Removal of Ionic Dyes from Water by Solvent Extraction Using Reverse Micelles

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Several methods (e.g., UV/H₂O₂ oxidation, adsorption, flocculation—precipitation) are normally employed to remove dye from water. A new technique based on liquid/liquid extraction using reverse micelles is proposed whereby recovery of solvent and reuse of dye is possible. Experiments were conducted by mixing a known quantity of dye in aqueous phase and solvent-containing surfactants in a simple mixer. The separation of solvent phase, containing encapsulated dye in reverse micelles, from aqueous phase due to gravity results in separation of dye from water. The removal of different ionic dyes (e.g., eosin yellow, methylene blue, malachite green, methyl orange, orange G) from aqueous phase in the presence of different cationic and anionic surfactants (e.g., sodium dodecylbenzene sulfonate, sodium bis(2-ethylhexyl) sulfosuccinate, hexadecyltrimethylammonium bromide, and cetyl pyridinium chloride) in different solvents (e.g., amyl alcohol, benzyl alcohol, methyl benzoate, and isoctane) were studied by conducting experiments. The percentage removal of dye from aqueous phase increases with the decrease in dye concentration or with the increase in surfactants concentration. Furthermore, the percentage COD removal of dye is increased with the increase in surfactant concentration. The nature of solvent has minimal effect on percentage removal of dye. The ratio of solvent to aqueous phase volume required for the removal of dye decreases with the increase in surfactant concentration. It is possible to back-extract dye into aqueous phase and recover solvent by using counterionic surfactants. The separation of aqueous phase from the aqueous-phase solvent dispersion is faster for amyl alcohol as compared to benzyl alcohol and methyl benzoate. A theoretical model based on ion-exchange reaction between surfactants and dye is used to analyze the experimental data.

Introduction

The effluent water from carpet manufacturing, dyeing, textile, pulp, and paper industries contains various types of dyes which should be removed before discharging the effluent to the environment to avoid health hazards and destruction of the ecosystem. The investigation on the removal of dyes from effluent wastewater of various industries has been going on for several years. There are three major technologies available to remove dyes from water (i.e., oxidation, adsorption, and flocculation—precipitation). Only recently membrane separation technology has been used for the separation of dyes from water. Among the oxidation methods, UV/ozone or UV/H₂O₂ is one of the best technologies for the total removal of dye from wastewater (1, 2). These methods are only effective for low concentrations of organic matter present in water. In other words, significant dilution of the water containing dye is necessary as a facility requirement for the effective use of the oxidation method. The separation of dyes based on adsorption on peat, wood (3), silica (4), bagasse pith (5), activated carbon and slag (6), and bagasse fly ash (7) have been proposed, and the adsorption kinetics have been studied in detail. These adsorption methods are capable of removing the dyes from concentrated wastewater. However, regeneration of most of the adsorbents is difficult except for activated carbon. The adsorption treatment using activated carbon as adsorbent is quite expensive (2, 3). On the other hand, in the flocculation—precipitation process, the dye forms a complex (8) with the flocculant; thus, the reuse of dye is not possible. Thus, it is desirable to use a new technique for the removal of dyes from water that is simple, cost-effective, and permits reuse of the dyes.

A novel method using colloidal gas apheres (CGA) is proposed by Roy et al. (9) for the separation of organic dyes from water. CGA is a gas bubble encapsulated in a thin, aqueous, soapy shell. CGAs are used in a flotation column to remove dyes from water. The dyes are encapsulated in the soapy shell of the CGAs due to Coulombic attraction between the dye and the surfactant molecules. Basu and Malpani (10) studied the effect of process parameters on the percent removal of dyes from water using CGA. The CGA method is found to be inefficient as compared to the present method described here (i.e., solvent extraction using reverse micelles). The successful use of CGAs for the removal of dyes by encapsulating in the soapy shell led to the idea of the use of reverse micelles for the removal of dyes in a similar manner. The reverse micelles are nanometer-sized aggregates of surfactant molecules surrounding microscopic water core in nonpolar solvents. These inverted aggregates are drawn together by hydrogen bonding in the presence of minimal amounts of water, and they are thermodynamically stable. The reverse micelles have been successfully used to extract proteins (11, 12) and enzymes (13, 14) by liquid—liquid extraction. Recently, Pandit and Basu (15) demonstrated the use of reverse micelles in the removal of dyes from water. Prior to this, no work has been reported on the application of reverse micelles in removing dye from water in the context of wastewater treatment. In this approach, the dye is solubilized in the aqueous core of the reverse micelles, which are present in the solvent phase. The organic phase is subsequently separated from the aqueous phase by gravity, leading to the significant removal of the dye. The purpose of the present study is to investigate in detail the application of solvent extraction using reverse micelles in removing organic dyes from water. In particular, the issues related to solvent phase volume, phase-separation time, percentage COD removal, and data analyses by ion-exchange reaction model are presented. The use of reverse micelles allows the recovery of solvent and dye through back-extraction using counterionic surfactants. Although back-extraction of dye and recovery of the solvent were successfully accomplished (16), the results are not presented here.

