

Binding of Hydrophobic Counterions by Polyelectrolyte and Their Hydrophobic Association around Polyion

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ABSTRACT: The binding of *p*-ethylbenzenesulfonate ions (EBS^- 's) by poly(allylammonium) cation (PAAH^+) and their hydrophobic association around PAAH^+ have been investigated in aqueous solutions through ^1H NMR and Cl^- activity measurements. At a constant PAAH^+Cl^- concentration, all ^1H NMR signals of EBS^- exhibited up-field shift (ring current shift) with the increase in the NaEBS concentration. However, any chemical shift change did not observe in each signal of PAAH^+ . These results show that EBS^- 's atmospherically bound to PAAH^+ associate each other due to their hydrophobic interaction. The association of EBS^- 's is depressed by the decrease in the charge density of the polyion and broken by the addition of another simple salt (NaCl) to the $\text{PAAH}^+\text{Cl}^-/\text{NaEBS}$ system. Moreover, it was found that the counterion exchange from Cl^- 's to EBS^- 's around PAAH^+ is efficiently promoted by the association of EBS^- 's.

KEY WORDS Poly(allylammonium) Cation / Hydrophobic Counterion / Atmospheric Binding / Association of Hydrophobic Counterions / Counterion Exchange /

The properties of polyelectrolyte solutions depend, very much, on the electrostatic interactions between charges fixed along the polymer backbone. These interactions are also very sensitive to the presence of counterions. The addition of electrolyte to the medium screens out the repulsive interactions between charges through the counterion binding and/or condensation around the polyion with a high electrostatic potential. This counterion binding (condensation) is an important feature of polyelectrolyte solutions.¹ Thus, the solution properties are considerably modified accompanying the changes in the chain conformation, water structure, degree of hydration around the polyion, and so on. On the one hand, when hydrophobic salt is used as an added electrolyte,²⁻⁴ the hydrophobic counterion, which has both hydrophilic and hydrophobic moieties, may have a different influence upon

these electrostatic interactions. Especially, interactions among hydrophobic counterions should be also taken into account when polyion/hydrophobic counterion system is examined, although this interaction would be negligible in the absence of polyion.⁵

In the previous work,⁶ the interaction of three hydrophobic ions, *i.e.*, benzenesulfonate (BS^-), *p*-methylbenzenesulfonate (MBS^-), *p*-ethylbenzenesulfonate (EBS^-) with PAAH^+ cation was investigated by ^1H NMR and viscosity measurements. It was found that EBS^- 's accumulated electrostatically around the polyion can associate each other through their hydrophobic interaction. But, BS^- and MBS^- , which are slightly less hydrophobic than EBS^- , did not show any sign of such hydrophobic association. This indicates that the hydrophobicity of counterion plays an important role in the association of counterions

around polyion. However, the mutual relation of the attractive interaction between polyion and counterions, the repulsive interaction between charges along the chain or counterions, and the hydrophobic interaction between counterions has not been cleared in details yet.

Under these circumstances, we present here a contribution to the understanding of the binding and/or association of hydrophobic counterions around the polyion. We pursued ^1H NMR and Cl^- activity measurements on the poly(allylammonium) cation/ EBS^- system in order to elucidate the effects of the charge density of the polyion and the coexistence of another simple salt (NaCl) on these binding and/or association of hydrophobic counterions around the polyion.

EXPERIMENTAL

Materials

Poly(allylammonium) chloride (PAAH^+Cl^-) used in this study was obtained from Nitto Boseki Co., Ltd. It was purified by reprecipitation with methanol contained 0.5 M HCl and dried *in vacuo* at room temperature for one week.⁷ The weight-average molecular weight of PAAH^+Cl^- was determined by light scattering to be 1.0×10^5 in 0.2 M NaCl . Sodium *p*-ethylbenzenesulfonate (NaEBS) of analytical grade was purchased from Tokyo Kasei Co., Ltd., which was used without further purification. D_2O (99.9%) was obtained from Matheson, U.S.A. Company. NaOD (99.5%, Merck) was used to control the neutralization α of PAAH^+ . For chloride ion activity measurement, deionized and doubly distilled water was used as solvent. Concentrations were expressed in C_p (monomer mol dm^{-3}) for polymer and C_s (mol dm^{-3}) for salts.

