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Divalent Metal Ion Binding to Polyelectrolytes with Different Polyion Structure and Functional Groups

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ABSTRACT: Polyion–counterion interactions have been investigated in the mixed counterion system $M^{2+}/M^+/Cl^-$/polyion ($M^{2+} = Mg^{2+}, Ca^{2+}$; $M^+ = Na^+, K^+$; polyion = poly(styrenesulfonate) ($\xi = 2.80$), polygalacturonate ($\xi = 1.61$), and (carboxymethyl)cellulose ($\xi = 1.32$ (HZ 900), $\xi = 1.32$ (Z), and $\xi = 1.19$, where HZ 900 and Z represent (carboxymethyl)celluloses with different distributions of methylcarboxyl substituents but with the same overall degree of substitution). Activities of Mg^{2+} and Ca^{2+} were determined by means of a previously described dye spectrophotometric method at ionic strength $I = 0.01$ mol/L and polyion concentration C_p (expressed as mol univalent anionic charges/L) = 0.001. The results are plotted as binding isotherms, θ_2 vs. $C_{M^{2+}}/C_p$ ($\theta_2 = C_{2b}/C_p$; C_{2b} is the bound divalent metal ion concentration), and Scatchard plots, K_2 vs. θ_2 ($K_2 = \theta_2/(C_{M^{2+}} - C_{2b})$) for $I = 0.01$, and results are correlated with the two-variable theory of Manning. Both Mg^{2+} and Ca^{2+} bind to the same extent to poly(styrenesulfonate) with the polyion showing a small specificity for K^+ over Na^+ ($\theta_2(Mg^{2+}/Na^+$ or $Ca^{2+}/Na^+) > \theta_2(Mg^{2+}/K^+$ or $Ca^{2+}/K^+)$). In contrast, for polypectate $\theta_2(Ca^{2+}/M^+) \gg \theta_2(Mg^{2+}/M^+)$, indicating the specific nature of the Ca^{2+}–polypectate interaction. As predicted for the (carboxymethyl)cellulose polyanions, $\theta_2(M^{2+}/M^+; \xi = 1.32\ (\text{HZ 900})) = \theta_2(M^{2+}/M^+; \xi = 1.32\ (\text{Z})) > \theta_2(M^{2+}/M^+; \xi = 1.19)$ with $\theta_2(Ca^{2+}/M^+) > \theta_2(Mg^{2+}/M^+)$. Results for the M^{2+}–poly(styrenesulfonate) interaction, like those for M^{2+}–dextran sulfate, are in good agreement with the two-variable theory, pointing to a delocalized or territorial nature of the metal ion interaction with the sulfonated or sulfated polyions. In contrast, results for M^{2+}–carboxylated polyanions interactions are in excess of theoretical predictions, indicating the restricted nature of the metal ions in the vicinity of the polyanions.

Introduction

Divalent metal ion interactions with the biological polyelectrolytes dextran sulfate and heparin at high ionic strengths have recently been reported from this laboratory,[1-3] with binding data in these "mixed counterion" systems correlated with the two-variable theory of Manning.[4] The divalent metal ions Mg^{2+}, Ca^{2+}, Zn^{2+}, and Mn^{2+} were shown to bind in a delocalized or territorial manner[5] with dextran sulfate, in good agreement with the two-variable theory, although a univalent counterion specificity of the binding was observed.[6] While Mg^{2+} interaction with heparin was also of a delocalized nature, Ca^{2+} interaction was much greater than predicted, indicating the specific nature of the Ca^{2+}–heparin interaction.

Both dextran sulfate and heparin are polyelectrolytes with a predominance of sulfated charged groups on the polyanion backbone, although heparin also contains carboxylated charged groups. For these polyelectrolytes, the charge-density parameter, ξ, defined by $\xi = e^2/\epsilon kTb$ (e is the protonic charge, ϵ is the dielectric constant, k is Boltzmann's constant, T is the absolute temperature, and b is the average distance of separation between neighboring charged groups on the polymer backbone) is considerably greater than unity. A more thorough evaluation of the two-variable theory will necessitate a study of the influence of the charge-density parameter and the nature of the charged groups on the polyanion backbone and their influence on divalent metal ion interaction. Theory predicts that counterion–polyion interaction is a function of the charge-density parameter and independent of the nature of the charged groups.[4] In this paper, we report Mg^{2+} and Ca^{2+} interaction to (carboxymethyl)cellulose (CMC) and polygalacturonate ("polypectate", PP), polyelectrolytes with carboxylate charged groups where the charge-density parameter, ξ, varies from 1.19 to 1.61. In addition, counterion interaction to a sulfonated polymer, poly(styrenesulfonate) (PSSA), with a charge-density parameter identical with that of dextran sulfate, is further examined. Results will be compared to the two-variable theory with the appropriate ξ values.

