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Effects of Hydrophobic Hydration on Counterion Binding of Polycations

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ABSTRACT: For aqueous solutions of poly(4-vinylpyridine)s quaternized with ethyl, propyl, and butyl chlorides (P4VPEt, P4VPPr, P4VPBu) and poly(allylamine) hydrochloride ((PAA)HCl), density measurements were performed to obtain the apparent molar volume, V_{app}, of the polymers. Observed increase or decrease in the V_{app} values with increasing concentrations of added salts, namely, NaCl, NaI, $NaNO_3$, sodium benzenesulfonate (NaBS), sodium ethylbenzenesulfonate (NaEBS), has been ascribed to perturbation of hydrophobic and/or hydrophilic (ionic) hydrations of pertinent polyions and counterions by counterion exchange. Cl^- ion activities were measured to evaluate extra binding energies (ΔE_{ex}) of the coexisting counterion species. Variation in ΔE_{ex} values according to the polyion systems has been interpreted consistently with the hydration change behaviors.

Introduction

Hydration around a polyelectrolyte in aqueous solution is composed of a few kinds of hydrations, i.e., ionic hydration for charged groups and counterions, hydrogen bonding to polar groups, and hydrophobic hydration around alkyl main and side chains. Since these three hydration (structure)s are incompatible with each other, solvent water molecules close to the boundary region between those groups may have unfavorable structures and interaction energies compared to any types of intact hydration waters. In other words, repulsive forces should be operative between two solutes or two moieties of one large solute having different types of hydration when they are so close that the hydration shells intrude into each other. In the case of small ionic solutes, such interactions become appreciable at a higher concentration region, leading to deviations of thermodynamic properties such as activity coefficients and partial molar volumes of relevant ions from those predicted by Debye–Hückel limiting law. Desnoyers et al.[1] qualitatively explained such deviations observed for a series of alkali and tetraalkyl halides, dependent on the combination of cation and anion, in terms of relative (de)stabilization of hydration structures produced by overlap of the hydration spheres. According to their hydration sphere interaction model, not only repulsive forces between hydrophilic and hydrophobic solutes but also attractive interactions are assigned to solutes of like hydration properties.

These discussions on small ionic solutes seem to be valid for counterion binding in polyelectrolyte solutions. According to Strauss et al.,[2] dehydration accompanied by counterion binding of alkali-metal cations to a polyanion increases with the decrease in the cation size for polyacrylate (PAA) but decreases for poly(styrenesulfonate) (PSS). Mattai and Kwak[3] have also found that the counterion binding degrees of Mg^{2+} and Ca^{2+} ions onto PSS and dextran sulfate are quantitatively predicted by Manning's two-variable theory,[4] whereas those for polypectate and (carboxymethyl)cellulose are appreciably higher than the predictions. We have reported that counterion activity coefficients of Mg^{2+} and Ca^{2+} are reproduced by our counterion condensation model (IMM),[5] which assumes extra attractive interaction energies (ΔE_{ex}) as 0 kcal/mol for (PSS)Na, 6–1.2 kcal/mol for sodium poly(L-glutamate) ((PLG)Na),[6] and −1.5 and −3.9 kcal/mol for (PAA)Na,[7] respectively. These three examples imply that small and hard counterions such as Li^+, Na^+, Mg^{2+}, and Ca^{2+} interact more strongly with relatively small and hard carboxyl anion groups on polymers than with relatively large and soft sulfate or sulfonate groups, and vice versa. Such an interpretation is consistent with the solvation cosphere interaction model for small ionic solutes,[1] namely, water molecules in the cosphere of hydrations of the counterion and charged group are stabilized when extents and types of structurization of hydration spheres are alike and are destabilized when they are not alike.