Measurements

^1H NMR experiments were performed at 270 MHz on a JEOL GSX270 spectrometer in pulse Fourier Transform mode (Instrument Center for Chemical Analysis, Hiroshima

University). The measurements were carried out at $27 \pm 1^\circ\text{C}$ in D_2O (99.9%). Chemical shift was given in ppm relative to the external tetramethylsilane (TMS) standard.

Chloride ion activity measurement was carried out on an Orion 940 ion meter equipped with a chloride ion selective electrode (Orion model 94 17B) and a double junction reference electrode (Orion model 90 02). Potential measurements were performed at a constant temperature ($25 \pm 0.1^\circ\text{C}$) under nitrogen atmosphere. Calibration curves for Cl^- ion were determined before each data set with standard solutions of sodium chloride. All potentials were taken after a constant readings were obtained (20–30 minutes).

RESULTS AND DISCUSSION

Binding of EBS^- 's by PAAH^+ and Their Hydrophobic Association around PAAH^+

Two models are generally accepted for the interaction between polyion and hydrophobic counterions.⁸ One of them is the electrostatic interaction and the other is the hydrophobic interaction between the non-polar moieties of the polyion and the bound counterions. The interaction between polyion and hydrophobic counterions can be successfully probed by NMR spectroscopy. Figure 1 shows the NaEBS concentration dependence of the ^1H NMR spectra of the PAAH^+Cl^- ($C_p = 1.17 \times 10^{-2}$ M)- NaEBS system in D_2O solution. Any chemical shift change was not observed in each signal of PAAH^+ . This result indicates that EBS^- 's are bound to the polyion not so as to give any change in the magnetic environment of polyion protons. Accordingly, it seems that the interaction between PAAH^+ and EBS^- 's is neither the direct hydrophobic interaction nor the strong electrostatic interaction such as site binding. Because, upon the above interactions, ^1H chemical shift of the polyion protons should be changed. Probably, the interaction between PAAH^+ and EBS^- 's may be such an atmospheric binding as interposing some

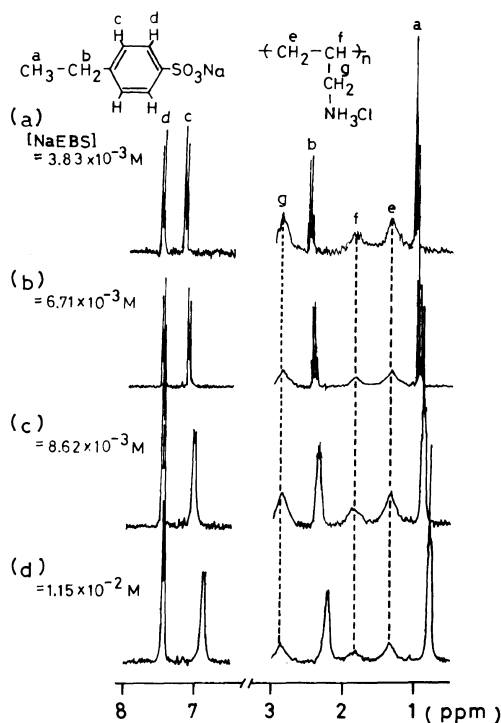


Figure 1. NaEBS concentration dependence of the ^1H NMR spectra of NaEBS and PAAH^+Cl^- in D_2O solution. $[\text{PAAH}^+\text{Cl}^-] = 1.17 \times 10^{-2} \text{ M}$.

hydration layers between PAAH^+ moieties and EBS^- 's. The presence of such hydration layer between the charged backbone and the electrostatically accumulated counterions is verified from the recent neutron and X-ray scattering studies on poly(methacrylic acid) solution.⁹

On the other hand, each signal of EBS^- exhibited an up-field shift with increasing concentration of NaEBS. In addition, a line broadening of EBS^- proton signals was observed at the higher concentrations of NaEBS ($C_s = 8.62 \times 10^{-3} \text{ M}$ and $C_s = 1.15 \times 10^{-2} \text{ M}$). Similar up-field shift and line broadening have never been observed in the systems containing less hydrophobic counterions: $\text{PAAH}^+\text{Cl}^-/p$ -methylbenzenesulfonate, $\text{PAAH}^+\text{Cl}^-/\text{benzenesulfonate}$ and $\text{PAAH}^+\text{Cl}^-/n$ -butanesulfonate.⁶ These results indicate that the up-field shift of EBS^- signals is due to the inter-