Table I
Structural Parameters for (Carboxymethyl)cellulose (CMC), Polypectate, and Poly(styrenesulfonate) (PSSA)

polymer	deg of substitution	ξ
CMC (commercial)	0.86	1.19
CMC (HZ 900)[a]	0.96	1.32
CMC (Z)[a]	0.96	1.32
polygalacturonate	0.99	1.61
PSSA	0.99	2.80
dextran sulfate	2.00	2.80

[a] These polymers have the same degree of substitution but differ in distribution of the substituents between ring- and C6 OH groups.

Experimental Section

Origin, purification, and concentration determination of dextran sulfate and poly(styrenesulfonate) solutions are as described earlier.[7,8] Polygalacturonate (polypectate), a gift from Dr. R. Kohn, Slovak Academy of Sciences, Bratislava, is the same sample used in a previous study on surfactant binding.[9] Uronic acid content is 90.5%, degree of esterification, 1%. The 9.5% neutral sugars are not assumed to lower the average charge density of the backbone, thus the ξ value of this polyion is calculated on the basis of a 1% esterification and 4.35-Å length of the α,D-galacturonic acid unit.[9,11] Two samples of CMC (designated "HZ900" and "Z") were supplied by ENKA Industrial Colloids Division, Arnhem, Holland. The difference between these two samples, which have equal degrees of substitution, is in the different distribution of methylcarboxyl substituents on the C_2, C_3, and C_6 positions. The extent of substitution at the various positions was determined by the suppliers by hydrolysis of the CMC and subsequent analysis by HPLC. A third, commercial CMC samples was obtained from Koch-Light Laboratories, Colnbrook, UK. Its degree of substitution was determined to be 0.86.[8] Table I lists the various structural parameters of the polymers used.

Mg^{2+} and Ca^{2+} activities were determined by means of a dye spectrophotometric method.[10] Briefly, this method uses a relatively weak dye–metal ion equilibrium as an activity probe for the metal ion. By working at very low dye concentration relative

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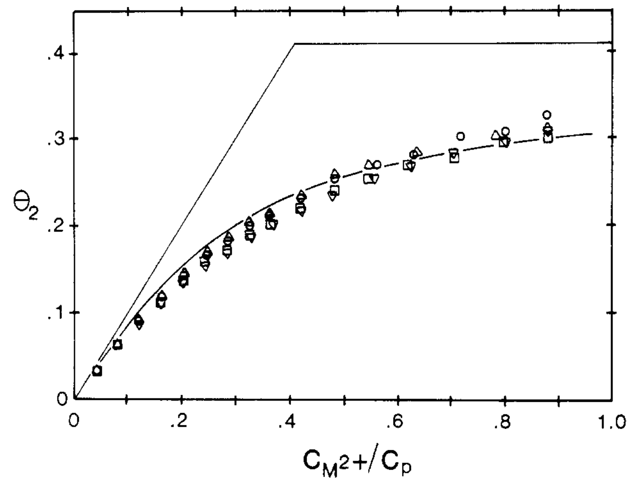

Figure 1. θ_2 vs. $C_{M^{2+}}/C_p$ for the system $MgCl_2$ (or $CaCl_2$) + NaCl (or KCl) + poly(styrenesulfonate) ($\xi = 2.80$) for $C_p = 0.001$ mol/L and $I = 0.01$: (○) Mg/Na; (▽) Mg/K; (△) Ca/Na; (□) Ca/K. Upper line, condensation model;[12] lower curve, two-variable theory.[4]