To counterion binding systems in which hydrophobic interactions are involved may be applied the same rule;[8-10] Miyamoto and Imai[8] ascribed a specific interaction between tetrabutylammonium cation and poly(isobutyl vinyl ether-*co*-maleic acid), which were suggested from the counterion activity data, to hydrophobic interaction with the alkyl side chain of the polyion. It is known[9] that large tetraalkylammonium cations as counterions of PLG stabilize its helical conformation probably through the hydrophobic interaction with hydrophobic moieties on the polymer. In these studies emphasis has been laid on hydrophobic interaction. As far as we know, few studies have discussed effects of incompatibility of ionic and hydrophobic hydrations on the counterion binding. In a previous study,[11] we performed potentiometric titrations for poly(4-vinylpyridine) (P4VP) and poly(2-vinylpyridine) (P2VP) with HCl and benzenesulfonic acid (HBS). The higher pK_a values for P2VP titrated with HBS rather than with HCl and the former temperature dependence different from that for P4VP suggested that the protonation to the pyridine ring of P2VP is stabilized by counterion binding of BS^- partially through hydrophobic interaction but not for the P4VP/BS^- system. This was attributed to the difference or the protonated sites of the two PVP; since the protonation site on P2VP is closer to the hydrophobic main chain, hydrophobic BS^- ions are more accessible to the polymer charges than Cl^-, to stabilize the charged state. On the other hand, in P4VP, the hydrophobic core is covered with the hydrophilic (ionic) hydration shell, which prevents the core from having hydrophobic interaction with BS^- counterions.

In the present study, we examine hydration change detected by apparent molar volume, V_{app}, of P4VP quaternized with ethyl, *n*-propyl, and *n*-butyl chlorides in aqueous solutions in the presence of hydrophilic (Cl^-, I^-, and NO_3^-) and hydrophobic (BS^- and ethyl benzene-

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sulfonate, EBS$^-$) counterion species. Referring to the results for polyallylamine (PAA), which is supposed to be hydrophilic, we deduce the effects of overlap of incompatible or compatible hydrations on the counterion binding.

Experimental Section

P4VP ($M_v = 2.3 \times 10^5$) was purchased from Kouei Kagaku Co., Ltd. The polymer sample was purified by twice-repeated precipitation from ethanol into diethyl ether and dried in vacuo at room temperature. The P4VP sample dissolved in nitromethane (10 g, 150 mL) was quaternized by an excess amount of ethyl n-propyl, and n-butyl bromide (molar ratio = 1.5), respectively, at 46 °C for 3–7 days. Precipitates obtained in the quaternization were dissolved in ethanol and then reprecipitated in diethyl ether. The quaternization degrees were estimated as 100% from the disappearance of the ^{1}H NMR peak at 6.7 ppm ascribed to the β-proton on the unquaternized pyridine residue. Abbreviations for the 100% quaternized P4VP's are P4VPEt, P4VPPr, and P4VBu, respectively. Exchange of counteranion to Cl$^-$ was performed by the ultrafiltration method; an aqueous solution of the quarternized P4VP was ultrafiltrated through an Ultrafilter UP-20 (Toyo Rushi Co.), which fractionates molecular weight less than 20 000, in the presence of a large excess of NaCl (10 times). This process was repeated four times, followed by five times of ultrafiltration for the polymer solution diluted by distilled water. This procedure resulted in poly(4-vinylalkylpyridinium) chloride containing a trace of Br$^-$ ions (<0.1 mol%). Poly(allylamine)hydrochloride ((PAA)HCl) ($M_v = 6.0 \times 10^4$) from the Nittobo Co. was also purified by ultrafiltration with a UP-20 membrane. The polymer samples thus purified were collected by freeze-drying. NaCl, NaNO$_3$, and NaI of analytical grade of Kanto Kagaku Co. were used without further purification. NaBS and NaEBS of reactive grade were recrystallized from water and dried in vacuo.