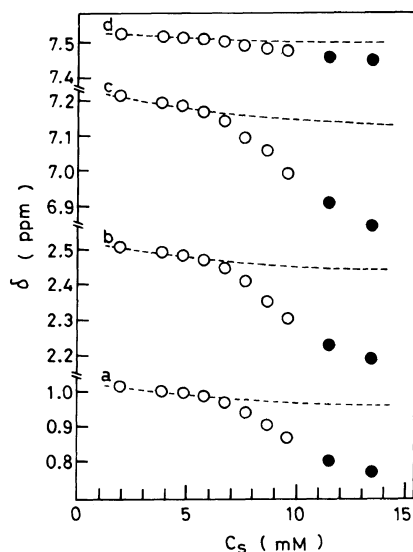


Figure 2. NaEBS concentration dependence of ^1H chemical shift of NaEBS in D_2O solution containing $1.17 \times 10^{-2} \text{ M}$ PAAH^+Cl^- . The small letters indicate a, methyl-; b, methylene-; c, *meta*-; and d, *ortho* protons. The solid symbols indicate a turbid solution. Dashed lines show the calculated values, where $\delta_m = 1.02$, $\delta_d = 0.80$ for methyl proton, $\delta_m = 2.51$, $\delta_d = 2.25$ for methylene proton, $\delta_m = 7.21$, $\delta_d = 6.92$ for *meta*-proton, $\delta_m = 7.52$, $\delta_d = 7.45$ for *ortho*-proton and $K = 20$.

molecular ring current effect of benzene rings of associated EBS^- 's around PAAH^+ rather than the binding of EBS^- 's to PAAH^+ . In addition, it can be presumed that the stacking interaction between benzene rings and the hydrophobicity of counterion play an important part in the association of counterions around the polyion. In the absence of PAAH^+Cl^- , the sharp ^1H NMR signals of EBS^- were observed, showing that EBS^- itself does not exhibit self-association in pure water. Accordingly, it is suggested that the association of EBS^- 's is induced by the presence of PAAH^+Cl^- . And, EBS^- 's associate each other due to their hydrophobic interaction including the stacking interaction around PAAH^+ .

Figure 2 shows how the ^1H chemical shift of EBS^- in the $\text{PAAH}^+\text{Cl}^-/\text{NaEBS}$ system varies with the NaEBS concentration. Dotted curves represent the results calculated by a

simple equilibrium model (this is discussed in detail later). The change of ^1H chemical shift of EBS^- is small at low concentration of NaEBS , but it becomes very large with increasing the NaEBS concentration. The precipitation of the polymer also takes place at higher NaEBS concentrations. The accumulation of EBS^- around the polyion with increasing the NaEBS concentration leads to the favorable hydrophobic association of EBS^- 's. In addition, as mentioned above, the hydrophilic envelope (NH_3^+ groups) of PAAH^+ atmospherically interacts with the ionic head (SO_3^- group) of the counterion directing its hydrophobic tail to the outside.¹⁰ Therefore, the environments around PAAH^+ become more hydrophobic as a whole, which leads to precipitation.

The order of magnitude of the ring current shift is *m*-proton > methylene proton > methyl proton > *o*-proton. The change of the chemical shift of *o*-proton is fairly smaller than that of other protons. The magnitude and order of the ring current shift are highly dependent on the mutual orientation of the aromatic ring planes of the associated EBS^- 's. As is shown in the previous paper,⁶ the structure of associated EBS^- 's is assumed as follows. The aromatic rings are overlapped each other, skewing by about 60° due to the charge repulsion of sulfonate groups and the steric hindrance of ethyl groups. The smaller change in chemical shift of *o*-proton may be attributable to the effect of the magnetic anisotropy of $\text{S}=\text{O}$ double bond in the sulfonate group, which probably leads to a rather decreased magnetic shielding.¹¹

Effect of the Charge Density of Polyion on the Association of EBS^- 's

Figure 3 shows the effect of the charge density of the polyion on the ^1H chemical shift of EBS^- in $\text{PAAH}^+\text{Cl}^-/\text{NaEBS}$ system. The abscissa in Figure 3 represents the degree of neutralization α of PAAH^+ ($-\text{NH}_3^+ \rightarrow -\text{NH}_2 + \text{H}^+$). The counterion binding to poly-