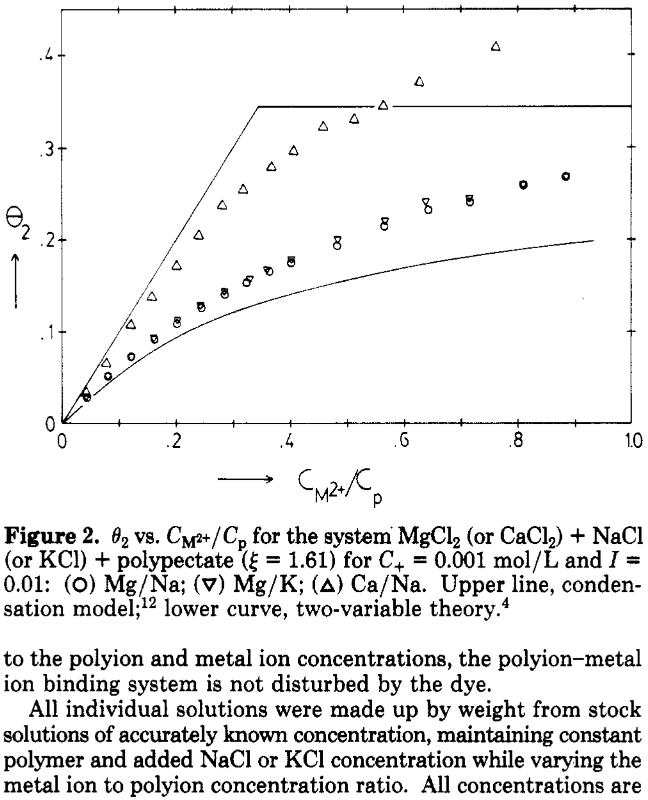

Figure 2. θ_2 vs. $C_{M^{2+}}/C_p$ for the system $MgCl_2$ (or $CaCl_2$) + NaCl (or KCl) + polypectate ($\xi = 1.61$) for $C_+ = 0.001$ mol/L and $I = 0.01$: (○) Mg/Na; (▽) Mg/K; (△) Ca/Na. Upper line, condensation model;[12] lower curve, two-variable theory.[4]

to the polyion and metal ion concentrations, the polyion–metal ion binding system is not disturbed by the dye.

All individual solutions were made up by weight from stock solutions of accurately known concentration, maintaining constant polymer and added NaCl or KCl concentration while varying the metal ion to polyion concentration ratio. All concentrations are expressed as moles per liter.

Results and Discussion

Since the ionic strength dependence of counterion–polyion interaction has been previously established,[1-3] we have chosen to compare the binding to the various polymers at the relatively high ionic strength of 0.01 mol/L for comparison with the two-variable theory. In Figures 1–3, we present experimental data in the form of binding isotherms for the systems $P^- + Mg^{2+}$ (or Ca^{2+}) + Na^+ (or K^+) at $C_p = 0.001$ mol/L and ionic strength of 0.01, where C_p is the polymer concentration. The graphs are plots of θ_2 vs. $C_{M^{2+}}/C_p$, where θ_2 is defined as the fraction of bound divalent metal ions per charged polyion group and is calculated via measured activities[10] and $C_{M^{2+}}$ is the total divalent metal ion concentration. The theoretical lines in Figures 1–3 were calculated from a condensation model[12] (single upper line) and from the two-variable theory[4] (solid or broken lines at $I = 0.01$ for different θ values).

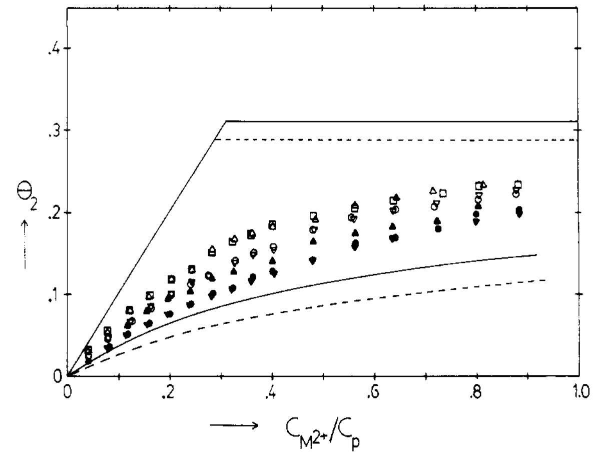

Figure 3. θ_2 vs. $C_{M^{2+}}/C_p$ for the system $MgCl_2$ (or $CaCl_2$) + NaCl (or KCl) + (carboxymethyl)cellulose for $C_p = 0.001$ mol/L and $I = 0.01$: (○) Mg/Na; (▽) Mg/K; (△) Ca/Na; (□) Ca/K. Open symbols, CMC HZ900 and Z, $\xi = 1.32$. Closed symbols, "commercial" CMC, $\xi = 1.19$. Solid curve, two-variable theory for $\xi = 1.32$. Broken curve, two-variable theory for $\xi = 1.19$.

