Competitive counterion binding and hydration change of Na poly(acrylate)/$MgCl_2$, $CaCl_2$ in aqueous solution

Mitsuru Satoh*, Masahiko Hayashi, Jiro Komiyama and Toshiro Iijima†
Department of Polymer Science, Tokyo Institute of Technology, Ookayama, Meguro-ku, Tokyo 152, Japan

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Dehydration upon divalent counterion binding has been studied by means of counterion activity, density and sound-velocity measurements for aqueous solutions of Na poly(acrylate)/$MgCl_2$ or $CaCl_2$ and Na poly(L-glutamate)/$MgCl_2$. The dehydration number and dehydration fraction (ratio of dehydration number to total hydration number) of the following two types of binding reactions, $2(\text{–COO}^-\text{Na}^+)+\text{M}^{2+}\rightarrow(\text{–COO}^-)_2\text{M}^{2+}+2\text{Na}^+$ and $2(\text{–COO}^-)+\text{M}^{2+}\rightarrow(\text{–COO}^-)_2\text{M}^{2+}$, were estimated from compressibility data obtained from the density and sound-velocity measurements. It has been suggested that the dehydration fraction of the former reaction, which includes the hydration change of Na^+ ions upon reaction, serves as a measure of the relative binding strength of the divalent cations, while the dehydration fraction of the latter reaction serves as a measure of the binding mode.

(Keywords: competitive counterion binding; polyelectrolyte; hydration; counterion activity; compressibility)

INTRODUCTION

In most studies on counterion binding in polyelectrolyte solutions, dehydration of the charged groups upon binding has been observed[1–8]. In these studies, the observed hydration changes have often been correlated with the binding modes of the relevant ions, namely so-called 'site binding' or specific binding and 'atmospheric binding' or non-specific binding. Since the studies by Strauss *et al.*[1,2] on 'site binding' in polyelectrolyte solutions, dehydrative counterion binding has been linked to the site-binding mode. On the other hand, 'atmospheric binding' has been linked to counterion binding that is not accompanied by appreciable dehydration. However, it seems that actual dehydration behaviour upon counterion binding can hardly be elucidated by the extreme concepts included in these two binding modes. For example, certain multivalent counterions attracted to polyions through non-specific electrostatic interactions may lose their outer-sphere water of hydration upon 'atmospheric' binding, since these ions maintain multilayer electrostrictive hydration. As a matter of fact, counterion condensation theories[9–12], which were first developed for atmospheric counterion binding, have been successfully applied to polyion systems in which divalent counterions are bound with appreciable dehydration (e.g. poly(styrene sulphonate), dextran sulphate/Mg^{2+}, Ca^{2+})[13,14]. Therefore, it seems necessary to reconsider the correlation between counterion binding modes and dehydration behaviour.

In a recent paper, we have reported a theoretical and experimental study on competitive counterion condensation between mono- and divalent counterions in polyelectrolyte solutions[15]. Our theoretical model for non-specific counterion condensation, the intermediate model (IMM)[12], could quantitatively predict both mono- and divalent counterion activity coefficients in Na poly(styrene sulphonate) (PSSNa)/$MgCl_2$ or $CaCl_2$ systems. However, for Na poly(L-glutamate) (PLGNa)/$MgCl_2$, $CaCl_2$ systems, the theory turned out to overestimate the divalent counterion activity coefficients. It is known that counterion binding in the former polyion systems is non-specific, with slight dehydration, while the divalent counterion binding onto carboxylic polyanions is accompanied by substantial dehydration. Therefore, we suggested in the paper[12] the possibility that dehydration upon and the strength of divalent counterion binding are properly correlated through experimental activity coefficients; counterions specifically interacting with polymer charges would show lower activity coefficients than those predicted by the IMM and larger dehydration than non-specific cases.