The laboratory tests were conducted for the removal of the cationic dyes methylene blue and malachite green and the anionic dyes methyl orange, orange G, and eosin yellow from water using various surfactants and solvents. The effects of the different process parameters such as nature of dye, surfactant, solvent, and their concentrations on the percent-
age removal of dyes from water are studied in detail. A mathematical model based on ion-exchange reaction between the dye and the surfactant molecules is tested to analyze the removal of dyes from water by solvent using reverse micelles.

**Experimental Section**

**Materials.** The surfactants used to prepare reverse micelles were sodium dodecylbenzene sulfonate (SDBS, Sigma), sodium bis(2-ethylhexyl) sulfosuccinate (AOT, E. Merck), hexadecyltrimethylammonium bromide (HTAB, Eastman Kodak), and cetyl pyridinium chloride (CPC, E. Merck). The physical properties of the surfactants are given in Table 1.

The various dyes used to study the removal process were methyl orange, orange G, eosin yellow, malachite green, and methylene blue. The chemical structural formulas of all the dyes are shown in Chart 1, and the physical properties of the dyes are given in Table 2.

**Methods.** Dye Removal. The removal of organic dyes by liquid–liquid extraction using reverse micelles was conducted in two steps. In the first step, a given volume of the aqueous solution with known dye concentration was added to a known volume of the solvent containing a known quantity of the cationic or anionic surfactants. The range of surfactant concentrations used is around the critical micelle concentration (cmc) level for all the surfactants. The aqueous phase and the solvent phase were mixed thoroughly using a stirrer at a fixed rpm or using a shaker for 5 min. It was observed that equilibrium was reached within the stirring time.

In the second step, the two-phase dispersion was transferred to a graduated cylinder to separate the solvent and aqueous phases by gravity. A three-bladed axial type impeller was used. A graduated cylinder was connected to a beaker for the separation of solvent and aqueous phases by gravity. An UV spectrophotometer (Shimadzu, UV 1201) was used to measure the removal of dye from the aqueous phase. A Karl Fischer titrator (Mettlet DL 18) was used for the measurement of water uptake by the solvent phase. The graduated cylinder was used to quantify the phase separation. A stereo-zoom microscope (Leica) was used to measure the dispersed droplet diameter.

**Experimental Setup.** The schematic view of experimental setup is shown in Figure 1. A simple stirrer connected to

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### TABLE 1. Physical Properties of Surfactants

<table>
<thead>
<tr>
<th>no.</th>
<th>name</th>
<th>formula</th>
<th>MW</th>
<th>type</th>
<th>cmc (ppm)</th>
</tr>
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<tbody>
<tr>
<td>1</td>
<td>hexadecyltrimethylammonium bromide</td>
<td>CH₃(CH₂)₁₅-N⁺(CH₃)₃Br⁻</td>
<td>364.6</td>
<td>cationic</td>
<td>350</td>
</tr>
<tr>
<td>2</td>
<td>cetyl pyridinium chloride</td>
<td>C₁₆H₃N⁺-C(CH₂)₁₅-CH₂Cl⁻·H₂O</td>
<td>358</td>
<td>cationic</td>
<td>525</td>
</tr>
<tr>
<td>3</td>
<td>sodium dodecylbenzene sulfonate</td>
<td>CH₃(CH₂)₁₅-C₆H₄SO₃²⁻·Na⁺腐败</td>
<td>348.5</td>
<td>anionic</td>
<td>500</td>
</tr>
<tr>
<td>4</td>
<td>sodium 2-diethylhexyl sulfosuccinate</td>
<td>(CH₃CH₂CH₂CH₂CH₂-C₆H₅CH₂COO)₂CH₃CH₂-SO₃²-Na⁺</td>
<td>444</td>
<td>anionic</td>
<td>1110</td>
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</tbody>
</table>