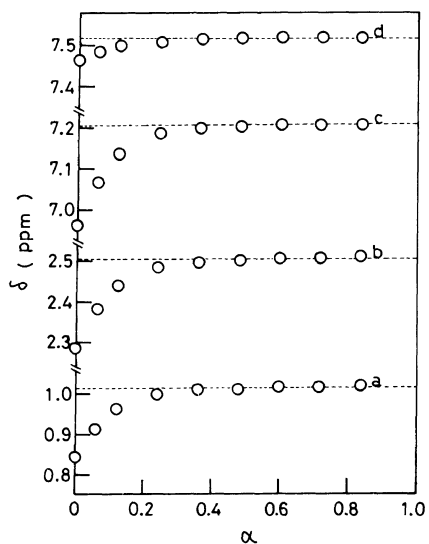


Figure 3. The effect of the charge density of PAAH^+ on the ^1H chemical shift of $8.92 \times 10^{-3} \text{ M NaEBS}$ in the presence of $1.17 \times 10^{-2} \text{ M PAAH}^+\text{Cl}^-$. The small letters indicate a, methyl-; b, methylene-; c, *meta*-; and d, *ortho*- protons.

ion depends on its charge density.¹² At $\alpha=0$, PAAH^+ is a fully charged vinylic polyelectrolyte forming a high electrostatic field around it. Therefore, the added EBS^- 's are accumulated around the PAAH^+ moieties. This accumulation of the counterions by the polyion induces the hydrophobic association of the counterions. However, as the charge density of the polyion decreases (α increases), ^1H signals of EBS^- exhibit a down-field shift from the higher position at $\alpha=0$. And, even at $\alpha=0.4$, they shift back to each original position as in the absence of PAAH^+Cl^- . This result shows that the association of EBS^- 's is not induced under the condition that the charge density of the polyion is low (for example $\alpha > 0.4$). On the other hand, according to Mannings's counterion condensation theory,¹³ since the charge density parameter ξ is 1.71 at $\alpha=0.4$, some counterions should be condensed around the polyion. However, the present experimental result suggests that even if the counterions exist in high concentration around the polyion, their mutual interaction seems to

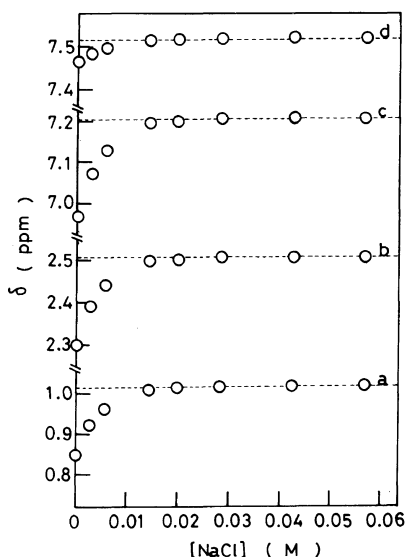


Figure 4. The effect of NaCl on the ^1H chemical shift of 8.92×10^{-3} M NaEBS in the presence of 1.17×10^{-2} M PAAH $^+\text{Cl}^-$. The small letters indicate a, methyl-; b, methylene-; c, *meta*- and d, *ortho*- protons.

be nil at $\alpha = 0.4$.

Effect of the Added Salt (NaCl) on the Association of EBS $^-$'s

Figure 4 shows the effect of added NaCl on the ^1H chemical shift of EBS $^-$ in the presence of PAAH $^+\text{Cl}^-$. When NaCl is added to the PAAH $^+\text{Cl}^-$ /NaEBS system, ^1H signals of EBS $^-$ shift to the low magnetic field and on further addition of NaCl they shift back to the original position as in the absence of PAAH $^+\text{Cl}^-$. This result shows that the association of EBS $^-$'s is broken by the added Cl^- 's. The charges on the polyion are shielded by an excess of NaCl approached to the polyion. Association of EBS $^-$'s is depressed as a result of the shielding of charges on the polyion. Concurrently, EBS $^-$'s are preferentially removed from the PAAH $^+$ moieties by Cl^- 's. Until now, the counterion binding to polyion has been interpreted in terms of the size of counterion¹⁴ and/or the state of hydration of both polyion and counterions.^{15,16} The affinity of bulky and hydro-