Density measurements were carried out with a Precision density meter DMA-O2C (Anton Paar) at 25 ± 0.005° C. The calibration was made with ultrapure nitrogen gas (Kayama Oxygen Co.) and distilled water. The experimental error was within 2×10^{-6} g·cm^{-3}. The polymer concentration, C_p, was adjusted to 0.01 base·mol·dm^{-3}, and the molar ratio of added salts, C_s/C_p, was varied from 0 to 4.0. The apparent molar volume of the polymer, V_{app}, was calculated by eq 1 where M is the

$$V_{app} = \{M + 1000(d_0 - d)/C_p\}/d_0 \qquad (1)$$

molecular weight of the monomer unit, d is the density, and subscript 0 means a solvent or salt solution. The experimental results for V_{app} were reproducible within 0.3 cm^3·base·mol^{-1}. The density measurements were repeated at least two times to obtain an average V_{app} value.

Activities of Cl$^-$ ions in respective polymer/added salt systems were estimated by an Orion ion analyser 901 using an ion-selective electrode, an Orion 94-17 with a reference electrode, an Orion 90-02, at 25 ± 0.05 °C. Volume change due to addition of salt solution to a sample polymer solution was corrected to estimate the activity coefficient.

All the polymer and salt solutions were gravimetrically prepared by using deionized and afterward distilled water.

Results and Discussion

Parts a–c of Figure 1 show dependences of V_{app} on the molar ratio, C_s/C_p, of hydrophilic counterions added to P4VPEt, -Pr, and -Bu, respectively. V_{app} in each system increases with the increase in C_s. (V_{app}'s for the P4VPBu/NaI system are plotted only at $C_s/C_p \leq 1.0$, because of the precipitation for the polymer solution at $C_s/C_p > 1.0$.) Since no effective counterion exchanges should occur for NaCl systems, the observed changes in V_{app} should be ascribed to the increase in ionic strength. According to the counterion binding theories,[4,5,12] the increase in ionic strength hardly affects the binding degree but gives rise to a decrease in the ionic atmosphere thickness or in the average distance between a bound counterion and polymer charges. This will result in partial liberation of the ionic hydration waters and will also cause a perturbation of hydrophobic hydrations around the alkyl chains and pyridine rings. Since the overlap of ionic hydration shells and that of an ionic hydration and a hydrophobic hydration give rise to volume increment and decrement, respectively,[1] the observed increase in V_{app} for Cl$^-$ implies that the former contribution overcomes the latter one. In the cases of NaI and NaNO$_3$ systems, Cl$^-$ ions bound onto the relevant polyions are exchanged with the second counterions added. Therefore, the large increases in V_{app} than Cl$^-$ suggest that I$^-$ and NO$_3^-$ counterions interact more strongly with polymer charges so as to liberate more ionic hydration waters and/or to relatively stabilize the hydrophobic hydration structures. For I$^-$ and NO$_3^-$, both reasonings seem to be valid; the weaker ionic hydrations of these counterions are favorable to the access of charged sites surrounded by hydrophobic hydrations, leading to more

