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Charge Transfer Complexing Between Indole Derivatives and Methylviologen and Effects of Sodium Dodecyl Sulfate on It

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The charge transfer complex formations between indole derivatives and methylviologen were investigated spectroscopically. In aqueous solutions near room temperature, the order of complex stability was tryptamine < tryptophan < indole < indole acetate, which is the reverse order of the magnitude of molar absorptivities. This was interpreted as involvement of contact charge transfer. The decrease of enthalpy of complex formation ($-\Delta H$) was highest in tryptamine, and lowest in indole acetate. ΔH and entropy of complex formation (ΔS) varied nearly in a linear fashion with isokinetic temperature 242°K. These results were attributed to the hydration-dehydration properties of the side chains in indole derivatives. Except indole acetate, the complex formations were greatly enhanced by the addition of sodium dodecyl sulfate (SDS). However, the direct relationship between the enhanced complex formation and SDS micelle formation was not found. The enhanced charge transfer interaction in SDS solutions was attributed to the increased ΔS by interaction between methylviologen and SDS in premicellar level. The order of complex stability in SDS solutions was indole acetate < tryptophan < tryptamine < indole, which reflects the hydrophobicity of indole derivatives as well as electrostatic interaction between indole derivatives and methylviologen associated with SDS.

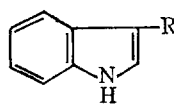
Introduction

Since Mulliken's suggestion of importance of charge transfer complexes in biological systems¹, studies have demonstrated that the complexes are indeed directly involved in various biochemical reactions, such as photosynthesis, phosphorylation and redox chains with flavin-nicotinamide chains.² One of the most important electron donor moieties in biologically active molecules is indole ring. Thus, the charge transfer complex formation of indole and/or its derivatives with various electron acceptors including pyridinium salts (mainly nicotinamide dinucleotide (NAD) or its analogs)³⁻⁷, tetracyanoethylene (TCNE)⁸, methylviologen⁹⁻¹¹, etc, has been investigated. The charge transfer interaction properties of indole ring with pyridinium salts were attributed to the coenzyme activity of NAD,⁵⁻⁷ and were also utilized as a conformational probe^{9,12} in the systems of biological interests.

Methylviologen (MV²⁺), commonly known as paraquat, is a dication, N,N'-dimethyl-4,4'-bipyridinium, and its salts are used widely as a weed killer.¹³ It has been found that the compound inhibits electron transfer in both the cytochrome chain of mitochondria and electron transfer chain of chloroplast.¹³ Recently, MV²⁺ and viologen polymers have attracted much attention as an electron catalyst in the hydrogen fuel production through the splitting of water by sunlight.¹⁴ The potential uses and biological properties of MV²⁺ are based on the high electron-accepting ability of the

dication: the estimated electron affinity of MV²⁺ is 1.24eV.¹⁵ In view of these interesting properties of MV²⁺, several investigators have reported the charge transfer complex formation of MV²⁺ with various electron donors.^{10, 11, 15, 16}

Despite the extensive uses of MV²⁺ in many biological systems as one-electron transfer agent and as redox indicators,¹⁷ studies on effects of neighboring charge and micro-environment on the interaction between donor moieties of biological molecules and MV²⁺ are scarce. For this reason, we considered it interesting to examine the charge transfer complex formation between indole derivatives and MV²⁺ systematically. To evaluate the contribution of electrostatic interaction to the complex formation and simulate the local environment of the indole ring in biological systems, the following indole derivatives with different charges in the side chain were chosen.



Indole (In) : R=H

3-Indole acetate (In. Ac) : R=CH₂COO⁻

Tryptamine-HCl (TA) : R=CH₂CH₂NH₃Cl

L-Tryptophan (Try) : R=CH₂CH(COO⁻)NH₃⁺

We have also studied the effects of sodium dodecyl sulfate (SDS), because reactions in micellar media are simple model systems for chemical processes occurring at interfaces in a living cell, and an anionic surfactant, SDS, is expected to have strong influence on the interaction properties of the

dication, MV^{2+} .