Figure 1 shows the binding isotherms for the system PSSA + Mg^{2+} (or Ca^{2+}) + Na^+ (or K^+), which will be called Mg^{2+}/Na^+, Mg^{2+}/K^+, Ca^{2+}/Na^+, and Ca^{2+}/K^+, respectively. The isotherms show the smooth increase in θ_2 with increasing divalent metal ion concentration, in agreement with the two-variable theory and contrary to the sharp change at $C_{M^{2+}}/C_p = 0.41$ for the simple condensation model. There is no apparent difference between $\theta_2(Mg^{2+}/Na^+)$ and $\theta_2(Ca^{2+}/Na^+)$, indicating that the interaction of Mg^{2+} and Ca^{2+} counterions with the sulfonated polyanion is identical. This is in agreement with earlier mean activity coefficient measurements of Kwak et al.[13] in the systems $MgCl_2$–MgPSSA and $CaCl_2$–CaPSSA, where no counterion specificity was observed. Measurements of surfactant binding to PSSA by Hayakawa and Kwak[14] have shown identical degrees of surfactant binding in the presence of $MgCl_2$ and $CaCl_2$. $\theta_2(Mg^{2+}/Na^+)$ or $\theta_2(Ca^{2+}/Na^+)$ is slightly greater than $\theta_2(Mg^{2+}/K^+)$ or $\theta_2(Ca^{2+}/K^+)$, while NaCl and KCl mean activity coefficient measurements in the system NaCl–NaPSSA and KCl–KPSSA[13,14] showed no appreciable differences between NaCl and KCl.

When a comparison of the binding isotherms for Mg^{2+}/Na^+ is made with the corresponding system for dextran sulfate, the agreement is quite good. For example, at $C_{M^{2+}}/C_p$ of 0.2, 0.4, and 0.5, $\theta_2(Mg^{2+}/Na^+)$ values in PSSA are 0.140, 0.225, and 0.256, respectively, while corresponding values for dextran sulfate are 0.134, 0.218, and 0.245, respectively.[1] The uncertainty in θ_2 is estimated at ±0.004 in all cases. Such an agreement is consistent with the charge-density requirement of the binding; both PSSA with a hydrophobic backbone and dextran sulfate with a more hydrophilic backbone give similar results for the degree of divalent metal ion binding, consistent with the identical charge-density parameter value of 2.80 for these polymers. However, while PSSA does not discriminate in its interaction with Mg^{2+} or Ca^{2+} and only slightly between Na^+ and K^+, dextran sulfate shows a preference for Ca^{2+} over Mg^{2+},[1] while the univalent counterion dependency is more pronounced.[6] The validity of the charge-density condition and the assumption of a delocalized nature of the binding is evident when experimental data are compared to the theoretical curve of the two-variable theory in Figure 1; the agreement is quite good over the whole region of the binding isotherm for Mg^{2+}/Na^+ and only slightly less so for Mg^{2+}/K^+ and Ca^{2+}/K^+. In the systems $MgCl_2$–MgPSSA and $CaCl_2$–CaPSSA good agreement was also found between the experimental data for $MgCl_2$ and $CaCl_2$ mean activity coefficients and Manning's limiting laws.[13,15]