In the present study, we examine the dehydration and counterion activity behaviour for Na poly(acrylate) (PAANa)/$MgCl_2$ or $CaCl_2$ systems. The counterion binding in these systems has been linked to the site-binding mode. The dehydration numbers for divalent counterion binding were estimated from compressibility data. Changes in the activity coefficients were measured as a function of the divalent ion/polyion concentration ratio, C_2/C_p. The latter results were also compared with the theoretical prediction by the IMM. We discuss the correlation between the degree of dehydration and the strength of counterion binding estimated from the activity data.

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* To whom correspondence should be addressed.

† Present address: Jissen Women's College, Oosakaue, Hino, Tokyo 191, Japan.

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EXPERIMENTAL

Sodium poly(acrylate) (PAANa, $M_v = 99000$) was purchased from Nihon Jun-yaku Co. Sodium poly(L-glutamate) (PLGNa, $Mv = 66000$) was obtained by saponification of poly(γ-methyl-L-glutamate) (Ajicoat A-2000)[16], kindly supplied by Ajinomoto Co., in an aqueous alcohol mixture. Low-molecular-weight substances in the polymer samples were removed by ultrafiltration through Ultrafilter UP-20 (Toyo Roshi).

The density and sound velocity of each polymer solution ($C_p = 0.025$ base mol l^{-1}) were measured at $25 \pm 0.005°C$ in the absence and presence of divalent cations (Mg^{2+}, Ca^{2+}, Ba^{2+}). The experimental errors were within 2×10^{-6} g cm^{-3} and 2 cm s^{-1} for the density and sound-velocity measurements, respectively. The molar ratio of the divalent salts to the polymers, C_2/C_p, was varied from 0 to 0.4 for poly(acrylic acid) (PAA) and 0 to 0.5 for poly(L-glutamic acid) (PLG). In the former systems, the addition of divalent cations induces polymer precipitation above $C_2/C_p = 0.4$. Details of the density and sound-velocity measurements have been described elsewhere[8].

Counterion activities were measured with ion-selective electrodes: Orion 97-11 for Na^+, Orion 93-32 for Mg^{2+} and Orion 93-20 for Ca^{2+} in conjunction with an Orion 90-02 double-junction reference electrode. Measurements were not performed on Ba^{2+} because no proper ion electrode was available. The electrode potential was measured by an Orion 901 Ionanalyser. Interference from H^+ was negligible since the pH values of PAANa and PLGNa aqueous solutions were higher than 7.0. All the activity measurements were performed at $25 \pm 0.01°C$.

RESULTS AND DISCUSSION

The apparent molar compressibility, ϕ_p, of a polyion is given by:

$$\phi_p = 10^3(\beta d_s - \beta_s d)/C_p d_s + \beta_s M_0/d_s \qquad (1)$$

where

$$\beta = 1/u^2 d \qquad (2)$$

is the adiabatic compressibility of the polymer solution, u is the sound velocity, d is the density, M_0 is the molecular weight of the monomer residue, and subscript s means the solvent. In the present study, 'solvent' means aqueous solution of alkaline-earth-metal chlorides and/or NaCl. The compressibility ϕ_p contains contributions from hydration water around the polyion. Since the molar compressibility of electrostrictional hydration water is negligibly small compared with that of bulk water $(\phi_w)^{17}$, ϕ_p decreases (becomes more negative) with increase in the ionic hydration.