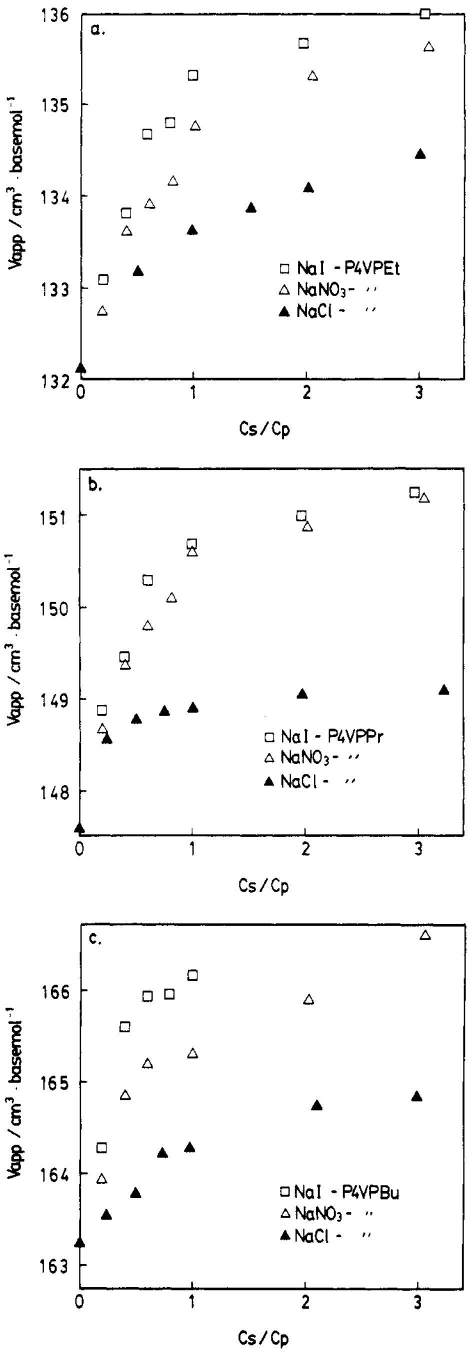

Figure 1. Variation of V_{app} of P4VP's with addition of hydrophilic counterions: (a) P4VPEt, (b) P4VPPr, (c) P4VPBu.

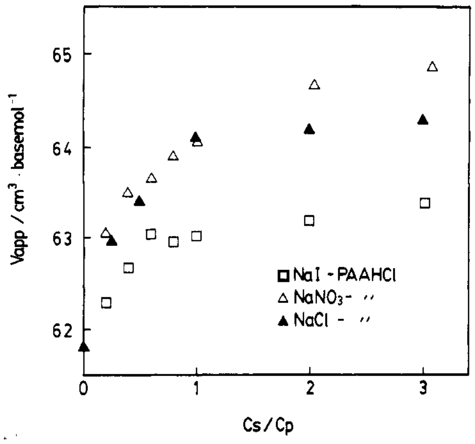

Figure 2. Variation of V_{app} of (PAA)HCl with addition of hydrophilic counterions.

effective neutralization of the polymer charge and hence to stabilization of the hydrophobic hydration. The fact that precipitation occurs in the presence of NaI at C_s/C_p >1.0 suggests that the effective neutralization of the polymer charge leads to substantial reduction of the polymer hydrophilicity.

Figure 2 shows results for (PAA)HCl/hydrophilic counterion systems. In this case, the order of degrees of the V_{app} increment is $I^- < Cl^- \leq NO_3^-$, contrary to that in P4VP systems, $Cl^- < NO_3^- < I^-$; the former increase in V_{app} is smallest for the I^- counterion. It is considered that this is caused by the weaker ionic hydration or smaller hydration number of I^-. The larger V_{app} of NO_3^- than that of Cl^- suggests that the structuredness of hydration around the former anion is most compatible, among the three anions, with that of the ammonium cation group on poly(allylamine).

By the addition of hydrophobic counterions (BS^- and EBS^-) to P4VP's, two types of dependence are observed. As seen in Figure 3a–c, one is an initial increase in V_{app} followed by a plateau for P4VPEt and P4VPPr/NaBS systems, and the other is followed by a decrease and at last by a precipitation. The initial increases in V_{app} (C_s/C_p < 1.0) by the addition of NaBS and NaEBS are comparable to those by NaCl (Figure 1a–c) except for the P4VPBu/NaEBS system. The decreasing trend of V_{app} becomes appreciable at a lower level of the counterion addition for systems of the more hydrophobic polyion and/or counterions, suggesting that hydrophobic interaction is involved with the counterion binding of EBS^- ions onto the quaternized P4VP's. Thus, the observed maximum of V_{app} should result from a balance between the positive and the negative contributions from liberations of ionic and hydrophobic hydration waters, respectively, upon the counterion binding; with the increase in the population of hydrophobic counterions in bound state, hydrophobic interactions between bound counterions and/or with the main chain become favorable, leading to the decrease in V_{app} and finally to precipitation. Namely, the precipitation in these cases is to be attributed mainly to the desolvation of hydrophobic hydration waters.