Binding isotherms for the system polygalacturonate (PP) + Mg^{2+} (or Ca^{2+}) + Na^+ (or K^+) are presented in Figure 2. An examination of the systems Mg^{2+}/Na^+ and Mg^{2+}/K^+ shows no observable preference for Na^+ over K^+, within the limits of experimental error. As we will also observe for the (carboxymethyl)cellulose systems, there is no apparent preference of the carboxylate group for Na^+ over K^+ in the mixed counterion system. We observe for the Mg^{2+}/Na^+, K^+ systems reasonable agreement with the theoretical curve at low $C_{M^{2+}}/C_p$ values ($C_{M^{2+}}/C_p < 0.2$), the deviation increasing at larger $C_{M^{2+}}/C_p$ values. It should be noted that relative to the PSSA/Mg^{2+}, Ca^{2+} systems as well as the dextran sulfate/Mg^{2+}, Ca^{2+}, Zn^{2+}, Mn^{2+} systems[1,2] the experimental data for the PP/Mg^{2+} system are in excess of theoretical predictions throughout the region of the binding isotherm. Since a similar deviation is observed for the CMC's, we will further discuss the carboxylate–metal ion interaction below. It is sufficient to indicate here that the delocalized interaction model is not quite valid for the carboxylated polymers but is more closely adhered to by the sulfated and sulfonated polymers.

Binding isotherms for the system polygalacturonate–Ca^{2+} in Figure 2 show the very strong interaction of the calcium ion with the galacturonate anion; values are considerably larger than the corresponding polygalacturonate–Mg^{2+} system and far in excess of the predicted values. Experimental points at higher $C_{M^{2+}}/C_p$ ratios are also in excess of the condensation model. Similar observations were made by Kohn[16,17] for the polygalacturonate–Ca^{2+} and polygalacturonate–Sr^{2+} interactions in the absence of added univalent salts; Ca^{2+} and Sr^{2+} activities were found to be unusually low in such systems. Rees and co-workers[18,19] as well as Kohn[16] have explained the high degree of interaction of the calcium ions as an intermolecular binding of Ca^{2+} ions with carboxyl groups of different chains in small aggregates. Rees et al.[18,19] have represented this cooperative interaction in terms of the "egg-box" model, where selectivity of binding is determined by the comfort with which cations of a particular size pack into the "box". Ca^{2+} appears to satisfy the size requirement; Mg^{2+} does not.

In Figure 3, binding isotherms are presented for the systems CMC + Mg^{2+} (or Ca^{2+}) + Na^+ (or K^+) for $\xi = 1.32$ (HZ 900), 1.32 (Z), and 1.19. As for the pectate case, there is not apparent preference for Na^+ over K^+ by the CMC polyanion. Data for divalent metal ion interaction to CMC are rather scarce. However, this nonspecificity of the carboxylate polyanion for univalent counterions is unlike that found in a number of systems in the absence of divalent ions. For example, in alginates Ander et al.[20] found from EMF measurements that $\gamma_{K^+} > \gamma_{Na^+}$ indicating a specificity sequence $Na^+ > K^+$. Ise et al.[21] arrived at a specificity sequence $K^+ > Na^+ > Li^+$ for the CMC–counterion interaction based on isopiestic measurements, while a reverse sequence was deduced by Tondre and Zana[22] from conductance and potentiometric measurements.

We find that the results for sample HZ900 and Z are indistinguishable within the limits of experimental error, and points from both samples are represented in the data presented in Figure 3. On the other hand, the difference between these two samples and the commercial CMC sample of lower charge density is about as expected, with θ_2 for all systems decreasing with ξ for a given concentration. These results, like those for PSSA and dextran sulfate,[1,2] confirm that the binding is strongly dependent on the average separation of charges on the polyanion backbone and apparently not on the precise location of the groups or on the exact geometry. The Ca^{2+} interaction in Figure 3 is greater than the Mg^{2+} interaction, possibly attributed to the smaller hydrated radius of the Ca^{2+} ion, as was found for the dextran sulfate case;[1] however, the difference between Mg^{2+} and Ca^{2+} is not as large as in the case of polygalacturonate.