In *Figure 1*, ϕ_p/ϕ_w vs. C_2/C_p plots are shown for PAANa/$MgCl_2$, $CaCl_2$, $BaCl_2$ and PLGNa/$MgCl_2$ systems. Since divalent counterions compete much more favourably with monovalent ones for binding onto polyions, dehydration due to divalent counterion binding is mainly responsible for the increase in $-\phi_p/\phi_w$ with the addition of divalent counterions. According to counterion condensation theories, including the IMM[12], one divalent counterion exchanges with nearly two moles (1.9–1.7) of monovalent counterion and almost all of the former condense onto the polyion at $C_2/C_p \leqslant 0.2$ (ref. 15). However, one mole–one mole exchange has also been predicted; Miyamoto and Imai[18] have applied the Fokker–Planck equation to thin rod-like polyions. They obtained a new additivity rule, i.e. $\Delta a_{Na} = \Delta(C_2 - a_2)$, which means that one bound divalent counterion releases one monovalent counterion. Therefore they used the ratio $\Delta a_{Na}/\Delta(C_2 - a_2)$ as a measure of the exchange pattern[19]: the ratios at $C_2/C_p < 0.25$ were 1.3 for poly(vinyl sulphonate)/Cu^{2+}, 1.7 for poly(styrene sulphonate)/Cu^{2+} and 2.0 for dextran sulphate/Cu^{2+} systems. The same ratios for PAANa/Mg^{2+} and Ca^{2+} estimated from the data in *Figures 2* and *3* are about 1.5–1.8 in the same C_2/C_p range. This indicates that one mole–two mole exchange rather than one mole–one mole exchange is to be assumed for the present systems. Therefore, the 'overall' dehydration number n^o_{DH} for the reaction:

$$2(\text{-COO}^-\text{Na}^+) + \text{M}^{2+} \rightarrow (\text{-COO}^-)_2\text{M}^{2+} + 2\text{Na}^+ \qquad (3)$$

was roughly estimated here from the initial slope of the plot in *Figure 1*.

The slopes of the ϕ_p/ϕ_w vs. C_2/C_p plots for PAANa/$BaCl_2$ and PLGNa/$MgCl_2$ systems were calculated by least-squares analysis on the data obtained at $C_2/C_p < 0.25$. In the case of the PAANa/$CaCl_2$ system, however, the least-squares calculation was done with all the experimental data, since the linear increase in ϕ_p/ϕ_w continues up to $C_2/C_p = 0.4$. The dehydration numbers n^o_{DH} in the absence of supporting NaCl are indicated in the third column of *Table 1*. The values for PAA systems in the

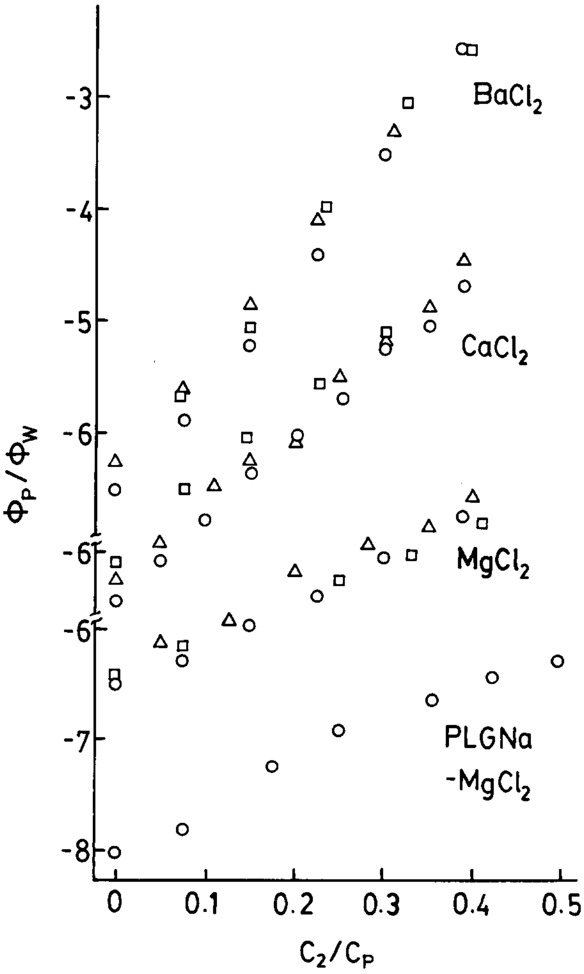

Figure 1 Dependence of ϕ_p/ϕ_w on C_2/C_p for PAANa/$MgCl_2$, $CaCl_2$, $BaCl_2$ and PLGNa/$MgCl_2$ systems: (○) $C_{NaCl} = 0$ M, (△) 0.025 M, (□) 0.05 M

