Effects of Polyelectrolytes on the Charge Transfer Complexing between Indole Derivatives and Methylviologen: Hydrophobic and Electrostatic Interactions

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The effect of anionic polyelectrolytes, poly(styrenesulfonate) (PSS) and poly(vinylsulfonate) (PVS), on the charge transfer complexing between indole derivatives and methyl viologen(MV^{++}) cation was investigated. The results were compared with effect of NaCl and an anionic surfactant, sodium dodecylsulfate (SDS). Both PSS and PVS enhanced the complex formation of neutral species (indole and indole acetate at low pH), zwitter ionic tryptophan, and positively charged tryptamine and tryptophan at low pH with MV^{++}. This result was attributed to the contribution of hydrophobic interaction, in addition to electrostatic interaction. The enhancing effect of PSS was much higher than that of PVS reflecting the higher hydrophobicity of PSS. The interaction between indole acetate anion and MV^{++} was greatly reduced by addition of PVS and PSS. The higher charge density of PVS was appeared as greater reducing effect indicating the importance of electrostatic force in this case. In all cases, the effect of polyelectrolytes showed maxima, and further addition of PVS and PSS decreased the effect. This behavior was explained in terms of distribution of indole derivatives and MV^{++} in domain of polyanions. The complex formation constants and molar absorptivities of complexes were determined, and the values were compared with those in water and SDS solutions.

Introduction

The effects of polyelectrolytes on chemical reactions and interactions have long attracted much attention of various fields of chemistry and the related disciplines.[1] Particularly, the resemblance of polyelectrolyte solutions to many biological fluids has yielded a large volume of studies on many systems of biological interests in the solutions. In most cases, the profound effects of polyelectrolytes have been attributed to electrostatic interactions between polyions and reacting or interacting species. However, the contribution of hydrophobic interaction was also recognized when reactants are large hydrophobic ones, such as triphenylmethane dyes.[2,3]

In view of the importance of charge transfer complexing in biological systems, the complex formation of indole and its derivatives, which are regarded as one of the most important electron donor moieties in biomolecules, with various electron acceptors has been investigated.[4] The influence of polyelectrolytes on charge transfer complexing of indole derivatives with coenzyme model compounds of nicotinamide adenine dinucleotide (NAD^+)[5] and flavin mononucleotide (FMN)[6] was reported. The strong influence of polyelectrolytes on these interionic interactions was explained by the "secondary salt effect", suggesting that electrostatic forces are most important to the stability of the complexes.

In an earlier article,[7] the authors' group showed that the interaction of indole and its derivatives with methyl viologen cation (MV^{++}) in the presence of an anionic surfactant, sodium dodecyl sulfate (SDS), is strongly affected by both hydrophobic and electrostatic interactions. This result implied that a polyelectrolyte would also influence the complex formation by hydrophobic interaction, provided that the polyelectrolyte is hydrophobic. Thus we chose poly(styrenesulfonate) (PSS) which is regarded as a hydrophobic polyelectrolyte,[2,3,8] and compared the effect of this polyelectrolyte to that of poly(vinylsulfonate) (PVS) on the complexation between indole derivatives and methyl viologen to clarify the hydrophobic interactions in the complexes in detail.

Experimental

Sodium poly(styrenesulfonate) (PSS) was obtained from Polyscience and recrystallized from ethanol. The 25% (w/v) suspension of sodium poly(vinylsulfonate) (PVS) purchased from Polyscience was diluted 5 times with distilled water, stirred overnight, and then filtered to obtain clear solution. The concentrations of PSS and PVS solutions were determined by passing *ca.* $0.1M$ solutions through acidified cation exchange resin columns, and titrating the released H^+ in eluents with NaOH solution. The concentrations are expressed in terms of molar concentrations of sulfonate groups.