Materials and Methods

Materials. Methylviologen dichloride ($MV^{2+}2Cl^-$) was prepared by method of Verhoeven et al⁹, but slight modifications of the procedure were adopted. 4,4'-Bipyridine (50 mmole; Tokyo Kasei) was reacted with methyl iodide (120 mmole) in 100ml of methanol to obtain red colored methylviologen diiodide ($MV^{2+}2I^-$). Aqueous solution of $MV^{2+}2I^-$ was stirred with the suspension of AgCl powder. After filtration of excess AgCl and AgI, the colorless solution was dried under reduced pressure to obtain white solid, crude $MV^{2+}2Cl^-$. The product was recrystallized in 95 % ethanol. Proton nmr and IR spectra of $MV^{2+}2Cl^-$ were identical to those of commercial sample (Tokyo Kasei). Prior to use, $MV^{2+}2Cl^-$ was dried in a vacuum oven at 50°C for 24 hours. Commercial reagent grade indole, indole acetate, tryptamine-HCl and L-tryptophan were used as received. SDS was recrystallized in methanol three times, after washing with ether.

Methods. Absorption spectra were taken on a Beckman DU-8B UV-Vis. spectrophotometer equipped with temperature-controlled cell compartment. The pH of solutions were ~7 except tryptamine, pH of which solution was adjusted to 2 with HCl.

Calculation. Absorption data obtained by varying the concentration of the acceptor (MV^{2+} : A) at constant donor (indole derivatives: D) concentration, while keeping the condition of $C_A \gg C_D$, were analyzed by Benesi-Hildebrand equation (1)¹⁰. This equation holds for formation of 1:1 complex.

$$C_{Di}/d = 1/\epsilon + 1/K\epsilon C_{Ai} \quad (1)$$

The complex formation constants (K) and apparent molar absorptivities (ϵ) were determined from the slopes and intercepts of the plots of C_{Di}/d vs. $1/C_{Ai}$. C_{Di} and C_{Ai} stand for initial concentrations of donor and acceptor, respectively. Also d represents the difference between the absorbance of a mixture and the sum of absorbances of individual components at a given wavelength.

The Gibbs free energy of a complex formation (ΔG) was evaluated from the complex formation constant;

$$\Delta G = -RT \ln K \quad (2)$$

and the enthalpy of a complex formation (ΔH) was determined from the plot of $\ln K$ versus $1/T$ according to equation (3).

$$\partial \ln K / \partial (1/T) = -\Delta H/R \quad (3)$$

The entropy of the complex formation (ΔS) was calculated from ΔG and ΔH using equation, $\Delta G = \Delta H - T\Delta S$, at each temperature.

Results and Discussion

Neither indole derivatives nor MV^{2+} showed appreciable absorption above 320nm, but mixtures of them colored pale-yellow and displayed a new diffused band with a ma-

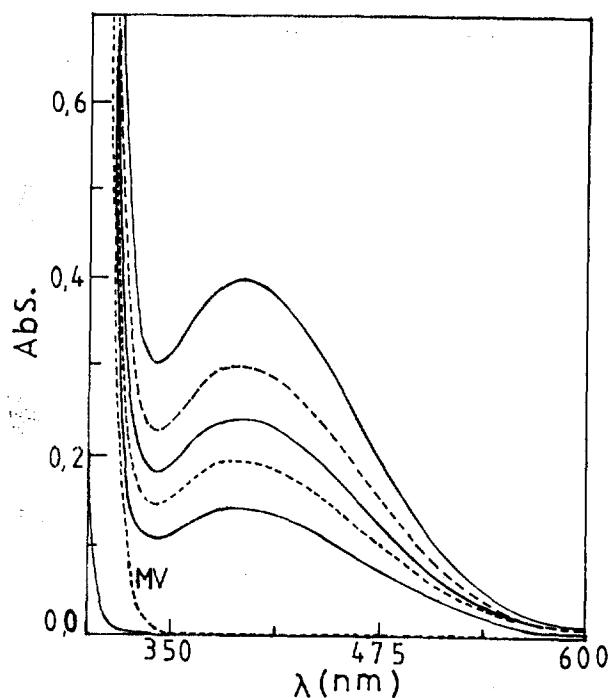


Figure 1. Absorption spectra of indole- MV^{2+} mixtures in water at 20°C. From top to bottom, MV^{2+} concentrations are 2.5×10^{-2} , 2.0×10^{-2} , 1.75×10^{-2} , 1.42×10^{-2} , 1.00×10^{-2} , 2.5×10^{-2} (MV) and 0M, respectively. Indole concentration is fixed at 2.5×10^{-3} M except MV which does not contain indole.

ximum near 390nm. This band agrees well with reported charge transfer band of indole- MV^{2+} complex.⁹⁻¹¹ Figure 1 shows the absorption spectra of indole- MV^{2+} system taken in water at 20°C. Other indole derivative- MV^{2+} systems exhibit the essentially same charge transfer band as indole- MV^{2+} . They differ only in the magnitude of absorbance values. Also the shape and position of the charge transfer bands were virtually unchanged with temperature and donor/acceptor ratio. These findings can be regarded as an evidence of the formation of same charge transfer complex, between indole ring and MV^{2+} , regardless of the nature of side chains of indole derivatives, temperature and donor/acceptor ratio.