Table 1 Hydration (n_H) and dehydration (n_{DH}) numbers and dehydration fractions (f_{DH})

Ion or process	n_H	n^o_{DH}	n^i_{DH}	f^o_{DH}	f^i_{DH}
Na^+	4.4^a				
Mg^{2+}	10.0^a				
Ca^{2+}	9.0^a				
Ba^{2+}	11.0^a				
$PAACOO^-$	4.2^b				
$PAACOO^- + Na^+$	8.6^c, 6.3^d	(1.5^g)	2.3^b		0.27
$2PAACOO^-Na^+ + Mg^{2+}$	23^e, 18^f	3.7 (8.7^g, 10^h)	8.3	0.16	0.45
$2PAACOO^-Na^+ + Ca^{2+}$	22^e, 17^f	7.2 (13^g)	12	0.33	0.68
$2PAACOO^-Na^+ + Ba^{2+}$	24^e, 19^f	8.7 (12^h)	13	0.37	0.69
$2PLGCOO^-Na^+ + Mg^{2+}$	27^e, 18^f	4.6	4.6	0.17	0.25

[a] Estimated by Bockris *et al.* on compressibility data (ref. 24)
[b] Estimated by the present authors (ref. 8)
[c] Values for the unbound state (ref. 8)
[d] Values for the bound state (ref. 8)
[e] Values containing n_H of the bound Na^+
[f] Values for the free COO^- and M^{2+}
[g] Estimated by Strauss *et al.* (ref. 1)
[h] Estimated by Ikegami *et al.* (ref. 6)

presence of 0.025 M and 0.05 M NaCl are lower, at most by ~10%, than the tabulated values.

If Na^+ ions are bound to the carboxyl anion groups with some dehydration, the n^o_{DH} values corresponding to reaction (3) include the hydration change due to the liberation of the bound Na^+ ions. To obtain the 'intrinsic' dehydration number n^i_{DH} corresponding to the hypothetical process of divalent counterion binding:

$$2(\text{-COO}^-) + M^{2+} \rightarrow (\text{-COO}^-)_2M^{2+} \quad (4)$$

twice the dehydration number for Na^+ ion binding must be added to the n^o_{DH} values. As reported in our preceding paper[8], Na^+ binding onto PAA occurs with partial dehydration of ~2.3 mole/bound ion pair at its full neutralization state. On the other hand, the dehydration number in the case of Na^+ ion binding onto PLG anion seems to be trivial, for the following reason. As seen in *Figure 1*, ϕ_p/ϕ_w for PLGNa at $C_2/C_p = 0.0$ is ca. -8.1, which is smaller than that of PAANa, -6.5. This implies that PLGNa is less dehydrated upon Na^+ binding than PAANa. As a matter of fact, the ϕ_p/ϕ_w value of PLGNa is very close to a calculated ϕ_p/ϕ_w value, -8.2, for hypothetical PAANa in which all the bound Na^+ ions, the fraction of which is estimated to be ~0.64 by the IMM, retain their hydration intact. Therefore we conclude that Na^+ ions are bound to PLG anion without significant hydration changes. In the fourth column of *Table 1* are shown n^i_{DH} values thus obtained.

For comparison, some literature values for n^o_{DH} are shown in parentheses. Strauss *et al.*[1] measured the volume change, ΔV, for the binding reactions of Na^+, Mg^{2+} and Ca^{2+} onto the tetramethylammonium salt of poly(acrylic acid) (PAATMA). The n^o_{DH} values in parentheses were obtained by dividing the reported ΔV values by 2.7 ($cm^3\ mol^{-1}$), the molar volume contraction of water due to electrostrictive hydration[20]. The n^o_{DH} values thus obtained for Mg^{2+} and Ca^{2+} binding are in good agreement with the present estimations for n^i_{DH}. This seems reasonable because the hydration change of TMA cation upon counterion binding has been assumed to be negligible[4]. Ikegami *et al.*[6] estimated n^o_{DH} values for Mg^{2+} and Ba^{2+} binding to the tetrabutylammonium salt of poly(acrylic acid) (PAATBA). It is found that the dehydration numbers of Mg^{2+} and Ba^{2+} are appreciably larger or smaller than the respective n^i_{DH} values. This may be attributed not only to the difference in the experimental methods (compressibility and refractive index) but also to the hydrophobic interaction between TBA cation and the polyanion[4,21].