Indole (Kanto), indole acetate (Gibco) and DL-tryptophan (BDH Chemicals) were recrystallized from ethanol. Indole acetate was stored in a freeze before use. Tryptamine (Tokyo Kasei) was converted into tryptamine-HCl by dissolving it in HCl solution and then evaporating water and excess HCl. The salt was recrystallized from ethanol-ethyl acetate (1:1). Preparation of methyl viologen dichloride ($MV^{++}2Cl^-$) was described elsewhere.[7]

Absorption spectra were taken on a Beckman DU-8B UV-Vis spectrophotometer with mixing tandem double cells of light pathlength of 0.882cm, which are partitioned into two equal compartments. Unless otherwise specified, they were taken at 25°C. Solutions of MV^{++} and indole derivatives containing desired amounts of electrolytes at given pH were prepared. One solution was placed in one half, and the other solution was placed in the other half of a reference cell. Both sides of a sample cell was filled with the mixture of above two solutions, and the

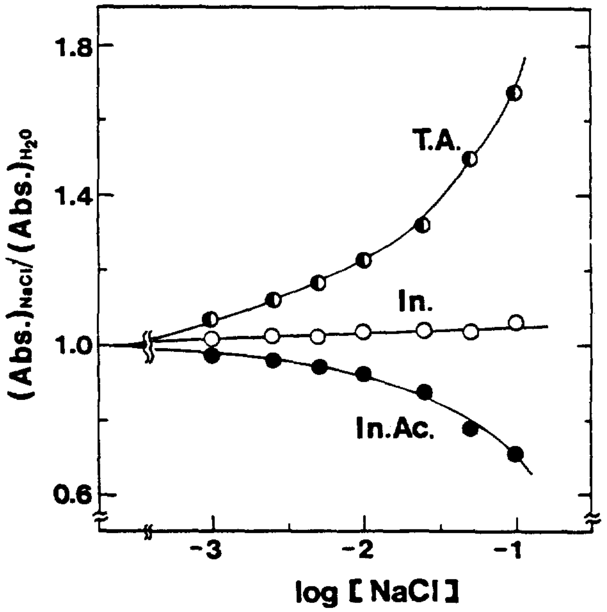

Figure 1. Relative changes in absorbance at 390 nm of 5 mM indole derivatives-5 m*M* MV^{++} mixtures with NaCl concentration at 25°C.

difference spectra of the complex formation were taken. The pH's of solutions were adjusted with sodium cacodylate/HCl (final concentrations were 1mM). The complex formation constants (K) and molar absorptivities (ε) of the complexes were calculated from spectral data taken at 390nm by Benesi-Hildebrand method employed in a previous report.[7]

Results and Discussion

The difference spectra of the complex formation between indole derivatives and MV^{++} showed a diffused band with a peak at about 390 nm as reported.[7] The shape and position of the band were virtually same for all indole derivatives-MV^{++} complexes studied and unchanged with addition of electrolytes. However, the addition of electrolytes resulted in change of the magnitude of absorbance of the bands, which depended largely on the charge of indole derivatives and nature of electrolytes, suggesting the sensitivity of the stabilities of the complexes on these factors.

Figure 1 shows the relative changes in absorbances at 390 nm of 5m*M* indole derivatives-5m*M* MV^{++} mixktures with NaCl concentrations. The absorbances of the mixtures in the absence of NaCl were 0.13 for indole, 0.38 for indole acetate and 0.04 for tryptamine-MV^{++}. The solutions of these mixtures were adjusted to pH 7 for indole and for indole acetate (pK$_a$ = 4.75) and 3 for tryptamine (pK$_a \simeq$ 10.5) to yield neutral, anionic and cationic species, respectively.

The changes of absorbances reflect the changes of degree of complexation, *i.e.*, complex formation constants (K). However, the dependencies of K's on NaCl cannot be directly evaluated from this figure, because the molar absorptivity (ε) of a complex decreases with increasing K value (see Table 1). This figure shows typical salt effects on interionic interactions, and the results accord well with our previous ascertainment that electrostatic forces contribute greatly to the stabilities of complexes between indole derivatives and MV^{++}.[7]