Complex formation data were plotted according to Eq. 1 as shown in Figure 2 for data taken at 20°C. Good agreement of experimental results with Eq. 1 suggests that the indole derivatives form 1:1 complexes with MV^{2+} . Molar absorptivities (ϵ) and complex formation constants (K) were evaluated by the method described in the preceding section, and summarized in Table 1.

The order of K 's in water in experimental temperature range is In.Ac > In > Try > TA, as expected from the charges of side chains: the negatively charged In.Ac. forms the most stable complex, while positively charged TA. forms the least stable one with MV^{2+} . The difference in complex stability between In and Try can be attributed to the steric hindrance of the side chain of Try. in the interaction of indole ring with MV^{2+} .

TABLE 1: Parameters of Charge Transfer Complex formation between Methylviologen and Indole Derivatives in Water at 20 °C

Donor	$K (M^{-1})$	$\epsilon (M^{-1} \text{cm}^{-1})$	ΔG	ΔH	ΔS
Tryptophan	4.9	833	-0.93	-3.22	-7.83
Indole	8.1	741	-1.22	-2.82	-5.46
Indole acetate	47.3	422	-2.25	-1.19	+3.62
Tryptamine	1.6	1540	-0.26	-7.75	-25.6

*absorbance values are taken at 390nm. ** ΔG and ΔH are in Kcal/mole and ΔS is in cal/deg/mole.

TABLE 2: Parameters of Charge Transfer Complex Formation Between Methylviologen and Indole Derivatives in 0.015M SDS at 30 °C

Donor	$K (M^{-1})$	$\epsilon (M^{-1} \text{cm}^{-1})$	ΔG	ΔH	ΔS
Tryptophan	56.2	240	-2.43	-2.24	+0.63
Indole	870	372	-4.08	-1.45	+8.68
Indole acetate	18.1	760	-1.74	-4.37	-8.68
Tryptamine	462	310	-3.69	+2.98	+22.01

*absorbance values are taken at 390nm. ** ΔG and ΔH are in Kcal/mole and ΔS is in cal/deg/mole.

The effect of the charge in the side chains on K values agrees well with the results of Verhoeven et al⁹, who reported the complex formation constants of 3-methylindole, N-acetyl-L-tryptophanamide and L-tryptophan-methyl ester with MV²⁺ as 7, 5.6 and 2.7, respectively. The smaller K value in N-acetyl-L-tryptophanamide than 3-methylindole was explained as greater steric hindrance in the former compound. Similar effect of the charge in side chains on complex formation constants was also reported for complexes between indole derivatives and N-ethyl-theophylline nicotinamide⁶, and between tryptophan derivatives and N-methylnicotinamide⁵.

The magnitudes of ϵ 's are in order of TA > Try > In > In.Ac, which is the reverse of that of K 's. This relationship can be interpreted as involvement of contact charge transfer. Orgel and Mulliken²⁰ proposed that, in addition to absorptivity of a complex, the random encounters of donor and acceptor (contact charge transfer) also contribute to the apparent molar absorptivity of the complex, and the contribution of "contact" absorption is inversely proportional to K . However, the exact relationship between ϵ and $1/K$ was not revealed in this study. This might reflect the sensitivity of the contact charge transfer and the geometry of a complex on the nature of side chains of indole derivatives.

Logarithms of complex formation constants (K) obtained in water were plotted against $1/T$ in Figure 3, and enthalpies of the complex formation (ΔH) were evaluated from slopes of the graphs. ΔG and ΔS of complex formations were also calculated from corresponding K and ΔH values employing equations 2 and 3. These results were listed in Table 1. The thermodynamic parameters listed in Table 1 are those of typical weak charge transfer interactions.