In the last two columns in *Table 1* are the two types of dehydration fractions, $f^o_{DH} = n^o_{DH}/(n^o_H)_{total}$ and $f^i_{DH} = n^i_{DH}/(n^i_H)_{total}$. The total hydration numbers, $(n_H)_{total}$, for $2(\text{-COO}^-Na^+)$ or $2(\text{-COO}^-) + M^{2+}$ were estimated from n_H values of the components in the second column. The n_H value of $PAACOO^-$ was substituted for that of $PLGCOO^-$. We consider that the dehydration fractions, f^o_{DH} and f^i_{DH} are more directly correlated with the binding mode or strength than are the dehydration numbers. Since f^o_{DH} is the overall dehydration fraction including rehydration of Na^+ repelled by divalent counterions, it may serve as a measure of the binding strength of competitive counterion binding. The f^i_{DH} values will provide information on the binding mode and strength of the divalent counterions in the absence of Na^+ ions. The high f^i_{DH} values of Ba^{2+} and Ca^{2+} binding suggest that these counterions form contact ion pairs or solvent-shared ion pairs with the carboxyl anions. The present dehydration numbers, for example, indicate that only five or six hydration water molecules remain to dangle about one Ca^{2+} and two carboxyl anions in the binding state. The f^i_{DH} values of PAA^-/Mg^{2+} and PLG^-/Mg^{2+}, which are lower than those for Ca^{2+} and Ba^{2+}, seem to be significant in that a fraction of the hydration water molecules may participate in the formation of a solvent-shared ion pair[22]. It should be remarked that, even though one mole–one mole exchange is assumed, these interpretations need no alteration in qualitative sense. In the following, the experimental results on counterion activity coefficients and their correlation with the dehydration fractions are examined.

In *Figure 2*, the a_2/C_2 values obtained for $PAANa/MgCl_2$ and $CaCl_2$ systems are plotted against C_2/C_p. Ca^{2+} ion activity was also measured in the presence of 0.025 M and 0.05 M NaCl. The theoretical curves obtained by the IMM, as shown in *Figure 2*, disagree essentially with the experimental data for the Ca^{2+} ion. The theoretical curve for 0 M NaCl still deviates upwards from the experimental a_2/C_2 values of the $PAANa/MgCl_2$ system. Such an overestimation of a_2/C_2 by the IMM has also been found for