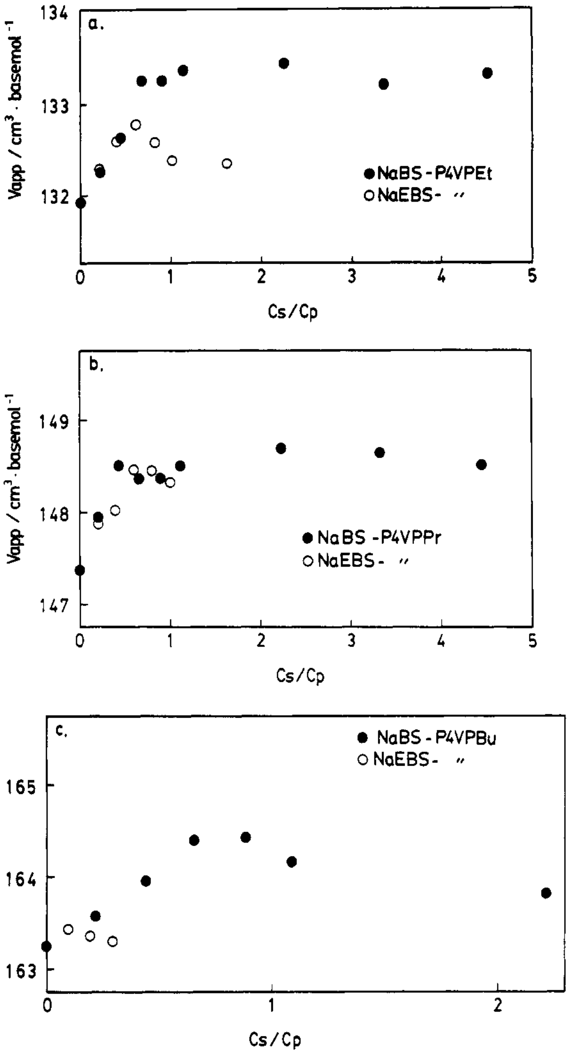

Figure 3. Variation of V_{app} of P4VP's with addition of hydrophobic counterions: (a) P4VPEt, (b) P4VPPr, (c) P4VPBu.

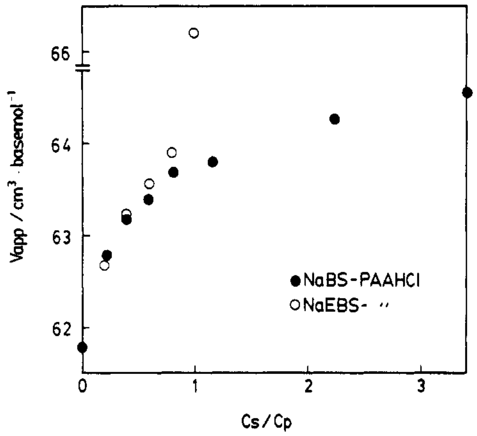

Figure 4. Variation of V_{app} of (PAA)HCl with addition of hydrophobic counterions.

In Figure 4, V_{app} is plotted for (PAA)HCl/NaBS or NaEBS systems. In the case of less hydrophobic BS^-, the behavior of V_{app} is essentially the same as those of (PAA)HCl/NaCl or $NaNO_3$ systems, suggesting that the hydrophilic envelope of the polyion allows the counterion molecule to interact only at the ionic site (SO_3^- group) with the polyion. However, addition of NaEBS gives rise to, contrary to the case of P4VP's, a rapid increase in V_{app} at around $C_s/C_p = 1.0$, just beyond which precipitation takes place. The precipitation suggests that the hydrophobic counterions interact with the polymer main chain. Since a substantial amount of ionic hydration waters surrounding the polyion should be liberated upon the hydrophobic interaction between bound counterions and the polymer main chain, the rapid increase in V_{app} means that the negative contribution to V_{app} change due to the hydrophobic interaction is overwhelmed by the positive one due to the liberation of the ionic hydration waters. Furthermore, the liberation of such ionic hydration appears to be a reason why precipitation occurs at the relatively early stage of the counterion addition for this hydrophilic polymer.