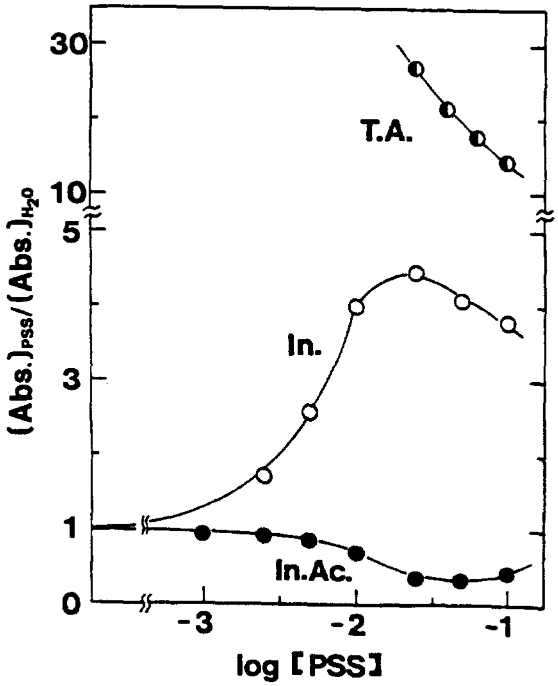

Figure 2. Variations in absorbance at 390 nm of 5 m*M* indole derivatives-5 m*M* MV^{++} mixtures with PSS concentration. The pH of indole acetate was 7, and that of tryptamine was 3. Temperature of indole was 35°C, and others were 25°C.

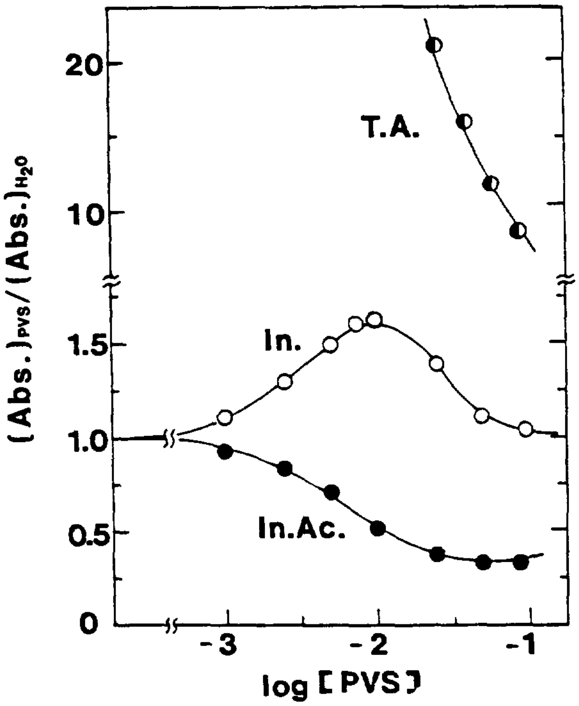

Figure 3. Variations in absorbance of indole derivatives-MV^{++} mixtures with PVS at 25°C. Other conditions are the same as in Figure 2.

The effects of polyelectrolytes, PSS and PVS, on the complex formations were found to be quite different from those of NaCl. Figures 2 and 3 show the effects of PSS and PVS, respectively. The most significant difference between NaCl and polyelectrolytes was observed in the effects on the interaction between neutral indole and MV^{++}. In contrast to NaCl, the addition of the polyelectrolytes strongly enhanced the complex formation, and showed a maximum in the relation between the stability of the complex and polyelectrolyte concentration. A explanation about the effect of polyelectrolytes on the indole-MV^{++} system is hydrophobic interaction. The polyelectrolytes and possibly polyelectrolyte-MV^{++} aggregates can provide hydrophobic regions, in which the hydrophobic indole can be incorporated and effectively interacts with MV^{++}.

The hydrophobic interaction is supported by the difference in the effects of PSS and PVS. PSS bears phenyl group and is more hydrophobic than PVS. The greater hydrophobicity of PSS, compared to PVS, seems to appear as greater stability of the indole-MV^{++} complex in PSS solution. The strong association of indole with MV^{++} in PSS provided by the hydrophobicity of the macroanion resulted in precipitate formation at low temperature and low PSS concentration. For example, precipitates were formed when $[PSS]<10^{-2}M$ at 25°C, and the indole-MV^{++} data in figure 2 were taken at 35°C.

The large enhancing effects of PSS and PVS on the complex formation between positive ions, tryptamine and MV^{++} at pH = 3, can also be seen in Figures 2 and 3. The data in these figures for the mixture were taken with polyelectrolyte concentrations above 25m*M*, because of precipitate formation below the concentration. The effects of PSS and PVS on tryptamine-MV^{++} interaction reflect, in part, the electrostatic contribution of the polyelectrolytes. However, since both PVS and PSS are completely sulfonated, the charge density of PVS is higher than that of PSS, and PVS is expected to influence the complex formation in greater extent than PSS from electrostatic point of view. Thus, the observation of much greater enhancement of the complex formation in PSS than in PVS solution can be regarded as an evidence that hydrophobic interaction also plays an important role in the complex formation.