Comparison of the experimental data for CMC with the theoretical curves in Figures 2 and 3 shows that counterion binding is much greater than the predictions of the two-variable theory. It has been observed that in biopolymers with higher carboxyl content, specific interactions between counterions and acid groups may occur.[24] For some polyions, the "site binding" model[25] has been invoked. For example, density measurements by Strauss and Leung[26] have indicated that site binding of alkali and alkaline earth metal ions takes place to varying degrees with several polyelectrolytes, including the polyacrylate anion. For this polyanion, Eldrige and Treloar[27] found that the hexaminecobalt(III) cation is site bound by three carboxylate groups on a single polymer chain. ESR measurements by Westra and Leyte[28] show no site binding for the Mn^{2+}–poly(acrylic acid) interaction. However, although the metal ions remain fully hydrated on interaction with the polyacid, there is a restricted mobility, i.e., a decrease in the rate of molecular motion in the direct vicinity of the hydrated model ions. ESR measurements by Karenzi et al.[25] show that for the polyacrylate anion only a fraction of the condensed counterions is able to site bind; poly(styrenesulfonate) did not produce any site binding. Recently, Raman spectroscopic studies by Koda et al.[29] have indicated that while Cu^{2+}, Zn^{2+}, and Mn^{2+} interact with the polyacrylate anion in a specific type of interaction with bond formation, this is not the case for Mg^{2+} and Ba^{2+}. In several cases where the carboxylate interaction gives an affinity sequency of $Li^+ > Na^+ > K^+$ for the alkali metal ions,[22,23,26] the order can only mean that the hydration layers of the metal ions are released or at least partially penetrated and the affinity sequence is in the order of their crystallographic radii.

The above discussion serves to illustrate that for carboxylated polyelectrolytes, the polyanion–metal ion interaction is generally stronger than is the case for the sulfated or sulfonated polymer. Our experimental data for the carboxylated systems confirm this, when comparison is made with the theoretical curves that do not incorporate any specific interaction. The data of Westra and Leyte[28] as well as Karenzi et al.[25] are important in pointing at the restricted nature of the metal ions in the region of the polyion. Such a restriction will reduce the entropy of the counterion in the condensed phase as well as the rate of exchange betwen "bound" and free ions. This will affect the free energy terms from associated uni- and divalent cations in eq 28 or ref 4.

One possible approach for taking into account specific interactions is modification of eq 13 of ref 4 for calculation of the condensation volume, V_p. (V_p is the volume around the polyion in which the counterions are mobile but territorially bound.) A reduced V_p will shift the theoretical binding isotherms upward, producing better correspondence with the experimental data. Note that Manning, in a recent discussion,[30] introduces a specific interaction term that always appears in combination with V_p. Thus, a nonzero value for $\mu_i°$ would be compensated for by a change in V_p (see eq 30 of ref 30), and the binding fractions

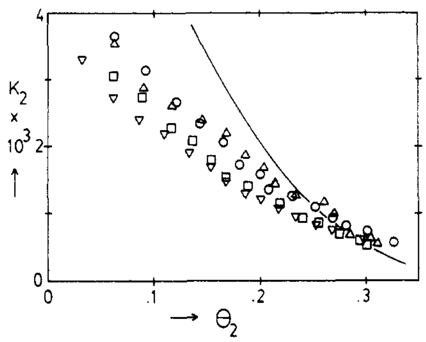

Figure 4. Scatchard curves K_2 (L/mol) vs. θ_2 in the system $MgCl_2$ (or $CaCl)_2$ + NaCl (or KCl) + poly(styrenesulfonate) for $C_p = 0.001$ mol/L and $I = 0.01$. Symbols as in Figure 1; theoretical curve, two-variable theory.[4]

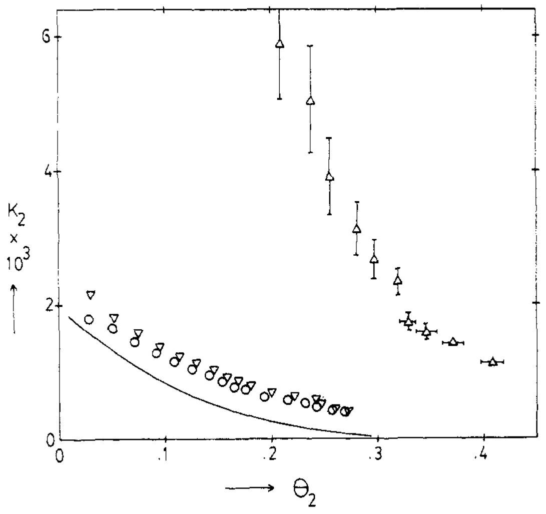

Figure 5. Scatchard curves K_2 (L/mol) vs. θ_2 in the system $MgCl_2$ (or $CaCl_2$) + NaCl (or KCl) + polypectate for $C_p = 0.001$ mol/L and $I = 0.01$. Symbols as in Figure 2; theoretical curve, two-variable theory.[4]