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### TABLE 2. Physical Properties of Dyes

<table>
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<th>name</th>
<th>formula</th>
<th>MW</th>
<th>type</th>
<th>λ&lt;sub&gt;max&lt;/sub&gt; (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
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<td>C₁₄H₁₄O₃SNa</td>
<td>327</td>
<td>anionic</td>
<td>510</td>
</tr>
<tr>
<td>2</td>
<td>orange G</td>
<td>C₁₆H₁₀N₂O₇S₂Na₂</td>
<td>452</td>
<td>anionic</td>
<td>472</td>
</tr>
<tr>
<td>3</td>
<td>eosin yellow</td>
<td>C₂₀H₁₄Cl₅Na₂</td>
<td>692</td>
<td>anionic</td>
<td>517</td>
</tr>
<tr>
<td>4</td>
<td>methylene blue</td>
<td>C₁₆H₁₈Cl₃NaCl</td>
<td>373.5</td>
<td>cationic</td>
<td>660</td>
</tr>
<tr>
<td>5</td>
<td>malachite green</td>
<td>C₂₃H₂₅Cl₂</td>
<td>365</td>
<td>cationic</td>
<td>619</td>
</tr>
</tbody>
</table>
in an UV spectrophotometer (Shimadzu, UV 1201) to determine the amount of dye separated. The dye present in the solvent was also analyzed to check the mass balance. The dye removal experiments followed by analyses of the samples were conducted several times to check the repeatability and the accuracy of measurements. The variation of experimental data was within the range of 2–3%. Consequently, the experimental data are presented with error bars. Water uptake by the reverse micelles in the organic phase was measured by using a Karl Fisher titrator (Mettler DL18). An open reflux method was used for the analyses of chemical oxygen demand (COD) of water.

The cationic surfactants, HTAB and CPC, were used for the extraction of the negatively charged methyl orange, eosin yellow, and orange G. The anionic surfactants, SDBS and AOT, were used for the separation of the positively charged methylene blue and malachite green. Experiments were performed to study the effect of different parameters such as surfactant concentration, dye concentration, and solvent type on the extent of the dye removal.

Phase Separation. The experiments on phase separation were performed using different solvents (e.g., amyl alcohol, benzyl alcohol, and methyl benzoate) for the removal of eosin yellow by using HTAB at two different concentrations. After mixing solvent with aqueous phase dispersion for a constant period of time at fixed rpm, it was transferred to a graduated cylinder. The interface formed at the bottom moved up in the case of amyl alcohol since it is lighter than water. In other cases, the heavier solvent phase (e.g., benzyl alcohol and methyl benzoate) moved downward. The volume of the clear water phase separated was noted as a function of time. The dispersed droplet diameter was measured using a stereo-zoom microscope fitted with a CCD camera.

Model

Various models (17–19) have been proposed for the extraction of proteins, amino acids, and metal ions by using reverse micelles. In particular, model for dye removal by reverse micellar extraction is not reported in the literature. Normally, protein molecules are complex in nature as compared to dye molecules; thus, straight-away application of an existing model for protein or amino acid extraction may not work for the prediction of dye removal by reverse micelles. The experimental data of the present study and the investigation conducted by Pandit and Basu (15) reveal that the removal of dye from water by reverse micelles is mainly controlled by the electrostatic interactions between the dyes and the surfactant headgroups. Thus, this process may be thought of as a phenomenon based purely on ion-exchange reactions between the dye and the surfactant in the reverse micelles.