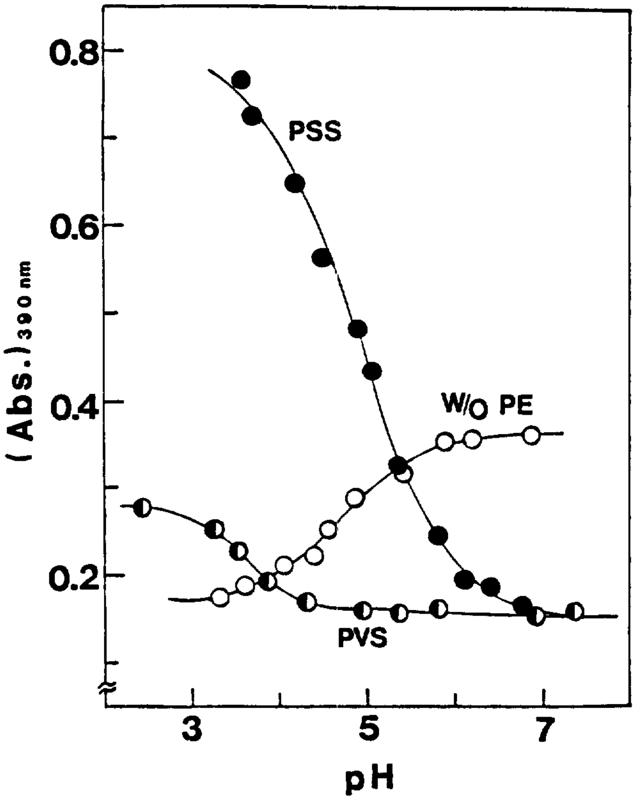

Figure 4. Changes of absorbance of 5 m*M* indole acetate-5 m*M* MV^{++} mixtures in the absence (O) and presence of 25 m*M* polyelectrolytes with pH at 25°C.

As expected from the negative charge of indole acetate at pH = 7, the complexation of the anion with MV^{++} decreased by addition of PVS and PSS. The larger effects of polyelectrolytes than that of simple electrolyte NaCl can be ascribed to the high potential field of the macroanions.[6] In this case, the effect of PVS was slightly larger than that of PSS. This accords well with the difference in the charge densities of the polyanions, and indicates that the effect of the polyelectrolytes on the complex formation is mainly electrostatic.

In contrast to the NaCl effects, the effects of PVS and PSS on indole derivatives-MV^{++} interactions exhibit maxima, and further addition of the polyelectrolytes decreases the enhancing or reducing effects on the complex formations. For indole-MV^{++} and tryptamine-MV^{++} systems, the interacting species are strongly bound to the polyanions by electrostatic and/or hydrophobic interactions. As concentrations of polyelectrolytes are increased, the average number of donor-acceptor pairs decreases. This leads to decreased charge transfer interaction. Similar explanation cannot be applied to indole acetate-MV^{++} systems, in which negatively charged indole acetate anion stays away from domains of polyanions by electrostatic force. The excluded volume effect of macroions resulting in higher effective concentration of indole acetate at high polyelectrolyte concentration can explain the increased a ssociation of indole acetate with MV^{++} at high polyelectrolyte concentration.

The hydrophobic and electrostatic contributions of polyelectrolytes on the indole derivatives-MV^{++} interactions were clearly revealed in optical titrations of indole acetate-MV^{++} mixture (Figure 4). In the presence of PSS, the absorbance of the given mixture increased sharply with decreasing pH near pK_a. The opposite pH dependency of absorbance was shown in the absence of polyelectrolytes. The much smaller absorbance value of indole acetate-MV^{++} mixture at low pH in PVS than in PSS solution also confirms the large contribution of hydrophobic

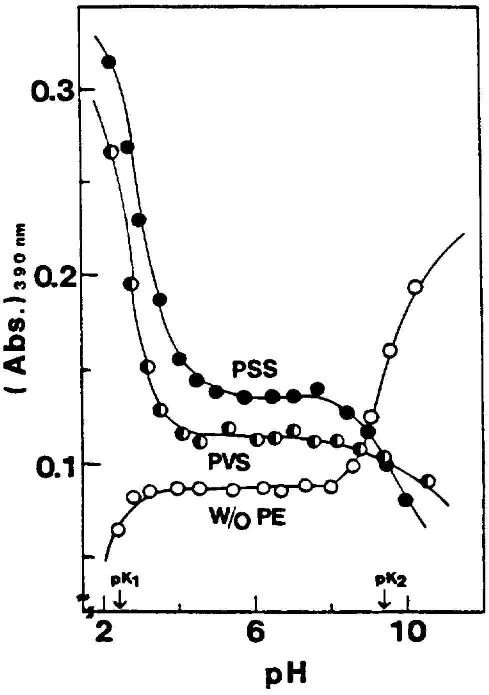

Figure 5. Changes of absorbance of tryptophan-MV^{++} mixtures with pH. Conditions are the same as in Figure 4.