The differences in ΔH 's among indole derivative-MV²⁺ complexes as shown in Table 1 are of particular interest. It is expected that the side chains of indole derivatives interact with MV²⁺ electrostatically as well as sterically, in addition

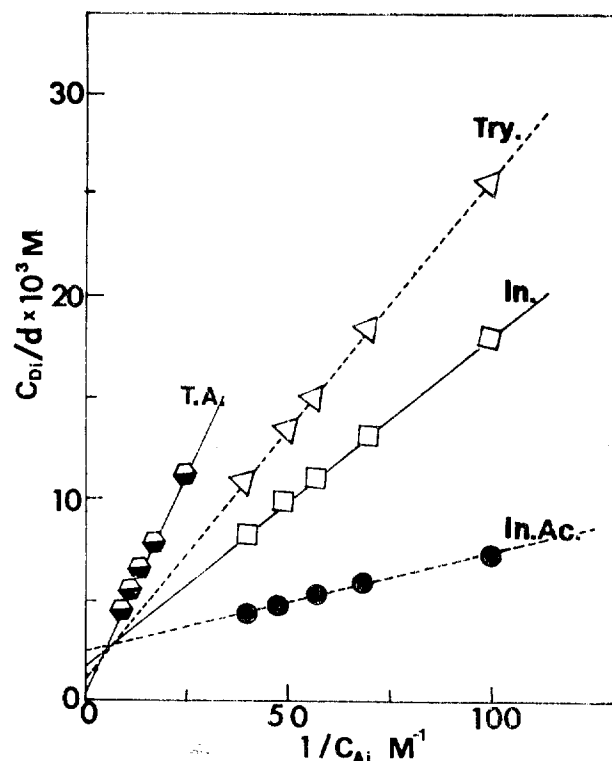


Figure 2. Plots of complex formation data of MV²⁺-indole derivatives according to Eq. 1. Data were taken in water at 20°C at 390nm for solutions containing 2.5×10^{-3} mole/l indole derivatives varying MV²⁺ concentration.

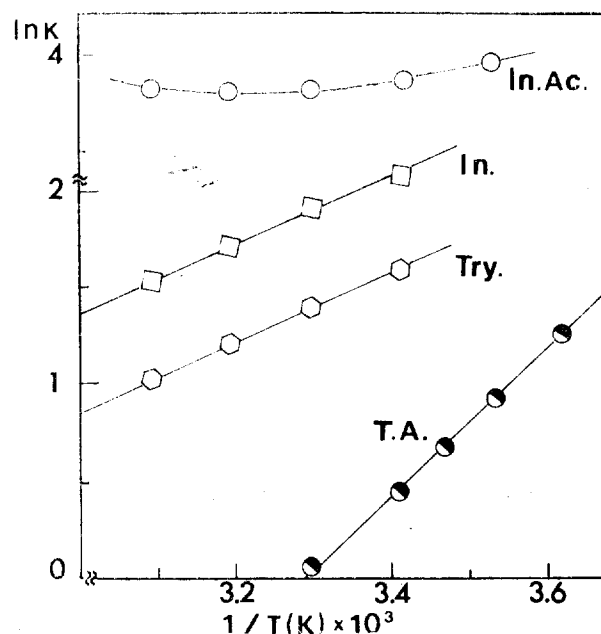


Figure 3. Variations of complex formation constants in water with temperature.

to the charge transfer interaction. Considering electrostatic interaction, indole acetate might form the most stable complex and $-\Delta H$ of the complex formation could be the greatest. On the other hand, tryptamine is expected to form the least stable complex with the smallest $-\Delta H$

value. However, our results in Table 1 reveal that $-\Delta H$ is the greatest in case of tryptamine and the smallest in indole acetate. This finding could be rationalized by solvation of side chains in H_2O medium. Both COO^- and NH_3^+ groups of indole acetate and tryptamine, respectively, are expected to be highly solvated. When indole acetate forms a complex with MV^{2+} , COO^- group may overlap with the positively charged MV^{2+} leading to desolvation of the COO^- group. The enthalpy change associated with this process could be positive, but the entropy of desolvation might be large enough to overcome this enthalpy increase to result in large decrease in Gibbs free energy. Thus, among indole derivatives studied, indole acetate forms the most stable complex, but $-\Delta H$ and $-\Delta S$ are the smallest. On the other hand, NH_3^+ group of tryptamine may stay away from bipyridinium ring of MV^{2+} , and association of H_2O and/or counter ions with the NH_3^+ group could result in large $-\Delta H$ and $-\Delta S$, compared to other compounds. However, in our experimental temperature range, the enthalpy decrease associated with side chain orientation in complex formation of tryptamine seems not large enough to compensate the decrease in entropy to provide extra stability of the complex in water.