The volume changes observed for the systems so far mentioned are at most 4.5 cm^3/mol in the last system. If all the volume changes were ascribed to the liberation of electrostrictly hydrating waters, the molar volume of which is assumed to decrease by 2.7 $cm^3 \cdot mol^{-1}$ compared with that of bulk,[13] the dehydration number would be estimated to be ca. 1.7. However, since the changes in V_{app} contain negative contributions from destabilization and/or liberation of hydrophobic hydration waters, actual numbers of water molecules pertaining to any hydration changes upon the counterion binding should be larger. This means that one cannot estimate the relative binding strength from these volume change data. In order to obtain the desired information, we performed counterion activity measurements for Cl^-; the stronger the interaction of an added counterion with a polyion, the higher the activity of coexisting Cl^- ions. According to our counterion condensation model (IMM),[5] the relative difference in the interaction energies can be estimated from the extra interaction energy, ΔE_{ex}, which has been incorporated into the model to fit experimental counterion activities.[6,7] Since our original model considers nonspecific long-range electrostatic interaction for the counterion binding energy, ΔE_{ex} contains and explains the other contributions; short-range and specific interactions between bound counterion(s) and polymer charge(s) that accompany hydration changes, e.g., solvent-shared or contact ion-pair formation and the hydrophobic interactions. The validity of our model in treating counterion activities has been demonstrated for, for instance, sodium poly(L-glutamate)/Mg^{2+} or Ca^{2+} systems, in which both of the monovalent and divalent counterion activities are reproduced by assuming a single ΔE_{ex} value for the counterion binding of respective divalent ions.[6] Parts a–c of Figure 5 show variations of the activity coefficient, γ_{Cl}, and theoretical curves fitted by IMM including ΔE_{ex}'s for the addition of NaBS, NaEBS, and $NaNO_3$, respectively. As seen in the figures, γ_{Cl} values in the absence of the added salts are dependent on polymer species; (PAA)HCl < P4VPEt ≤ P4VPPr ≤ P4VPBu. These polymers have the same axial charge spacing ($b = 2.5 \times 10^{-8}$ cm). Then, discrepancy in the counterion activity between (PAA)HCl and P4VP's may be attributed to a difference in "effective" charge densities. Since the charged site of quaternized P4VP is apart from the main chain compared with (PAA)HCl, the former effective charge density is lower than the latter, as discussed in a previous study on pH titrations for P4VP and P2VP.[11] Furthermore, the small differences in γ_{Cl} for the P4VP's seem to reflect repulsive mismatches of the hydration structure of Cl^- with those of the hydrophobic polyions. Although such specificity in the counterion binding should be adjusted, in the present content, by assuming ΔE_{ex} values for respective Cl^-/polyion pairs, we included that effect into the differences of b values for simplicity's sake. Thus, we used the following b (10^{-8} cm) values to reproduce the experimental Cl^- activities in the absence of the other salt. $b = 2.5$ for (PAA)HCl, 3.25 for P4VPEt, 3.3 for P4VPPr, and 3.4 for P4VPBu. γ_{Cl} for (PAA)HCl can be predicted without adjusting the b value.