TABLE 1: Molar Absorptivities and Complex Formation Constants of Indole Derivatives with MV^{++} in Various Media at 25°C

Donor	H_2O^a		PVS^b		PSS^b		$0.015\dot{M}$ SDS^a	
	K	ε	K	ε	K	ε	K	ε
Indole	8.1	741	27^c	—	152	377	870	372
Indole acetate (pH = 7)	47	422	5.5^c	—	12	685	18	760
Tryptamine (pH = 3)	1.6	1540	56	400	99	392	462	310

All values are taken at 390 nm and in $cm^{-1}M^{-1}$. K values are in M^{-1}. [a]taken from reference 13; [b]PVS and PSS concentrations are 50 m*M* for tryptamine, and 25 m*M* for others; [c]estimated from absorbance values of 5 m*M* donor and 5 m*M* MV^{++} mixtures (see text for detail).

interaction between neutral species, indole acetate, and MV^{++} in PSS solutions.

Similar pH effect on the complex formation was also studied for tryptophan-MV^{++} mixtures and shown in Figure 5. The pH dependencies of absorbance of the charge transfer band of tryptophan-MV^{++} mixture match well with acid-base property of tryptophan, of which pK_1 is 2.38 and pK_2 is 9.39. The effects of PVS and PSS on tryptophan-MV^{++} mixture are similar to those on tryptamine-MV^{++} when $pH<pK_1$, on indole acetate-MV^{++} when $pH>pK_2$ and on indole-MV^{++} at pH 4-8, reflecting the charge of tryptophan which varies with pH. However, the difference in the enhancing effect between PVS and PSS is much smaller in tryptophan-MV^{++} than in tryptamine-MV^{++} or indole-MV^{++} systems. The enhancement of complexation by polyelectrolytes at pH 4-8, where tryptophan behaves as a zwitter ion, is also much smaller than that in indole-MV^{++}. These results seem to reflect less hydrophobic character of tryptophan than indole as explained for SDS effects on indole derivatives-MV^{++} complexation.[7]

A series of difference spectra of complex formation with varying concentration of MV^{++} were taken at given pH, given concentrations of indole derivatives and polyelectrolyte. The Benesi-Hildebrand plots,[7] $l\cdot C_{Di}/\text{Abs.} = 1/\varepsilon + 1/(K\cdot\varepsilon\cdot C_{Ai})$, of absorption data at 390nm yielded good straight lines, except for indole-MV^{++} and indole acetate-MV^{++} in PVS solutions. The K and ε values of the complex formations were determined from the plots and listed in Table 1. K values of indole-MV^{++} and indole acetate-MV^{++} in PVS solutions were estimated from absorbance data taken for 5 mM donor and 5 mM MV^{++} mixtures assuming that ε values are the same as those in PSS solutions: as ε values of a given type of charge transfer complex decreases with increasing K value, the K of indole-MV^{++} complexation would be slightly over-estimated while that of indole acetate -MV^{++} is underestimated. The K and ε values of complex formations in water and 0.015 M SDS are also included in Table 1 for comparison.

Table 1 reiterates and summarizes our conclusions on the polyelectrolytes effects on indole derivatives-MV^{++} interaction. Both PVS and PSS strongly enhance the charge transfer interactions of neutral indole and positively charged tryptamine with MV^{++}. The effect of PSS on these interactions is much larger than that of PVS because of greater hydrophobicity of PSS. The reducing effect of PVS for the interaction between negatively charged indole acetate and MV^{++} is greater than that of PSS due to higher charge density of the polyanion. This table also shows close similarity between hydrophobic anionic polyelectrolyte, PSS, and anionic surfactant, SDS, on their effects on the charge transfer complex formations between indole derivatives and MV^{++}.

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