For a series of indole derivative- MV^{2+} systems, no direct relationship between ΔG and ΔH is evident. However, ΔH values change approximately in a linear fashion with ΔS , as found in other systems^{8b}. The slope of ΔH versus ΔS plot (not shown) was $242^\circ K$, which represents the so-called "isokinetic temperature." This result suggests that stabilities of complexes studied in this report may be equal at $\sim -30^\circ C$, and below this temperature the order of stabilities would be $TA > Try > In > In. Ac.$

Except In. Ac., the interactions between indole derivatives studied and MV^{2+} were greatly enhanced in the presence of an anionic surfactant, sodium dodecyl sulfate (SDS). Such enhanced interactions could be easily noticed by deepening the color of solution (orange-yellow) by addition of SDS. The spectroscopic and thermodynamic properties of complex formation between indole derivatives and MV^{2+} were investigated in 0.015M SDS solution, which is above the critical micelle concentration (CMC) of SDS. The charge transfer bands in SDS solution exhibited a maximum at ca. 400nm, which is 10nm longer than those obtained in water. The shift in absorption maximum indicates that the microenvironment of the complexes is more hydrophobic in SDS solutions than in water.

The absorption spectra of indole derivatives and MV^{2+} mixtures in 0.015M SDS solutions were taken and analyzed by the same methods as those employed for data taken in water. Parameters of complex formation at $30^\circ C$ were summarized in Table 2. Comparing data in Tables 1 and 2, besides the great enhancement of complex stabilities, the reduction in molar absorptivities in SDS solutions also can be noticed. One exception to this is In. Ac., which bears negative charge. However, any relationship between the nature of side chains of indole derivatives and K , and between K and ϵ are not immediately evident from these data.

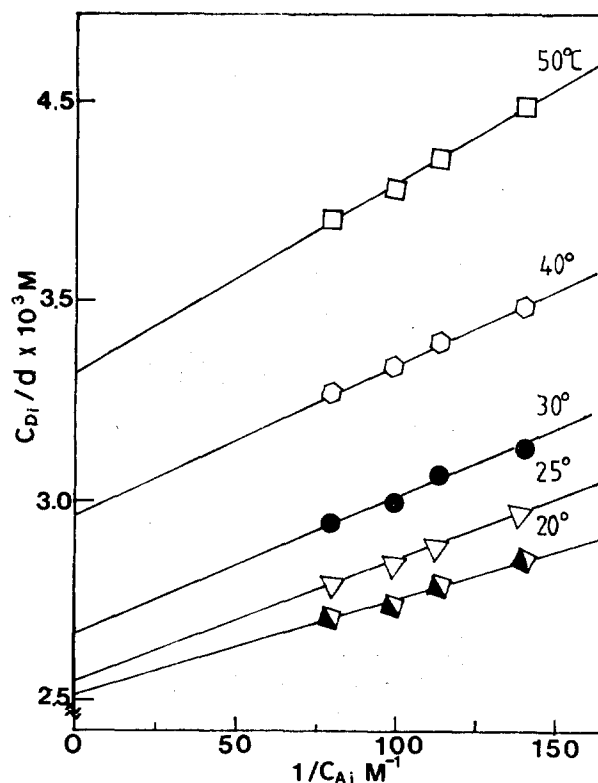


Figure 4. Plots of complex formation data of indole- MV^{2+} in 0.015M SDS according to Eq. 1 at temperature shown. Indole concentrations were $1.25 \times 10^{-3} M$ and absorption data were taken at 390nm.

The plots of complex formation data for indole- MV^{2+} system in 0.015M SDS were shown in Figure 4. This Figure shows that ϵ as well as K values decrease with increasing temperature. Other systems also reveal the same trend: ϵ decreases with temperature in nearly same proportion as indole- MV^{2+} . The reduced ϵ values in SDS solutions can, partly, be attributed to the absence of contact charge transfer in SDS solutions. The variations of complex formation constants with temperature in SDS solutions were graphed in Figure 5, and thermodynamic parameters of complex formations in the solutions were summarized in Table 2. Comparing Table 1 and 2, it can be noticed that ΔH values are insensitive to SDS or rather increased in SDS solutions. Table 1 and 2 also show that ΔS values in SDS solutions are positive, while those in water are negative. Only In. Ac. exhibits opposite trend. From these facts, it is concluded that the great enhancement of charge transfer interaction in SDS solutions is not an enthalpy effect, but results from increased entropy of the complex formation.