Ion-Exchange Reaction Model. In the ion-exchange reaction model, it is assumed that the surfactants in the reverse micelles are chemically active because of the strong electrostatic effect of the surfactant headgroups. The dye molecules react with the surfactant headgroups to form complexes. In the present model, one molecule of the dye reacts with one molecule of the oppositely charged surfactant to form a dye–surfactant complex, which further dissociates to release the counterion in the water pool of the reverse micelle. The solubilization process depends on the identification of these specific ion-exchange reactions. Since dye is slightly soluble in some of the solvents, the solubility of dye in the absence of surfactants is accounted for by introducing the partition coefficient term. There are essentially four distinct regions in a reverse micellar system where a dye molecule may be present. They are as follows: (i) the bulk of the organic phase, (ii) the interfacial region between the surfactant hydrophilic headgroup and the water pool of the reverse micelles, (iii) the water pool inside the reverse micelles, and (iv) the bulk of the aqueous phase. The different regions are schematically shown through a diagram available in the Supporting Information. It is assumed that a negligible amount of dye is present at the solvent–aqueous phase interface after the separation of solvent and aqueous phases. Furthermore, it is assumed that all the surfactant molecules in the organic phase take part in reverse micelles formation at equilibrium and that the concentration of the surfactant in the aqueous phase is negligible. These assumptions are reasonable since COD of water does not increase with the increase in surfactant concentration in the system. In the water pool of the organic phase, the dye concentration is defined as the moles of dye per unit volume of water pool. On the other hand, the concentrations of the surfactant and the surfactant–dye complex in reverse micelles are defined as moles per unit volume of water-free solvent phase. The dye concentration in the reverse micellar water pools is the same as the bulk aqueous phase. The anionic methyl orange, orange G, and eosin yellow form complexes with the cationic surfactants, HTAB and CPC. Similarly, the cationic methylene blue and malachite green form complexes with the anionic surfactants, SDBS and AOT. The ion-exchange reaction and the equilibrium constants involved are given in the Supporting Information.

Mass Balances. The mass balances for the dye and the counterion are given by

\[ K_d^{s/w} C_{D_s}^{s/w} + C_D + rC_{SDCI} + rC_{SD} = C_D^0 \] (1)

\[ C_{CI} + rC_{CI,b} + rC_{SCCI} = C_{CI}^0 + rC_{S}^0 \] (2)

where \( K_d^{s/w} \) is the concentration partition coefficient of dye between solvent and aqueous phase in the absence of surfactants, \( C_{D_s}^{s/w} \) is the concentration of dye in the bulk aqueous phase after dissolving with solvent phase in the absence of surfactants, \( C_D \) is the molal concentration of the dissociated dye–surfactant complex at the reverse micellar interface, \( C_{SDCI} \) is the molal concentration of the dye–surfactant–counterion complex at the reverse micellar interface, \( rC_{CI,b} \) is the molal concentration of counterion bound to the surfactant headgroup at the reverse micellar interface, \( C_D^0 \) is the initial concentration of the counterion in the aqueous phase, \( r \) is the organic phase to aqueous phase volume ratio, \( C_{CI}^0 \) is the initial surfactant concentration in the solvent phase, and \( C_D^0 \) is the initial concentration of dye in the aqueous phase. \( C_D \) is the concentration of dye in the bulk aqueous phase, which is the same as that in the reverse micellar water pools. The first term in eq 1 corresponds to transfer of dye to the solvent phase due to solubility. \( K_d^{s/w} \) is assumed not to be influenced by the presence of surfactants aggregates. In the present case, the initial counterion concentration in the aqueous phase (\( C_{CI}^0 \)) is zero. The concentration of the bound counterion to the surfactant at the reverse micellar interface is given by

\[ C_{CI,b} = C_S^0 - \left( C_D - C_D^0 - K_d^{s/w} C_D^0 \right)/r \] (3)

By combining eqs 1–3 along with the expression for equilibrium constants for ion-exchange reactions given in the Supporting Information, the final model equation is given by

\[ C_D^0 - C_D = K_d(2C_D^0 - C_D) + C_D + K_d^{s/w} C_D^0 \] (4)

\[ C_D^0 + C_D - K_d(2C_D^0 - C_D) + C_D + K_d^{s/w} C_D^0 \]
FIGURE 2. Effect of different cationic surfactants (HTAB and CPC) on the removal of eosin yellow from the aqueous phase.

