Spectroscopic Evidence for the Formation of
"Hydrophobic Ion Pairs"

by

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The optical spectra of picrate ions, which have been employed to evaluate the tightness of ion pairs in organic solvents, were taken in aqueous micelles (CTAB, SDS, and Brij-35) and cationic polysoaps, and were compared with those in organic solvents. The spectrum ($\lambda_{\text{max}}$ 355 nm in water) was hardly affected by the addition of anionic (SDS) and nonionic (Brij-35) surfactants above the cmc's and by a cationic polysoap with no dodecyl-group content (4VP-D-0). On the other hand, the addition of a cationic surfactant (CTAB) above the cmc and cationic polysoaps with high dodecyl-group contents (4VP-D-22 and EVI-D-41) gave rise to significant bathochromic shifts which were accompanied with a new absorption maximum at around 410 nm. It was suggested, based on the analogy with the spectra in organic solvents, that picrate ions form "hydrophobic ion pairs" with cationic surfactants such as CTAB, 4VP-D-22, and EVI-D-41, but the ion pairs in the hydrophobic region are not free as in dipolar aprotic solvents. Interestingly, the formation of a free ion pair with CTAB was observed slightly below the cmc.

Recently, a variety of anionic nucleophiles have been found to be unusually active in cationic hydrophobic aggregates such as micelles and polysoaps. Anionic nucleophiles reported are alkoxides,\(^1\)-\(^3\) phenolates,\(^6\),\(^7\) hydroxamates,\(^7\)-\(^14\) thiocyanates,\(^5\),\(^15\)-\(^21\) and imidazole anions.\(^22\)-\(^24\) The unusual activation of anions cannot be explained by the term of proximity effect, since the decarboxylation of carboxylic acids (unimolecular reaction) is also subject to the unusual rate acceleration.\(^25\),\(^26\) It is thus reasonable to consider that some enthalpy term is associated with the lowering of the free energy of activation. We suggested that the phenomenon largely stems from the formation of "hydrophobic ion pairs" between anions and cationic hydrophobic aggregates which are relatively dehydrated in the hydrophobic domain.\(^7\),\(^10\),\(^26\),\(^27\) The concept is illustrated in Fig. 1. An anionic nucleophile in protic media is well stabilized by solvation through hydrogen bonding, and it must lose the surrounding protic molecules before it can form a covalent bond. It may be said, therefore, that the reactivity of anions in protic media is considerably suppressed. On the other hand, the anion in aprotic media is free from hydrogen bonding. The crucial importance of aprotic solvents in activation of anions has been established by Par-
Here, we wish to address a spectroscopic evidence for the formation of "hydrophobic ion pairs". The optical spectra of picrate ions, which give the potential information for the tightness of ion pairs, were taken in the presence of micelles and polysoaps.

Results and Discussion

In the first place, the absorption spectra of picrate ions were taken in various organic solvents in order to dissect the nature of the spectra. As shown in Table 1 and Fig. 2, considerable bathochromic shifts were observed in dipolar aprotic solvents such as dimethylsulfoxide and dimethylformamide. On the other hand, apolar solvents resulted in hypsochromic shifts which were accompanied with a shoulder at around 400 nm. Smid et al. found that the addition of 4′-carbomethoxybenzo-15-crown-5 to the tetrahydrofuran solution of potassium picrate (λmax 357 nm) causes the shift of the absorption maximum to 380 nm as well as the disappearance of the shoulder. It was proposed that the shift stems from the formation of the free picrate anion. The proposition is compatible with the similar spectral shifts observed in dimethylsulfoxide and dimethylformamide (Table 1). Thus, the shift of the absorption maximum would be considered as a measure of tightness of the ion pairs. On the other hand, the relative magnitude of the shoulder (ODs / ODmax: see footnote of Table 1) would reflect solvent polarity.

The spectra of picrate ions taken in the presence of hydrophobic aggregates are summarized in Table 2 and Fig. 3. The addition of anionic (SDS: sodium dodecylsulfate) and nonionic (Brij-35) surfactants above the cmc's did not affect the spectrum at all. 4VP-D-0 which has no dodecyl group...
in the polymer structure did not influence the spectrum. On the other hand, slight bathochromic shifts were observed on the addition of EVI-D-9, EVI-D-41, and 4VP-D-22, the shifts being almost independent from the polymer concentration. The spectrum in the presence of EVI-D-9 did not show a distinct shoulder at around 400 nm, while the magnitude of the shoulder increased with increasing EVI-D-41 and 4VP-D-22 concentrations (Table 2). Obviously, the latter two polymers possess the hydrophobic region like conventional micelles. This is consistent with our kinetic observation that EVI-D-41 and 4VP-D-22 are classified as micelle-like polymers and EVI-D-9 as a polyelectrolyte-like polymer. Since the bathochromic shift was observed even in the presence of EVI-D-9, the micelle-like environment may not be a prerequisite to the shift of maximum. This problem will be discussed later.