Many investigators attributed the enhanced charge transfer complexing in a surfactant solution to the local concentration effect by association of charged species in Stern region of ionic micelles.^{7,10} To clarify whether the SDS micelle formation is indeed directly related to the observed enhanced complexing in SDS solutions or not, the effect of SDS concentration on complex formation was studied and the results were shown in Figure 6. This figure indicates that the charge transfer complexing, measured as absorbance at 390nm,

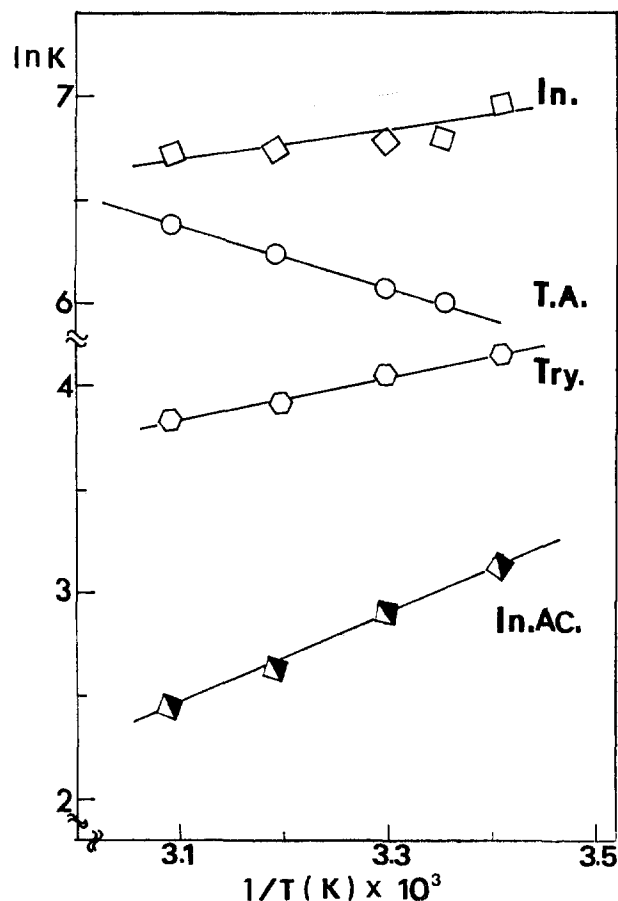


Figure 5. Variations of complex formation constants in 0.015M SDS with temperature.

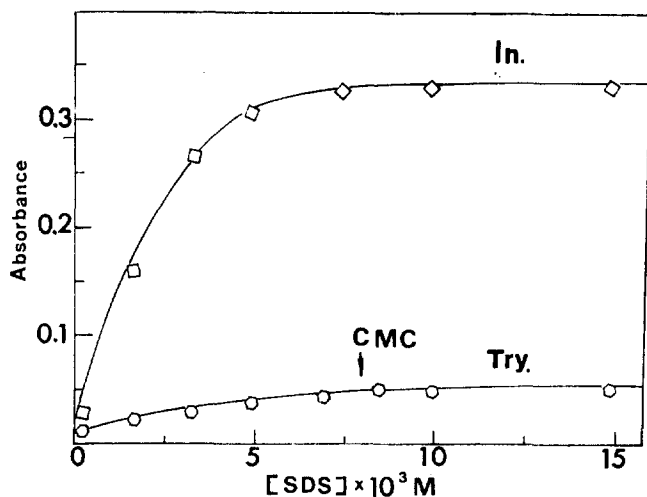


Figure 6. Effects of SDS on the absorbance at 390nm of indole derivatives ($1.25 \times 10^{-3} M$) and MV²⁺ ($2.5 \times 10^{-3} M$) mixtures at 20 °C. CMC of SDS in water is shown in Figure.

increases with SDS concentration in an approximately linear fashion at low SDS concentration and saturates near CMC of SDS²², $8.1 \times 10^{-3} M$. The same study could not be performed for tryptamine because of precipitation when [SDS] is lower than $5 \times 10^{-3} M$. Thus, the enhanced charge transfer interaction in SDS solutions can be ascribed to interaction properties of reactants with SDS molecules, rather than SDS micelles:

Martens and Verhoeven¹⁰ reported similar trend in 3-methylindole–MV²⁺ system, but they explained the result as micelle formation.