Model Correlation. The dye concentration in the aqueous phase (C₀) after dye removal can be estimated from eq 4 for known equilibrium constants (Kᵣ, Kᵥ), the initial dye concentration in the aqueous phase (C₀), the initial surfactant concentration in the solvent phase (Cₛ), and organic phase to aqueous phase volume ratio (r). Kᵥ and Cₛ are known from experiment data on dye solubility in the absence of surfactants. Since the Kᵣ and Kᵥ values for different dye-surfactant combinations are not known, eq 4 cannot be used directly to evaluate dye removal from water. The eq 4 is transformed to a straight line equation of the form, y = mx + c where the slope m = (Kᵥ/Cₛ)₁/₂, the intercept c = -(Kᵥ/Kᵣ)₁/₂, y = 1/(Cₒ(Cₒ + Cₛ + KᵥCₛ/Cₛ)), and x = (Cₒ - Cₒ)/[1(Cₒ(Cₒ + Cₛ + KᵥCₛ/Cₛ))]. By fitting the experimental data to a straight line and determining the slope and the intercept, Kᵥ and Kᵣ values are estimated.

Special Case (Methyl Orange). Combining the mass balance equations for methyl orange and bromine ion along with the equilibrium constant expression for ion-exchange reaction of methyl orange (see Supporting Information) gives the final model equation as

\[
\frac{C₀^D - C₀}{KᵥCₛ^D(2rCₛ^D - C₀^D + C₀ + KᵥCₛ^D/Cₛ)} = 1 + \frac{KᵥCₛ^D}{KᵣCₛ^D + C₀^D - KᵣCₛ^D(2rCₛ^D - C₀^D + C₀ + KᵥCₛ^D/Cₛ)} \tag{5}
\]

It should be noted that eq 5 is slightly different from eq 4. The equilibrium constants, Kᵥ and Kᵣ, are determined from the slope and intercept of the straight-line plot of eq 5 as discussed earlier.

Results and Discussion

Effect of Surfactant. Figures 2 and 3 show the experimental results for the percentage removal of the anionic eosin yellow and the cationic methylene blue using amyl alcohol as solvent with different cationic surfactants (HTAB and CPC) and anionic surfactants (SDBS and AOT), respectively. It is seen from Figures 2 and 3 that the percentage removal of dye decreases with the increase in the dye concentration and that the percentage removal of dye increases with the increase in the surfactant concentration for both the anionic and cationic dyes. The solvent has a fixed capacity for encapsulating the dye molecules for a given surfactant concentration since the number of reverse micelles formed is constant. Thus, the percentage removal of the dye decreases with the increase in the dye concentration. The measured weight percent of water uptake in the amyl alcohol phase is ~7.5% for the reverse micelles of both cationic and anionic surfactants. An enhanced capacity of the solvent for the dye encapsulation is achieved by increasing the surfactant concentration and, consequently, increasing the number of reverse micelles formed. A slight increase in water uptake is noticed with the increase in surfactant concentration and in the range of variation of surfactant concentration studied in the dye removal experiments. Figures 2 and 3 also show that the percentage removal of the cationic and anionic dyes using two different anionic and cationic surfactants at a given concentration is about the same. This may be because one dye molecule is electrostatically attracted toward one surfactant molecule and thus results in the same percentage removal of dye. It should be noted that the removal of the dye is accomplished using oppositely charged dye and surfactant molecules. The dye is not removed from water if similarly charged dye and surfactant molecules are used (15) or if a very low concentration (<100 mg/100 mL) of surfactant is used.

COD Removal. Generally, COD measures the purity of water in the context of water pollution control. It is seen from Figure 4 that the COD of water after treating with liquid–liquid extraction process using reverse micelle decreases significantly (~80–90%) as compared to that of the original dye solution. Figure 4 shows that the percentage COD removal from the aqueous phase decreases with the increase in methylene blue concentration from 20 to 40 mg/100 mL.

FIGURE 3. Effect of different anionic surfactants (SDBS and AOT) on the removal of methylene blue from the aqueous phase.

FIGURE 4. Effect of surfactant and dye concentrations on the COD removal for cationic methylene blue.
From the experimental data presented in Figures 2 and 3, it is seen that the percentage removal of dye increases with the increase in the surfactant concentration. Thus, it would be interesting to determine the increase in percentage of COD or decrease in COD removal from aqueous phase due to the addition of the surfactant to the system. Figure 4 shows that the percentage of COD removal of methylene blue from the aqueous phase using reverse micelles of SDBS increases with the increase in the surfactant concentration. The additional addition of surfactants to the solvent phase increases the COD level of water due to the transfer of some minute amount of surfactants to the aqueous phase. However, the surfactants are primarily present in the solvent phase in the form of reverse micelles. Therefore, COD removal from the aqueous phase increases with the increase in the surfactant concentration since a larger quantity of dye is removed. This is further explained through quantitative measurements.

