in AOT reversed micelles were influenced by the water content in the organic phase [15]. The wavelength of maximum absorbance near 664 nm of MB in the AOT reversed micellar solution was shifted to a longer wavelength as the $W_O$ value increased. The absorption spectra of MB in the DEHPA/2-ethyl-1-hexanol/isooctane reversed micellar solution showed a similar shift (see Figure 7). This indicated that the micropolarity of the waterpool in the DEHPA reverse micelles was reduced as the $W_O$ value decreased. In addition, 2-ethyl-1-hexanol which is an amphiphilic molecule may take part in the formation of the reversed micelle together with DEHPA.

Table 1 shows the extraction ratio for various feed concentrations of MB, $C_{aq,0}$, and various volume ratios of the organic to the aqueous feed phase, $V_{org,0}/V_{aq,0}$. When $V_{org,0}/V_{aq,0}$ was unity and $C_{aq,0}$ was in the range of $10^{-5}$ to $10^{-3}$ kmol/m$^3$, the extraction ratio of MB was almost 100%. The extraction ratio decreased with an decrease in the volume ratio. However, MB was concentrated to 6-8 times as high as the feed concentration when $V_{org,0}/V_{aq,0}$ was 0.1.

3.3 Back Extraction of Methylene Blue

Figure 8 shows the effect of pH in the aqueous strip solution on the back extraction ratio of MB, $E_B$, from the organic solution. The $E_B$ values both with and without 2-ethyl-1-hexanol were about 100% at pH values below 5 and decreased with increasing pH above 5. Since the $pK_a$ value of DEHPA is 5.7, the number of dissociated DEHPA molecules decreased with decreasing pH, and thus MB would be released to the aqueous phase by the destruction of the DEHPA reversed micelles and by the disappearance of the
electrostatic attraction between DEHPA and MB. Consequently, 100% back extraction was achieved at these lower pH conditions.

Table 2 shows the back extraction ratio for various feed concentrations of MB, $C_{aq,0}$, and various volume ratios of the aqueous strip to the organic phase, $V_{aq,1}/V_{org,1}$. The back extraction ratio was about 100% independent of the feed concentration and the volume ratio in the pH range of 3.5-5.

Table 1. Methylene blue concentration in the organic phase after extraction, $C_{org,1}$, and extraction ratio, $E$, for various feed concentrations, $C_{aq,0}$, and various volume ratios of organic to aqueous phase, $V_{org,0}/V_{aq,0}$. Organic solution : $C_S = 0.05 \text{ kmol/m}^3$, $C_A = 0.05 \text{ kmol/m}^3$. Feed solution : $C_E = 0.2 \text{ kmol/m}^3$, pH = 6.5-8.0. $C_{org,1}$ was determined by mass balance.

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<th>$C_{aq,0}$ [mol/m$^3$]</th>
<th>$V_{org,0}/V_{aq,0}$ [-]</th>
<th>$C_{org,1}$ [mol/m$^3$]</th>
<th>$E$ [-]</th>
<th>error [%]</th>
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Table 2. Methylene blue concentration in the aqueous phase after back extraction, $C_{aq,2}$, and back extraction ratio, $E_B$, for various feed concentrations, $C_{aq,0}$, and various volume ratios of aqueous to organic phase, $V_{aq,1}/V_{org,1}$. Organic solution : $C_S = 0.05 \text{ kmol/m}^3$, $C_A = 0.05 \text{ kmol/m}^3$. Feed solution : $C_E = 0.2 \text{ kmol/m}^3$, pH = 7-8. Strip solution : $C_E = 0.2 \text{ kmol/m}^3$, pH = 3.5-5.0.

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<th>$C_{aq,0}$ [mol/m$^3$]</th>
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<th>$C_{aq,2}$ [mol/m$^3$]</th>
<th>$E_B$ [-]</th>
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4. Conclusion

We studied the extraction of MB by using a DEHPA/isooctane solution and obtained the following results. The dissociated DEHPA at higher pH leaked from the organic to the aqueous phase and then no reversed micelle formation occurred. It was confirmed that, by addition of 2-ethyl-1-hexanol to the organic phase, the leakage of DEHPA was suppressed and reversed micelles were formed. Therefore, the extraction of MB was performed by using a DEHPA/isooctane solution containing 2-ethyl-1-hexanol. MB was hardly
extracted at all at pH values below 5, whereas the extraction ratio of MB greatly increased with an increase in pH between 5 and 6 and reached almost 100% at pH values above 6.8. It was found that MB was solubilized as a MB-DEHPA complex in the organic solution in the pH range of 5-5.5, whereas MB was entrapped in waterpool of a reversed micelle at pH values above 5.5. The back extraction ratio of MB from the organic phase to the aqueous strip solution was about 100% at pH values below 5. DEHPA became an undissociated species as pH decreased and thus MB was released to the aqueous phase by the destruction of the reversed micelles and the disappearance of the electrostatic attraction between DEHPA and MB.

References