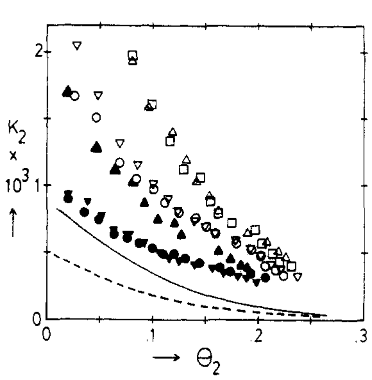

Figure 6. Scatchard curves K_2 (L/mol) vs. θ_2 in the system $MgCl_2$ (or $CaCl_2$) + NaCl (or KCl) + (carboxymethyl)cellulose for $C_p = 0.001$ mol/L and $I = 0.01$. Symbols as in Figure 3; theoretical curves, two-variable theory for $\xi = 1.32$ (solid curve) and $\xi = 1.19$ (broken curve).

would not be changed in this formalism.

The greater carboxylate–divalent counterion interaction appears related to the nonspecificity in the replacement of the univalent counterion. Note that in the case of sulfonated or sulfated polymers with a delocalized nature of the divalent ion binding the polyion does discriminate slightly between univalent counterions.

In Figures 4–6 the binding isotherm data are replotted in terms of Scatchard plots, K_2 vs. θ_2 ($K_2 = \theta_2/(C_{M^{2+}} - C_{2b})$; C_{2b} is the bound divalent metal ion concentration) at $I = 0.01$. Figure 4 for the system PSSA/M^{2+}/M^+ shows the predicted anticooperative nature of the binding, as was observed previously in other polyelectrolyte systems.[1-3,b] K_2 values for the system PSSA/Mg^{2+}/Na^+ are in good agreement with the corresponding dextran sulfate/Mg^{2+}/Na^+ system at similar ionic strengths. For example, the intrinsic binding constant, $K^0_{M^{2+}}$ for PSSA/Mg^{2+}/Na^+ obtained by extrapolating the Scatchard plot to $\theta_2 = 0$ gives a log $K^0_{M^{2+}}$ value of 3.68 ± 0.05 for $I = 0.01$, while the corresponding value for dextran sulfate/Mg^{2+}/Na^+ is 3.61 ± 0.05.[1] Within the limits of error, there is no apparent difference between $K_2(Mg^{2+}/Na^+)$ and $K_2(Ca^{2+}/Na^+)$ and between $K_2(Mg^{2+}/K^+)$ and $K_2(Ca^{2+}/K^+)$. Agreement between the experimental and theoretical K_2 values is quite reasonable; the difference is less than a factor of 2 at low θ_2 and agreement becomes even better at higher θ_2 values. In polygalacturonate solution, Figure 5, the system Mg^{2+}/Na^+, K^+ also shows the predicted anticooperative behavior. For the system Ca^{2+}/Na^+, there is hardly any free Ca^{2+} at low θ_2; the sensitivity of the dye spectrophotometric technique[10] therefore precludes obtaining reasonably accurate values of K_2 at lower θ_2. However, K_2 values at higher θ_2 show considerable differences between the magnesium and calcium curves and large deviations from the theoretical prediction, consistent with a strong binding of Ca^{2+} to polygalacturonate. In Figure 6 for the (carboxymethyl)cellulose systems, we again observe the anticooperativity of the Scatchard plots; K_2 values for Ca^{2+}/Na^+, K^+ are greater than for Mg^{2+}/Na^+, K^+ while there is very little difference between $K_2(Mg^{2+}/Na^+)$ and $K_2(Mg^{2+}/K^+)$ and between $K_2(Ca^{2+}/Na^+)$ and $K_2(Ca^{2+}/K^+)$. The theoretical K_2 values are again much smaller than the experimental values, showing the stronger interaction of divalent counterions with the carboxylated polyanion.

In conclusion, we have shown that the delocalized nature of counterion binding and its dependency on the charge-density parameter, as derived from the two-variable theory, are reasonably valid for the sulfonated and sulfated polyelectrolytes, poly(styrenesulfonate) and dextran sulfate. For the carboxylated polyanions, polypectate and (carboxymethyl)cellulose, counterion binding is in excess of predictions of the two-variable theory, although the charge-density requirement of the binding is valid. Modification of the entropy of mixing terms of the bound counterions in eq 28 of ref 4 and/or the use of the condensation volume, V_p, as an adjustable parameter in the two-variable theory can account for the restricted nature of the counterion in the condensed phase.