A material balance check was performed for the case of removal of 20 mg of methylene blue in 100 mL of aqueous phase using 45 mg of SDBS in 50 mL of amyl alcohol. The COD removal was 94% as against the 100% dye removal obtained from UV spectrophotometer analysis. This means that, although aqueous phase is contaminated with some organic matter, a completely decolored water was obtained. A similar experiment performed as mentioned above without using dye resulted in a similar COD value of water to that obtained when dye was present. The reason for not removing 6% of COD is due to the presence of some amount of surfactants and amyl alcohol in water. This fact was further verified by measuring COD after mixing 100 mL of aqueous phase with 50 mL of amyl alcohol in the absence of dye and surfactants. The 1.7% COD out of 6% not removed from water is accounted for by considering the slight solubility of amyl alcohol in water.

The surfactant is an indispensable component in the reverse micelle extraction process since the dyes are removed by solubilizing it in the self-assembling of surfactant molecules, called the reverse micelles. The increase in the surfactant concentration gives greater opportunity to a large number of dye molecules to solubilize in the reverse micelles. However, the increase in surfactant concentration may lead to stable solvent—aqueous phase dispersion, resulting in poor separation of phases. In protein extraction, normally a centrifuge is used for the separation of phases since the volume of liquid handled is very small. The dye removal from wastewater involves the processing of a large volume of liquid; hence, the centrifuge method cannot be adopted. The surfactant molecule plays both a positive and a negative role in the removal of dyes through the reverse micelles route. Thus, it is desirable to evaluate the required amount of surfactant needed for a given amount of dye removal, and this section clearly dealt with it. The effect of surfactant and solvent on the separation of phases is discussed later.

**Effect of Solvent.** The closed symbols in Figure 5 show the experimental data for the percentage removal of the anionic eosin yellow using three different solvents (amyl alcohol, benzyl alcohol, and methyl benzoate) containing 20 mg of HTAB. Figure 5 also shows the experimental data for the percentage removal of the cationic malachite green using two different solvents (isoctane and methyl benzoate). Eosin yellow and malachite green dyes are sparingly soluble in amyl alcohol, benzyl alcohol, and methyl benzoate whereas they are insoluble in isoctane. The effect of the nature of the solvent on the removal of dyes is studied by deducting the percentage removal in the absence of surfactant from that in the presence of surfactant. The open symbols in Figure 5 shows the percentage removal of dye in the absence of surfactants. The removal of dye in the absence of surfactants occurs due to the solubility of dye in the solvent. It is seen from the Figure 5 that the percentage removal of the dye from water for a particular surfactant concentration is almost the same for all the solvents. Thus, the experimental data reveal that the effect of the nature of the solvent on dye removal by reverse micelles separation is negligible. The water uptake by reverse micelles at a given surfactant concentration in different solvents is found to be same. Consequently, no difference in percentage removal of dye from the aqueous phase is obtained for different solvents. Therefore, the criterion for the choice of solvent depends on the easy separation of aqueous phase from solvent—aqueous phase dispersion in the presence of surfactants and not on the solvent effect in reverse micelles extraction process.

The surfactant to aqueous phase volume ratio (r) is varied from 1:10 to 1:1. Although the percentage removal of dye increases significantly with the increase in r from 1:10 to 1:2, no significant increase in the percentage removal is noticed beyond volume ratio 1:2. Furthermore, dye removal increases with the increase in surfactant concentration at a low value of r. As, for example, methyl orange removal increases from 55% to 80% when HTAB concentration in amyl alcohol increases from 10 to 20 mg at a value equal to 1:10. Therefore, a low surfactant quantity can be employed for the removal of dye from aqueous phase using reverse micelles. This is an

![FIGURE 5. Effect of solvent on the removal of eosin yellow (EY) and malachite green (MG) using HTAB and AOT in 50 mL of solvent.](image)

![FIGURE 6. Effect of surfactant concentration on aqueous phase separation time from solvent; 30 mg of eosin yellow was present in 100 mL of aqueous phase.](image)
important result from the point of economics of the removal process. The dye extracted in solvent is possible to back-
extract into water by using counterionic surfactants (16).
Thus, recovery of solvent and reuse of dye is possible.