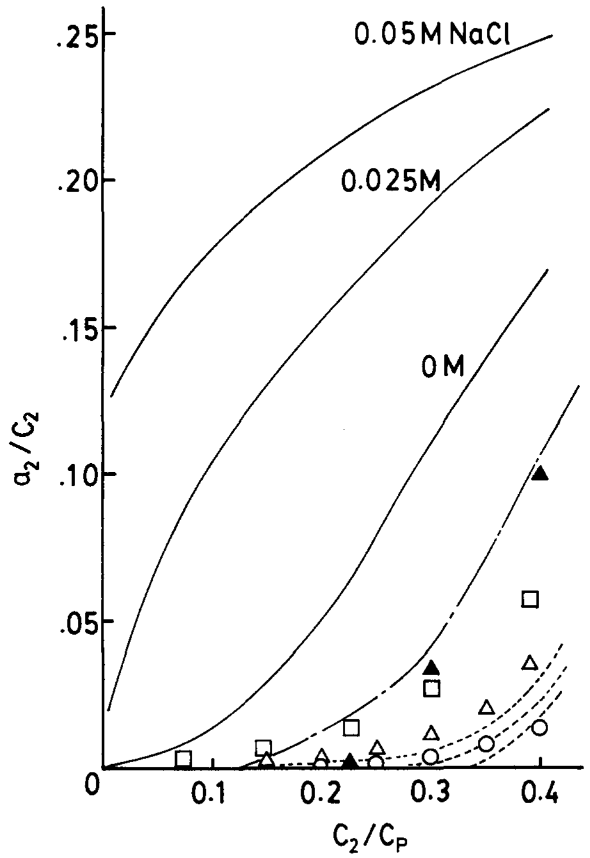

Figure 2 Activity coefficients of Mg^{2+} and Ca^{2+} and the theoretical estimations for PAANa system: (○) Ca^{2+}, $C_{NaCl}=0$ M; (△) Ca^{2+}, 0.025 M; (□) Ca^{2+}, 0.05 M; (▲) Mg^{2+}, 0 M. Theoretical curves are obtained by the IMM: (——) Ca^{2+} and Mg^{2+} ions; (– – –) Ca^{2+} with $\Delta E_{ex} = -3.9$ kcal mol^{-1}; (—·—·—) Mg^{2+} with $\Delta E_{ex} = -1.2$ kcal mol^{-1}

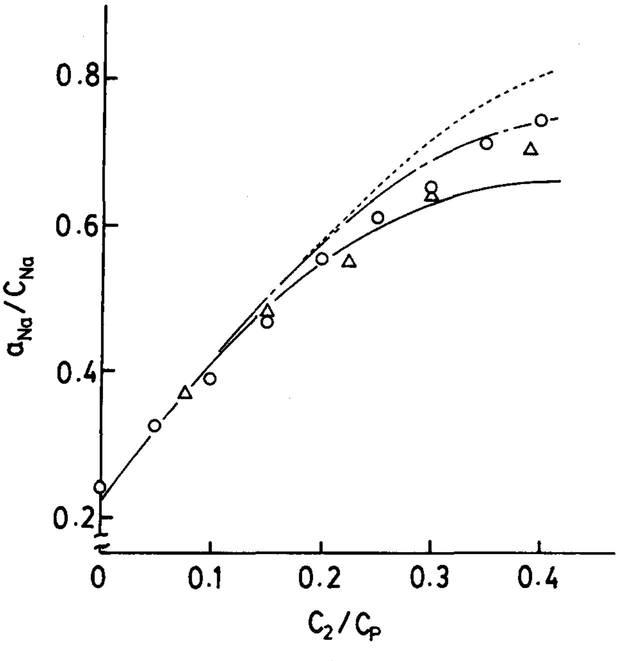

Figure 3 Activity coefficients of Na^+ and the theoretical estimations for PAANa/$MgCl_2$: (○) $CaCl_2$, (△) $MgCl_2$; (——) $\Delta E_{ex}=0$; (– – –) $\Delta E_{ex} = -3.9$ kcal mol^{-1}; (—·—·—) $\Delta E_{ex} = -1.2$ kcal mol^{-1}

PLGNa/$MgCl_2$, $CaCl_2$ systems[15]. In the previous paper, these discrepancies were corrected by assuming 'extra interaction energy ΔE_{ex}' for divalent counterion binding. With a value of -1.5 kcal mol^{-1} for ΔE_{ex}, both a_2/C_2 and a_{Na}/C_{Na} values could be quantitatively reproduced by the IMM. The same correction method was applied to the present results. The chain curve in *Figure 2* was drawn by assuming $\Delta E_{ex} = -1.2$ kcal mol^{-1} for Mg^{2+} in the PAANa system. The agreement with the experimental data is fairly good. This ΔE_{ex} value is comparable to that for Mg^{2+} in the PLGNa system, -1.5 kcal mol^{-1}. For Ca^{2+}, the corrected curves (broken curves) were drawn with $\Delta E_{ex} = -3.9$ kcal mol^{-1} so as to reproduce the experimental a_2/C_2 values in the absence of NaCl. This large negative ΔE_{ex} value implies that the binding of Ca^{2+} onto PAA^- is much stronger than those of counterion condensation mode. With these ΔE_{ex} values, corrected curves for a_{Na}/C_{Na} were drawn in *Figure 3*. The agreement with the experimental values is not effectively improved as compared with the original one. The higher a_{Na}/C_{Na} curve for the Ca^{2+} system is due to the higher interaction energy assumed for Ca^{2+} than for Mg^{2+}.