The strong electrostatic interaction between MV²⁺ and SDS even below CMC of SDS can reduce entropy of MV²⁺, and provide hydrophobic region in which hydrophobic indole derivatives can easily incorporate to interact with MV²⁺. In case of tryptamine, the association of this compound with SDS leading to formation of mixed aggregates of tryptamine–SDS and MV²⁺–SDS is also possible. These mechanisms can successfully explain the greatly increased stabilities of complexes in the presence of SDS.

The stability of indole derivative–MV²⁺ complexes in SDS solutions might be governed by charge and hydrophobicity of the indole derivatives. Indole, which is more hydrophobic than tryptophan can be more easily incorporated into SDS–MV²⁺ resulting higher stability of the complex formed. On the other hand, the negatively charged indole acetate forms the least stable complex.

Recently, Baxendale and Rodgers²¹ reported the presence of tris (2,2'-bipyridyl) ruthenium(II)–SDS clusters below CMC of SDS, which behave as micelle in that they incorporate aromatic molecules. The interaction between MV²⁺ and SDS could form clusters similar to those of Ru (bpy)₃²⁺–SDS. This cluster may provide hydrophobic regions for indole derivatives in complexing with MV²⁺. The effect of SDS described in this paper and by Baxendale and Rodgers²¹ implies that the generally accepted effects of micelles on chemical equilibria and reaction rates¹⁸ could also be realized even below CMC of a surfactant by the cluster formation. This mechanism may play important roles in biological systems and works on this aspect are under progress.

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Reactions of Aryl Halides with Phenoxides and Alkoxides by Phase Transfer Catalysis

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The reaction of aryl halides with phenoxides and alkoxides were investigated under phase transfer catalytic conditions. 2, 4-Dinitro- and 4-nitrohalobenzenes reacted readily with phenoxides in NaOH(aq)-benzene in the presence of Bu₄N⁺Br⁻, affording the products quantitatively. Although the aryl halides did not react with alkoxides under the same condition, the reactions were completed within 2 hours at room temperature when conducted under solid-liquid phase transfer catalytic condition. The reactivity of aryl halides was in the order, Ar=2, 4-dinitrophenyl > 4-nitrophenyl, and X=F > Cl, consistent with the S_NAr mechanism. The reactivity of oxyanions increased with the change of reaction condition from liquid-liquid to solid-liquid phase transfer catalysis. The results were explained with the concentration and the degree of hydration of the anion in benzene.

Introduction

Phase transfer catalysis (PTC) has been used in a variety of organic reactions^{1,2}. In nucleophilic substitution reactions, this technique has been most successfully applied to the Williamson ether synthesis. The reactions of alkyl halides with alkoxides or phenoxides to give ethers show significant improvement in convenience, reaction rate, and yield when conducted under phase transfer catalytic conditions^{1a,2a}. However, the synthesis of aryl ethers by phase transfer catalyzed nucleophilic aromatic substitution reaction has not been reported.

Recently, we studied the reactions of 2, 4-dinitrohalobenzenes with phenoxides in aqueous NaOH-benzene mixture as a model for the phase transfer polymerization³. The reactions proceeded readily at room temperature, affording the diaryl ethers quantitatively. As an extension to this work, we have investigated the reactions of aryl halides with phenoxides and alkoxides under liquid-liquid (L-L) and solid-liquid (S-L) phase transfer catalytic (PTC) conditions (Eq. 1).



Ar=2, 4-dinitrophenyl(1), 4-nitrophenyl(2)

X=F(a), Cl(b)

ROH=phenols, alcohols

PTC=NaOH(aq)/Bu₄N⁺Br⁻/C₆H₆,

NaH(s)/Bu₄N⁺Br⁻/C₆H₆

We have compared the reactivity of aryl halides, phenoxides, and alkoxides under various conditions. The concentration of oxyanions in benzene was also determined to provide an explanation for the relative reactivity of the anions.

Experimental

Melting points, uncorrected, were determined on a Electrothermal melting point apparatus. Proton nmr was recorded on a Varian Model EA-360A spectrometer and infrared spectra were obtained either with JASCO Model DS-710G or with Perkin-Elmer Model 710B spectrophotometer. For titration of the oxyanion concentration, Chemtrix