Phase Separation. The separation of aqueous and solvent phases is an important issue for the practical implementation
and economic viability of dye removal by liquid—liquid extraction using reverse micelles. The advantage and dis-
advantage of the presence of surfactant in the reverse micellar extraction process is already discussed in a previous section.
Figure 6 shows the effect of three different solvents (amyl alcohol, benzyl alcohol, and methyl benzoate) on the
separation of the aqueous phase from the solvent phase at different HTAB concentrations. The time required to separate
a fraction of clear aqueous phase increases with the increase in the surfactant concentration. It is seen in Figure 6 that the
3-fold increase in the HTAB concentration in 50 mL of amyl alcohol increases the time required for complete phase
separation from 20 to 60 min. This is because the Sauter mean diameter of amyl alcohol droplet decreases from 28 to
14 μm with the increase in HTAB concentration from 10 to 30 mg in 50 mL of amyl alcohol. Thus, an optimum surfactant
concentration should be used for dye removal by the reverse

FIGURE 7. Experimental data fitted with ion-exchange reaction model for the removal of anionic eosin yellow from 100 mL of aqueous
phase.

FIGURE 8. Experimental data fitted with ion-exchange reaction model for the removal of cationic malachite green from 100 mL of aqueous
phase.

mics such that the phase separation time is not high and as well as the percentage removal is not low.

By comparing data in Figure 6, it is seen that the amyl alcohol–aqueous phase dispersion separates faster than benzyl alcohol–aqueous phase and methyl benzoate–aqueous phase dispersions for a given HTAB concentration. A 150-mL mixture of amyl alcohol–water dispersion con-
taining 30 mg of HTAB separates into pure phases in 1 h, whereas other solvents take roughly 4–8 h for the separation.

To succeed as a viable alternative to the conventional dye removal process (e.g., UV oxidation, adsorption), the reverse
micelles extraction technique must use a solvent that is easily and cost-effectively separated from solvent–aqueous phase
dispersion in the presence of a surfactant. The other important criterion is that the reverse micelles should form
in the solvent phase. The dispersion of amyl alcohol in aqueous phase is easy to separate into pure phases in a
cylindrical column by gravity as compared to other solvents tested (e.g., benzyl alcohol and methyl benzoate). In some
cases, if a particular surfactant/solvent combination needs high surfactant concentration to remove large quantity of
dye from aqueous phase, a flotation column may be used to reduce the time of separation of aqueous phase from the
solvent–aqueous phase dispersion (20).

Analyses of Data. Figures 7 and 8 show the comparison experimental data and the ion-exchange reaction model
correlation (eq 4) for the removal of anionic eosin yellow and cationic malachite green from aqueous phase. The
experimental data shown by different symbols are fitted with straight lines for different dyes, solvents, surfactant types,
and their concentrations using least-squares fit method (average regression coefficient ≈ 0.93). The plot for methylene
blue and orange G is given in the Supporting Information. The $K_C$ and $K_D$ values for the dye—surfactant ion-exchange
reactions, determined from the slopes and intercepts of the straight lines, are shown in Table 3. The average error in
estimating $K_C$ and $K_D$ values for different dyes is ±2%. It is seen that $K_C$ and $K_D$ values are different for different dye—
surfactant–ion complex formation and its dissociation. These values are higher than that for similar ion-exchange reactions
of protein found in the literature (19). This may be because of the higher solubilization of dye than the protein molecules
in the respective reverse micelles. It should be noted that dye molecules are smaller than the protein molecules. The
**TABLE 3. Equilibrium Constant Values in the Ion-Exchange Reaction Model**