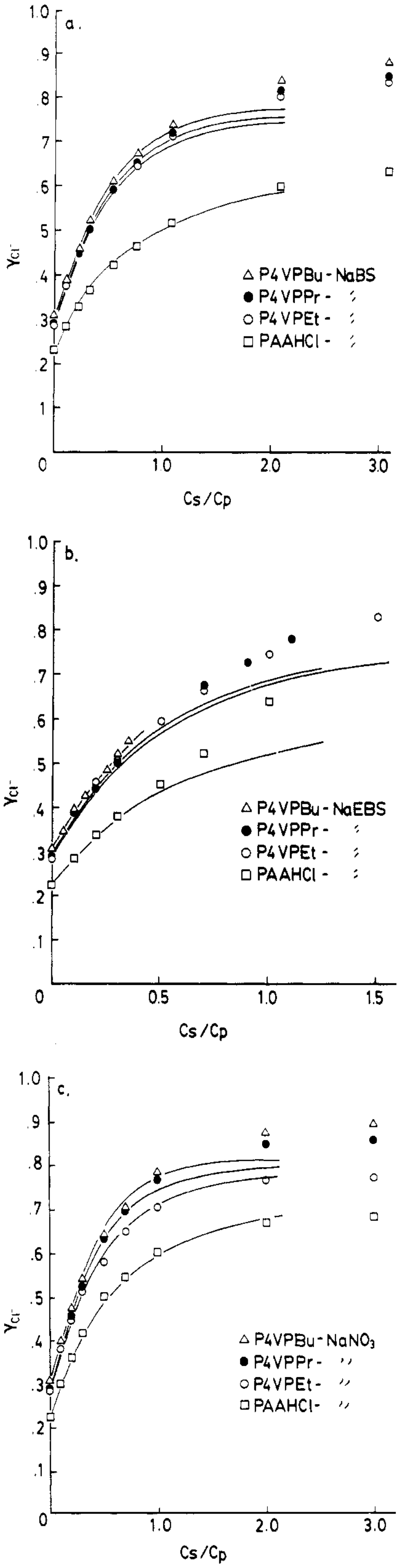

Figure 5. Variation of γ_{Cl} in P4VP's and (PAA)HCl aqueous solutions with addition of salts. Solid curves were drawn by our counterion condensation model (see text): (a) NaBS, (b) NaEBS, (c) $NaNO_3$.

In Figure 5a,c, the theoretical curves are drawn up to $C_s/C_p = 2.0$. This is because at higher C_s/C_p the theoretical estimation of γ_{Cl} becomes heavily dependent on the validity of the Debye–Hückel equation in the estimation of the simple ion interaction effect on γ_{Cl} as a background. In the case of NaEBS addition (Figure 5b), gradual upward deviations of γ_{Cl} from the theoritical curves, fitted to experimental data at $C_s/C_p \leq 0.5$, are observed. This suggests that the counterion binding strengths are enhanced with increasing the binding fraction. In fact, the deviations for the P4VPEt, P4VPPr, and (PAA)HCl systems become appreciable above $C_s/C_p \sim 0.75$, where decreases or a rapid increase in V_{app} begin to appear in the respective polymer systems. Thus, ΔE_{ex} values for EBS^-

Table I
ΔE_{ex} Estimated by the Counterion Condensation Model

counterion	polyion	ΔE_{ex}, kcal mol^{-1}	C_p/C_s at precipitn
BS^-	P4VPEt	−0.6	
	P4VPPr	−0.7	
	P4VPBu	−0.9	
	(PAA)HCl	+0.5	
EBS^-	P4VPEt	−0.6 (−2.0)[a]	2.0
	P4VPPr	−0.7 (−1.5)	1.2
	P4VPBu	−0.9 (−0.9)	0.4
	(PAA)HCl	+0.3 (−0.5)	1.2
NO_3^-	P4VPEt	−0.9	
	P4VPPr	−1.2	
	P4VPBu	−1.5	
	(PAA)HCl	−0.2	

[a] Parenthesized values are ΔE_{ex}'s estimated at C_s/C_p just before the precipitation.

systems were estimated also at C_s/C_p just before the precipitations to see the supposed enhanced interaction. These are summarized in Table I together with those of the other systems.