Table 2. Absorption maxima and shoulders in the presence of hydrophobic aggregates

<table>
<thead>
<tr>
<th>Additive</th>
<th>Concentration (mM)</th>
<th>$\lambda_{\text{max}}$ (nm)</th>
<th>$\lambda_{\text{shoulder}}$ (nm)</th>
<th>OD$<em>s$/OD$</em>{max}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water</td>
<td>355</td>
<td>yes</td>
<td>no</td>
<td>0.066</td>
</tr>
<tr>
<td>CTAB</td>
<td>0.10</td>
<td>380</td>
<td>yes</td>
<td>0.246</td>
</tr>
<tr>
<td></td>
<td>1.6</td>
<td>350</td>
<td>412</td>
<td></td>
</tr>
<tr>
<td>SDS</td>
<td>15.0</td>
<td>355</td>
<td>no</td>
<td></td>
</tr>
<tr>
<td>Brij-35</td>
<td>1.6</td>
<td>355</td>
<td>no</td>
<td></td>
</tr>
<tr>
<td>4VP-D-0</td>
<td>5.0</td>
<td>355</td>
<td>no</td>
<td></td>
</tr>
<tr>
<td>4VP-D-22</td>
<td>0.46</td>
<td>360</td>
<td>yes</td>
<td>0.077</td>
</tr>
<tr>
<td></td>
<td>0.93</td>
<td>360</td>
<td>yes</td>
<td>0.096</td>
</tr>
<tr>
<td></td>
<td>3.68</td>
<td>360</td>
<td>yes</td>
<td>0.165</td>
</tr>
<tr>
<td>EVI-D-9</td>
<td>5.00</td>
<td>358</td>
<td>no</td>
<td></td>
</tr>
<tr>
<td>EVI-D-41</td>
<td>0.71</td>
<td>358</td>
<td>yes</td>
<td>0.162</td>
</tr>
<tr>
<td></td>
<td>1.41</td>
<td>358</td>
<td>yes</td>
<td>0.174</td>
</tr>
<tr>
<td></td>
<td>4.98</td>
<td>358</td>
<td>413</td>
<td>0.223</td>
</tr>
</tbody>
</table>

In Fig. 4, the shifts of $\lambda_{\text{max}}$ are plotted as a function of CTAB concentration. Interestingly, the pronounced bathochromic shift to 380 nm occurred at $1.0 \times 10^{-4}$ M CTAB. Further increase in the CTAB concentration brought forth the hypsochromic shift down
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Fig. 3. Spectra of picrate ions in the presence of hydrophobic aggregates. Water (1), 0.1 mM CTAB (2), 1.6 mM CTAB (3), and 3.68 mM 4VP-D-22 (4). The concentrations of polymers were calculated based on the monomeric units.

Fig. 4. Shifts of $\lambda_{\text{max}}$ plotted as a function of surfactant concentrations.

to 350 nm and a new absorption maximum at 412 nm appeared (Fig. 3 and Table 2). The cmc of CTAB under the present condition is estimated to be $4 \times 10^{-4}$ M.\textsuperscript{14,24} It is implicated, therefore, that free ion pairs between CTAB molecules and picrate ions are formed slightly below the cmc and that the hydrophobic region presented by the micelle formation gives the relatively tight ion pairs. The spectra in the presence of the CTAB micelle most resemble that in tetrahydrofuran. Thus, what is necessary to form free ion pairs would be the microscopically hydrophobic environment around the ion pairs rather than the vast, micelle-like hydrophobic region.

In this connection, it is worth mentioning that the hydrophobic aggregates of trioctylmethylammonium chloride (TMAC), which probably form micro-micelles, enhance the nucleophilicity of bound anions more than the CTAB micelle.\textsuperscript{24} Table 3 shows the $\lambda_{\text{max}}$ values of picrate ions in the presence of TMAC. As anticipated, $\lambda_{\text{max}}$ values appeared invariably between 374-377 nm above $0.4 \times 10^{-4}$ M of TMAC. The result implicates that the aggregate \textit{a priori} be unable to form globular micelles and the increase in the TMAC concentration increases the number of micro-micelles, not the size of micelles. As a result, the microenvironment of TMAC aggregate can be similar to that of dimethylsulfoxide or dimethylformamide.

<table>
<thead>
<tr>
<th>[TMAC] (mM)</th>
<th>$\lambda_{\text{max}}$ (nm)</th>
<th>Shoulder</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>355</td>
<td>no</td>
</tr>
<tr>
<td>0.02</td>
<td>365</td>
<td>no</td>
</tr>
<tr>
<td>0.04</td>
<td>375</td>
<td>yes</td>
</tr>
<tr>
<td>0.06</td>
<td>377</td>
<td>yes</td>
</tr>
<tr>
<td>0.08</td>
<td>374</td>
<td>yes</td>
</tr>
<tr>
<td>0.10</td>
<td>374</td>
<td>yes</td>
</tr>
</tbody>
</table>

In general, sigmoidal dependence of bimolecular reaction rates followed by gradual rate suppression on surfactant concentrations has been rationalized in terms of concentration of reactants and dilution by micelles,\textsuperscript{30,31} and few reports espouse that the reactivity of reactants changes as a function of surfactant concentrations.\textsuperscript{32}
The present investigation manifests, however, that the reactivity of anions would change from that in dimethylsulfoxide to that in tetrahydrofuran with increasing CTAB concentration. Expectedly, a profile of anion reactivity vs. surfactant concentration would provide a similar sigmoidal curve. We thus propose that the bimolecular reaction rates should be considered not only as a function of the local concentration of reactants but also as a function of the anion reactivity, as long as anionic species are involved in the reaction concerned.

In conclusion, the hydrophobic environments of conventional micelles and polysoaps give rise to dehydration of bound anions, and ion pairs therein show rather tight nature. On the other hand, the environment of micro-micelles such as TMAC can produce loose, dehydrated ion pairs as in dipolar aprotic solvents. It is suggested, therefore, that the microscopically hydrophobic environment is favorable to the activation of anions.

Experimental

The preparation of polysoaps have been described.\textsuperscript{11,12} All the spectral measurements were carried out at 30°C with a Hitachi 200 spectrophotometer. The buffer solution (pH 7.1 with 0.02 with KCl) was used for the measurements in aqueous solutions.

References