<table>
<thead>
<tr>
<th>dye</th>
<th>surfactant</th>
<th>solvent</th>
<th>$K_C$ (mM$^{-1}$)</th>
<th>$K_D$ (mM$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>eosin yellow</td>
<td>HTAB</td>
<td>amyl alcohol</td>
<td>5.06</td>
<td>1.54</td>
</tr>
<tr>
<td></td>
<td>HTAB</td>
<td>benzyl alcohol</td>
<td></td>
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<tr>
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<td>CPC</td>
<td>amyl alcohol</td>
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<td></td>
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<tr>
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<td>CPC</td>
<td>benzyl alcohol</td>
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<tr>
<td>orange G</td>
<td>HTAB</td>
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<td>4.73</td>
<td>1.86</td>
</tr>
<tr>
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<td>HTAB</td>
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<tr>
<td></td>
<td>CPC</td>
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<td></td>
</tr>
<tr>
<td>methylene blue</td>
<td>SDBS</td>
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<td>2.29</td>
</tr>
<tr>
<td></td>
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<td>CPC</td>
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<tr>
<td></td>
<td>CPC</td>
<td>benzyl alcohol</td>
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<td></td>
</tr>
<tr>
<td>malachite green</td>
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<td>1.98</td>
<td>2.51</td>
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<td>isoctane</td>
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<td></td>
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</tr>
<tr>
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<td>amyl alcohol</td>
<td>31.0</td>
<td>4.17</td>
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<tr>
<td></td>
<td>CPC</td>
<td>methyl benzoate</td>
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</table>

*Temperature = 30 °C.*

different cationic or anionic surfactants used with the same number of charges for a particular dye have the same $K_C$ and $K_D$ values since the stoichiometry ratio in the ion-exchange reactions remain same. The solvent does not play any role in the ion-exchange reaction model; hence, the $K_C$ and $K_D$ values are not a function of the nature of solvent. Equation 5 is used to predict the removal of methyl orange from water. The excellent agreement of experimental data to a straight line validated the assumption that 2 mol of methyl orange reacted with 1 mol of HTAB. The information on plot for methyl orange is given in the Supporting Information. The other stoichiometry ratios for methyl orange and HTAB reaction do not satisfy the acceptable model correlation. The values of the equilibrium constants ($K_C$ and $K_D$) for methyl orange are shown in Table 3, and they are higher than the other dyes since the reaction stoichiometry is different. Dye removal by reverse micelles is predicted well by the ion-exchange reaction model.

**Acknowledgments**

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**Supporting Information Available**

Expression for equilibrium constants ($K_C$ and $K_D$) of ion exchange reaction between dye and surfactants, a schematic diagram on dye surfactant location in reverse micelles, and three figures pertaining to data analyses of orange G, methylene blue, and methyl orange dyes. This material is available free of charge via the Internet at http://pubs.acs.org.

**Nomenclature**

- AOT: sodium bis(2-ethyl) sulfosuccinate
- $C_D$: initial concentration of dye in bulk aqueous phase (mmol/L)
- $C_{SD}^{0}$: concentration of dye in bulk aqueous phase after mixing with solvent phase in the absence of surfactants
- $C_{SD}^{-}$: concentration of dissociated dye surfactant complex at reverse micellar interface (mmol/L)
- $C_{SDCl}$: concentration of dye–surfactant–counterion complex at reverse micellar interface (mmol/L)
- $C_{CI,b}$: concentration of counterion bound to surfactant headgroup at reverse micellar interface (mmol/L)
- $C_{Cl}$: initial concentration of counterion in bulk aqueous phase (mmol/L)
- $C_{Cl}$: final concentration of counterion in bulk aqueous phase (mmol/L)
- $C_{S}$: initial concentration of surfactant in organic phase (mmol/L)
- COD: chemical oxygen demand (mg/L)
- CPC: cetyl pyridinium chloride
- D: dye
- HTAB: hexadecyltrimethylammonium bromide
- $K_C$: equilibrium constant for ion-exchange reaction between dye and surfactant (mM$^{-1}$)
- $K_D$: equilibrium constant for dissociation reaction in ion-exchange reaction model (mM$^{-1}$)
- $K_S^{0,w}$: concentration partition coefficient of dye between solvent and aqueous phase in the absence of surfactants
- MG: malachite green
- MB: methylene blue
- MO: methyl orange
- $n_i^0$: initial concentration of dye in bulk aqueous phase (mmol/L)
- $n_i$: final concentration of dye in bulk aqueous phase (mmol/L)
- OG: orange G
- $r$: initial volume ratio of organic phase to aqueous phase
- SDBS: sodium dodecylbenzene sulfonate
- SDCI: dye–surfactant complex formed in ion-exchange reaction model
- T: absolute temperature (K)

**Literature Cited**


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