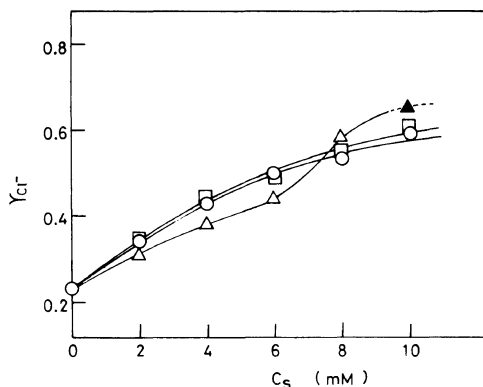


Figure 5. The dependence of the activity coefficient of Cl^- for 1.05×10^{-2} M PAAH $^+\text{Cl}^-$ on the hydrophobic salt concentration. (○), NaBS; (□), NaMBS; (△), NaEBS. The solid symbol indicates a turbid solution.

phobic EBS $^-$ to the hydrophilic polymer such as PAAH $^+$ seems to be much less than Cl^- . Therefore, when amounts of NaEBS added to the aqueous PAAH $^+\text{Cl}^-$ (a constant concentration) solution without NaCl are relative small, many Cl^- 's coexisting prevent an effective approach of EBS $^-$'s to the polyion moieties. However, large amounts of NaEBS is added to the solution, the association of EBS $^-$'s is subject to occur. The associated EBS $^-$'s has a property of di- and/or multivalent counterion and strongly interacts with PAAH $^+$. Consequently, counterion exchange from Cl^- 's to EBS $^-$'s around PAAH $^+$ may be much promoted. In order to obtain the information about this counterion exchange around PAAH $^+$, we measured the activity of Cl^- for PAAH $^+\text{Cl}^-$ in hydrophobic salt solutions.

The Activity Measurements of Chloride Ion for PAAH $^+\text{Cl}^-$ in Hydrophobic Salt Solutions

Figure 5 shows the dependence of the activity coefficient of Cl^- (γ_{Cl^-}) upon the concentration of added hydrophobic salts, *i.e.*, sodium benzenesulfonate (NaBS), sodium *p*-methylbenzenesulfonate (NaMBS) and NaEBS at a constant PAAH $^+\text{Cl}^-$ concentration. The comparison of the γ_{Cl^-} value in NaEBS solution

with that in NaBS and NaMBS solutions elucidate the counterion exchange promoted by the association of EBS^- 's. In the low salt concentration range, all γ_{Cl^-} values monotonously increase with the salt concentration. This behavior is a characteristic property of polyelectrolyte solution.¹⁷ In addition, the γ_{Cl^-} values decrease with the order of the hydrophobicity of the counterions. On the other hand, in the higher salt concentration range, the γ_{Cl^-} value in the $\text{PAAH}^+\text{Cl}^-/\text{NaEBS}$ system abruptly increases going over the values of other two systems, and after that the solution becomes turbid. The NaEBS concentration which the γ_{Cl^-} suddenly increased corresponds well to that ^1H chemical shift begins to change largely to up-field. The above result implies that the counterion exchange from Cl^- 's to EBS^- 's was much promoted by the association of EBS^- 's, causing an abrupt increase in the γ_{Cl^-} value.

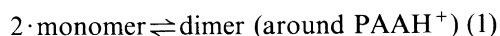
Generally, the stronger the interaction of an added counterion with a polyion, the higher the activity of coexisting Cl^- . When EBS^- 's associate each other around the polyion, the associated EBS^- 's have a character of divalent and/or multivalent counterion. Consequently, they strongly interact with PAAH^+ and preferentially remove Cl^- 's from the polyion moieties. At the same time, the ionic hydration around the charged groups on the polyion may decrease by the hydrophobic groups of EBS^- , which leads to the precipitation of the polyion.

Analysis of Association Behavior of EBS^- 's around PAAH^+ by Simple Equilibrium Model

As shown in Figure 1, ^1H NMR signals of EBS^- shift to up-field due to the association of EBS^- 's around PAAH^+ . Moreover, the line broadening was observed in each proton of EBS^- , especially in methylene proton. This broadening suggests that the motion of the methylene protons is highly restricted by the association of EBS^- 's. Judging from the change of above ^1H NMR signals of EBS^- , it seems that a rapid exchange is set up between

the free monomer and aggregate (dimer) of EBS^- around PAAH^+ . Accordingly, the higher fraction of associated EBS^- ions, the larger this change of ^1H NMR signals.