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Registry No. CMC, 9004-32-4; PP, 25249-06-3; PSSA, 50851-57-5; Mg, 7439-95-4; Ca, 7440-70-2; Na, 7440-23-5; K, 7440-09-7; dextran sulfate, 9042-14-2.

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Deuteration Effects on the Miscibility and Phase Separation Kinetics of Polymer Blends

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ABSTRACT: The substitution of deutereous polystyrene (PSD) for hydrogenous PS (PSH) in PS/poly(vinyl methyl ether) (PVME) blends raised the lower critical solution temperature (LCST) of the blend by about 40 °C. This deuteration effect has been qualitatively interpreted as resulting partially from the larger percentage of negative excess volume of mixing for PSD/PVME relative to that of PSH/PVME. Both blends have the same glass transition temperature (T_g) for the same composition. Optical microscopy was used to study the morphology of phase separation for PSD/PVME and PSH/PVME blends at the same degree of superheating. The composition for these blends is close to the critical composition, i.e., 30 wt % PS. The observed morphologies are consistent with the prediction of the Cahn–Hilliard theory for spinodal decomposition. It has been found that the kinetics of phase separation for the PSD blend is about 10 times faster than that for the PSH blend. This behavior can be qualitatively interpreted in terms of the William–Landel–Ferry (WLF) equation. Furthermore, dynamic parameters, maximum scattering vector magnitude (q_m) and time (t) of spinodal decomposition for the above blends studied by light scattering are scaled to the reduced wave number and time, Q_m and τ, respectively, in terms of the characteristic parameters—apparent diffusion constant (D_{app}) and $q_m(t=0)$. The phase separation process is found to be the same for PSD/PVME, PSH/PVME, and other systems such as metallic alloys, inorganic glasses, and small-molecule systems. Their exponent has the same value (1.0) according to the power-law approach. The difference in the phase separation kinetics between the PSD/PVME and the PSH/PVME blends is simply due to lower viscosity and higher diffusion constant for the PSD blend.

Introduction

The small-angle neutron scattering (SANS) technique has often been used to study the miscibility of polymer blends in the solid state by using the deuterium substitution technique.[1-10] The substitution of deuterium for hydrogen in one of the components of the polymer blend provides the difference in a scattering length necessary to obtain sufficient coherent scattering. In this type of substitution, it is usually assumed that the thermodynamic interaction between components is negligibly affected. That is, for hydrogenous (H) and deutereous (D) species of one component and a second component (S) the Flory interaction parameters χ_{HS} and χ_{DS} are assumed to be equal and χ_{HD} is assumed to be zero. The validity of the latter assumption in the case of hydrogenous and deutereous polystyrene (PSH and PSD) has been demonstrated through the observation of a zero second virial coefficient by SANS studies from Zimm plots.[11] It should be pointed out that a small difference in thermodynamic properties between PSH and PSD has been demonstrated[12] by studies on solutions of both polymers in hydrogenous and deutereous cyclohexane. A lower critical solution temperature (LCST) behavior[13] is seen for a blend of polystyrene (PS) and poly(vinyl methyl ether) (PVME); its value depends on the molecular weight of the components.[14] In our previous paper,[15] we have shown by using photometric light scattering that the substitution PSD for PSH in PS/PVME blends raised the LCST by about 40 °C. This phenomenon has also been verified by Halary et al. using the fluorescence technique.[16]

In this paper we further describe the comparison between PSD/PVME and PSH/PVME blends, considering their glass transition behavior, volume of mixing change, and phase separation behavior and its kinetics.

Experimental Section

Sample Preparation. A commercial sample of PVME (Scientific Polymer Products, Webster, NY, $M_n = 46\,500$, $M_w = 99\,000$, and $M_w/M_n = 2.13$) was solution blended with samples of anionically synthesized hydrogenous polystyrene ($M_w = 100\,000$, $M_w/M_n = 1.05$) or with deutereous polystyrene ($M_w = 119\,000$,

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