Finally, we compare the ΔE_{ex} values obtained for PAANa/Mg^{2+}, Ca^{2+} and PLGNa/Mg^{2+} systems with the respective dehydration fraction values, f^{o}_{DH} and f^{i}_{DH}. Since ΔE_{ex} is a measure of the strength of counterion binding on the basis of the condensation mode and hence implicitly includes the energy to repel Na^+ ions, it is expected that ΔE_{ex} may be correlated with the overall dehydration fraction f^{o}_{DH}, which contains the hydration change of the repelled Na^+ ions. As a matter of fact, not only the order of ΔE_{ex} values for PAANa/Ca^{2+}, Mg^{2+} and PLGNa/Mg^{2+} systems (-3.9, -1.2, -1.5 kcal mol^{-1}, respectively), but also the relative largeness is in accordance with that of f^{o}_{DH} values (0.33, 0.16, 0.17, respectively). Thus degrees of dehydration measured by f^{o}_{DH} seem to be related to the binding strength of divalent counterions for reaction (3) measured by ΔE_{ex}. If we also assume the same correlation for the f^{i}_{DH} values and the intrinsic binding strength for reaction (4), the higher f^{i}_{DH} value for PAA^-/Mg^{2+} than for PLG^-/Mg^{2+} means that the intrinsic binding strength for reaction (4) of Mg^{2+} with PAA^- is higher than that with PLG^-. In fact, the stronger binding of Mg^{2+} with PAA^- is manifest in precipitation at higher level of addition of Mg^{2+} ($C_2/C_p > 0.4$). It should be noted here that the above correlation is between the dehydration fractions and the 'extra' binding strength. No correlations are to be expected between these dehydration parameters and 'overall' counterion binding strength or binding degrees. This is because even for polyelectrolytes such as PLGNa and PSSNa, which are hardly dehydrated upon counterion binding, the thermodynamic binding degrees are as large as those of polyelectrolytes subject to dehydration counterion bindings, e.g. PAA.

From the above discussion, one may infer that divalent counterion binding is greatly affected by the species of coexisting monovalent counterions. Such ion specificity in competitive counterion binding has been reported by Kwak *et al.*[23]. These authors found that Ca^{2+} binding onto dextran sulphate in the presence of Na^+ is higher by 10–30% than in the presence of K^+. The specificity in counterion binding is explained by the relative binding affinity of the monovalent ions onto the polyelectrolyte: sulphate anion groups are apt to favour larger alkali cations in counterion binding[1].

CONCLUSIONS

In the present study, the correlation between counterion activity coefficients and dehydration was examined for divalent counterion binding in PAANa/$MgCl_2$, $CaCl_2$ and PLGNa/$MgCl_2$ systems. We have proposed a sophisticated correlation between f^o_{DH} and ΔE_{ex} instead of the direct correlation assumed for degrees of dehydration and site binding. According to the former correlation, the atmospheric counterion binding mode ($\Delta E_{ex}=0$) is assigned even to polyion systems in which dehydrative counterion binding occurs (e.g. for PSS^-/Mg^{2+}, Ca^{2+} systems, $\Delta E_{ex}=0$ and $n_{DH}=3\text{–}5$)[15]. The present study also indicates that the difference between f^o_{DH} and f^i_{DH}, in other words hydration changes accompanying the binding of competing monovalent counterions, is one significant factor that should be taken into consideration when comparing the binding strength of divalent counterions in terms of degrees of dehydration.

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