It is of interest to analyse the observed chemical shift of $\text{PAAH}^+\text{Cl}^-/\text{NaEBS}$ system in terms of a rapid exchange between the free monomer and dimer of EBS^- around PAAH^+ . The following simple equilibrium was adopted under the condition that the concentration of PAAH^+Cl^- is constant.



$$K = [\text{D}]/[\text{M}]^2 \quad (2)$$

where $[\text{M}]$ and $[\text{D}]$ represent the molar concentrations of the monomer and dimer forms, respectively. Then, the chemical shift, δ , can be expressed by a weight average of the chemical shifts for two forms.

$$\delta = X_m \delta_m + X_d \delta_d \quad (3)$$

where δ_m and δ_d denote the respective chemical shifts of the monomer and dimer forms with X_m and X_d being the corresponding molar fractions of EBS^- in the two forms ($X_m + X_d = 1$).

From the eq 2 and 3, the chemical shift can be expressed by

$$\delta = \delta_d + (\delta_d - \delta_m) \times \{1 - (1 + 8K[\text{EBS}^-]_t)^{1/2}\} / (4K[\text{EBS}^-]_t) \quad (4)$$

where $[\text{EBS}^-]_t$ is the total concentration of NaEBS and $[\text{EBS}^-]_t = [\text{M}] + 2[\text{D}]$.

To determine the K and δ_d 's which can reproduce the experimental results (the solid symbols in Figure 2), an iterative procedure was adopted, where the values of δ_m 's were taken as those in the absence of PAAH^+Cl^- . However, any pair of K and δ_d 's values covering adequately experimental results over the whole concentration range of NaEBS examined could not be obtained. For example, the dotted curves in Figure 2 represent the calculated results using the values of K and δ_d 's shown in Figure 2. In the lower NaEBS

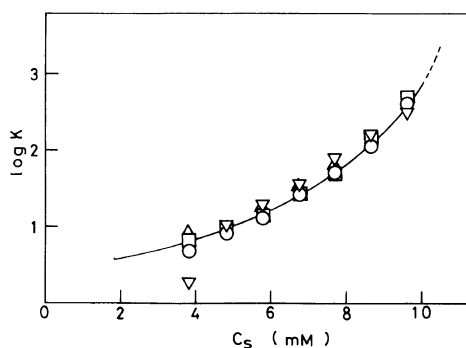


Figure 6. The dependence of the association constant K of EBS^- ions around PAAH^+ on the NaEBS concentration. The symbols indicate the values calculated for (Δ) methyl-, (\square) methylene-, (\circ) *meta*- and (∇) *ortho*-protons.

concentration range, the calculated values agree well with the experimental data, but the deviation from the experimental values becomes large at higher NaEBS concentrations. This implies that the simple equilibrium model (eq 1) is inapplicable to the present experimental data at higher NaEBS concentrations. Multiple aggregates such as trimer and tetramer may be formed under the condition that the local concentration of EBS^- around PAAH^+ is very high. In addition, since the EBS^- s are accumulated in high concentration around PAAH^+ , the association of EBS^- s may be cooperatively enhanced.

Thus, to clarify the cooperative association of EBS^- s around the polyion, it is worthwhile to examine the change of K with the NaEBS concentration. Using eq 2, 3, and 4, the value of K was evaluated from the observed NaEBS concentration dependence of each proton signal, and is shown in Figure 6 (for d_m 's and δ_d 's, the values shown in caption of Figure 2 were used). The value of K rapidly increases, as expected, with the increase in the NaEBS concentration. This strongly suggests the cooperative association of EBS^- s around the polyion, *i.e.*, an increase in the local concentration of EBS^- considerably enhances the association. Furthermore, it should be noted

that all the K values calculated from different proton signals are converged on a single smoothed curve. This also may give a powerful collaboration of our assertion that the observed chemical shifts of EBS^- in the presence of PAAH^+Cl^- are originated in a single process, that is, the ring current effect due to the association of EBS^- s.

CONCLUSION

In this study, EBS^- s found to be atmospherically bound by PAAH^+Cl^- and to associate each other around PAAH^+ through their hydrophobic interaction. Since the association occurs in the presence of PAAH^+ , it is influenced by the charge density of the polyion and the coexisting small ions (Cl^-). From a simple equilibrium model, the cooperative association of EBS^- s around PAAH^+ was demonstrated. In addition, as a result of the association of EBS^- s, the counterion exchange from Cl^- s to EBS^- s around PAAH^+ is efficiently promoted. At the same time, the ionic hydration of charged groups on the polyion may decrease by the hydrophobic groups of EBS^- , which leads to the precipitation of the polyion.

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