In BS^- and EBS^- bindings, the stronger interaction is estimated for the more hydrophobic polyions; P4VPEt < P4VPPr < P4VPBu. This is consistent with the hydrophobic interactions deduced from the V_{app} changes observed for these counterion binding systems. However, the ΔE_{ex} values for BS^- binding to the P4VP's are estimated to be the same as those for EBS^- that have been obtained by curve-fitting for the γ_{Cl} data at $C_s/C_p \leq 0.5$. This suggests that, at such a C_s/C_p region, bound EBS^- ions do not so deeply penetrate into the hydration shell of the polyions that the ethyl group of the counterion does not participate in hydrophobic interactions with the pertinent polyions. Contrary to these hydrophobic polymer systems, the ΔE_{ex} values for (PAA)HCl/BS^- and (PAA)/EBS^- systems are positive. Since ionic hydration, which is supposed to cover the whole polyion ((PAA)HCl), is incompatible with the hydrophobic hydration of the aromatic counterions, the slight repulsion in the counterion bindings compared to Cl^- is reasonable.

At the higher C_s/C_p region (>ca. 0.5), the hydrophobic interactions in the counterion binding of EBS^- onto P4VPEt and P4VPPr are enhanced (see the parenthesized ΔE_{ex} values in Table I). As discussed on the volume change data, it seems that the enhancement in ΔE_{ex} in the higher C_s/C_p region results from hydrophobic interactions with adjacent counterions and with the main chain. It should be noted here that the order of ΔE_{ex} values estimated for C_s/C_p just before the precipitations, which is apparently contradicting the above-mentioned hydrophobic interactions, does not directly reflect the relative strength among the polymer systems for the counterion binding. Namely, the higher the hydrophilicity of polyion, the more retarded the precipitation. For example, it is considered that the largest ΔE_{ex} value for P4VPEt stands for the hydrophobic interaction favored by such a high level of C_s addition or by the high density of bound EBS^- ions. In the case of the P4VPBu/EBS^- system, it seems that precipitation occurs due to the inherent hydrophobicity of the polymer at such an early binding stage of the hydrophobic counterion before hydrophobic interactions between bound counterions become favorable.

The ΔE_{ex} values estimated for P4VP's/NO_3^- suggest that the counterion binding strengths are significant and comparable to or higher than those for the hydrophobic counterions. This noticable attractive interaction of the nonhydrophobic counterion with the hydrophobic polyions seems to be consistently interpreted with the pertinent hydration changes. Namely, as discussed based on the V_{app} data, it is considered that NO_3^- ions having relatively weak ionic hydration are accessible to the hydrophobic surroundings of the P4VP's. The resultant effective neutralization of the polymer charge and stabilization of hydrophobic hydration lead to an enhanced counterion binding strength compared to Cl^- ions.

Conclusions

In this paper, effects of hydration sphere overlapping on the counterion binding have been examined for polyion/counterion systems of different degrees of hydrophobicity. Hydration changes measured by V_{app} variations are discussed consistently with the relative counterion binding strengths estimated by IMM. The NO_3^- or I^- binding with unexpected strengths to the P4VP's indicate that not only hydrophobic counterions but also less hydrophilic counterions, or those of weak ionic hydration, specifically interact with hydrophobic polyions. The contrast between hydration changes observed for (PAA)HCl and P4VP's is ascribed to the difference in the polyion's outer hydration shell; the former is supposed to be covered by an ionic one, and for the latter hydrophobic hydration should be exposed. As suggested by Turro et al.[14] and by our previous study on pH titrations of P4VP and P2VP,[11] this kind of local variation in the hydration environment of polyions is an important factor that determines the counterion binding specificity, other than the Debye–Hückel type interaction.

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Registry No. P4VPEt, 131458-62-3; P4VPPr, 70876-95-8; P4VPBu, 70876-96-9; (PAA)Cl, 71550-12-4; NaBS, 515-42-4; NaEBS, 30995-65-4; $NaNO_3$, 7631-99-4; Cl^-, 16887-00-6; NaI, 7681-82-5; NaCl, 7647-14-5.