Biophysical Chemistry, 31 (1988) 209–215
Elsevier

BPC 01269

A new model of counterion condensation in polyelectrolyte solutions

III. Theoretical predictions of competitive condensation between counterions of different valences

Mitsuru Satoh, Takehito Kawashima and Jiro Komiyama

Department of Polymer Science, Tokyo Institute of Technology, Ookayama, Meguro-ku, Tokyo 152, Japan

Received 4 November 1987
Accepted 7 April 1988

Polyelectrolyte; Counterion condensation; Activity coefficient

Our model has been extended for theoretical estimation of competitive condensation of counterions of different valences onto polyelectrolytes in solution. The estimations are compared with those obtained from Manning theory and with experimental data on counterion activity coefficients. The agreement with the data for sodium polystyrenesulfonate/$MgCl_2$, $CaCl_2$ is satisfactory.

1. Introduction

Counterion condensation in polyelectrolyte systems containing different kinds of counterions, particularly monovalent and divalent types, has been studied from the viewpoint of its biological importance as well as from theoretical interest. Record [1] studied the effects of counterion condensation of Na^+ and Mg^{2+} on the helix-coil transition of DNA. He observed that the melting temperature, T_m, attained a minimum as a function of Na^+ concentration in the presence of Mg^{2+}. The present authors [2] have also observed a similar dependence of the helix content of sodium poly(L-glutamate) in the presence of Mg^{2+}. This behavior was interpreted in terms of the decrease in degree of condensation of Mg^{2+} with increase in Na^+ concentration and with respect to the resulting modulation in degree of effective charge density. In the study of counterion condensation theories, many kinds of synthetic and biological polyions, with which no conformational transition takes place, have been employed in investigating the competitive binding of monovalent and divalent counterions. Kwak and co-workers [3–6] studied the condensation of divalent counterions onto dextran sulfate in the presence of excess monovalent salts. They found that the two-variable theory derived by Manning [7] is applicable to such systems. Miyamoto and Imai [8] reported that their new additivity rule, namely, that an increase in the activity of a monovalent counterion is equal to the increase in the difference between the concentration and the activity of the added divalent counterion, provides a good explanation for the counterion activities observed with the sodium poly(styrenesulfonate)/$CuSO_4$ system. This additivity rule was also found to be valid for the sodium poly(vinylsulfonate)/$CuSO_4$ system [9]. Shimizu et al. [10] measured the activity coefficients of counterions for the sodium salt of a copolymer of maleic acid and the ethyl vinyl ether/$CaCl_2$ system. The results were compared with Manning theory using a charge density

Correspondence address: M. Satoh, Department of Polymer Science, Tokyo Institute of Technology, Ookayama, Meguro-ku, Tokyo 152, Japan.

parameter ξ, which was obtained in the experiment. In the latter three examples, however, the degrees of condensation and activity coefficients of monovalent and divalent counterions have not been estimated theoretically. Recently, Manning has extended his condensation theory to general cases in which no restriction is imposed on the counterion species, ionic strength and the ratio of counterion and polyion concentrations [11]. However, the theory is a limiting law. For a finite value of the ionic strength, a priori knowledge of the condensed volume is necessary for estimation of the degree of condensation.

In our preceding paper [12], we have proposed a new model (the intermediate model) for counterion condensation as an extension of Manning theory. The theoretical estimations of the degree of condensation and counterion activity coefficients have been compared with those derived from the theories by Manning [13] and Iwasa and Kwak [14]. Qualitative agreement with experimental data has been found for the ionic strength dependence of the counterion activity coefficients, especially for systems in which interpolymer interactions can be neglected. The present paper describes a further extension of the intermediate model for polyelectrolyte solutions containing counterions of different valences. The theoretical predictions regarding the degree of condensation and counterion activity coefficients are compared with Manning theory derived for the general case and with experimental data for sodium poly(styrenesulfonate)(PSSNa)/$MgCl_2$-$CaCl_2$ and sodium poly(L-glutamate) (PLGNa)/$MgCl_2$-$CaCl_2$ systems obtained in the present study.

2. Polymer model and free energy calculation

The polymer model and the assumptions made for calculation of free energy adopted in this study are the same as those described in the preceding study [12]. We treat a system consisting of a polyion, ν_{1c}-ν_{1b} salt, ν_{2c}-ν_{2b} salt and solvent. Here, ν_i denotes the valence of the i-th added small ions and $\nu_{1c} < \nu_{2c}$. Subscripts c and b represent the counterion and by-ion, respectively. We assume that the counterion species of the polyelectrolyte is the same as that of the salt 1, and that the system contains only two kinds of counterions.

The free energy of the system, ΔG, is expressed as functions of the degrees of counterion condensation, θ, as follows.

$$\begin{aligned}\Delta G/RT &= C_{1c}\left(\ln C_{1c} + \ln \gamma_{1c}^{ii}\right) + C_{2c}\left(\ln C_{2c} + \ln \gamma_{2c}^{ii}\right) \\ &\quad + C_w \ln a_w + F_{ex}/RT \\ &\quad + C_p\{\theta_1 \ln \theta_1 + \theta_2 \ln \theta_2 \\ &\quad + (1 - \nu_{1c}\theta_1 - \nu_{2c}\theta_2)\ln(1 - \nu_{1c}\theta_1 - \nu_{2c}\theta_2) \\ &\quad - (1 - (\nu_{1c} - 1)\theta_1 - (\nu_{2c} - 1)\theta_2) \\ &\quad \times \ln(1 - (\nu_{1c} - 1)\theta_1 - (\nu_{2c} - 1)\theta_2)\} \qquad (1)\end{aligned}$$

where C represents molar concentration, γ the activity coefficient and a the activity. Subscripts p and w refer to the polyion and water (solvent), respectively. Superscript ii signifies a small ion-small ion electrostatic interaction. The final term on the right-hand side of eq. 1 expresses the mixing entropy for the assumed linear array of condensed counterions and polymer charges.

C_{1c}, C_{2c} and a_w are given by the following equations.

$$C_{1c} = n_{1c}C_1 + (1 - \nu_{1c}\theta_1)C_p/\nu_{1c} \qquad (2a)$$

$$C_{2c} = n_{2c}C_2 - \theta_2 C_p \qquad (2b)$$

$$a_w = C_w/(C_w + C_{1c} + C_{2c} + C_b) \qquad (2c)$$

where n_{ic} is the mole number of counterion in the i-th salt, i.e., $n_{ic}\nu_{ic} = n_{ib}\nu_{ib}$, and C_b $(= n_{1b}C_1 + n_{2b}C_2)$ the molar concentration of by-ions. In eq. 2c, the contribution of the polyion to a_w is neglected. F_{ex}, the excess free energy for electrostatic interactions between polymer charges and between small ions and polyions, is estimated with the screened coulombic Debye-Hückel potential:

$$F_{ex}/RT = C_p\xi(1 - \nu_{1c}\theta_1 - \nu_{2c}\theta_2)^2 \sum_{m=1}^{N-1}(1 - m/N) \times \exp(-\kappa m b)/m \qquad (3a)$$

$$\kappa^2 = 8\pi \times 10^{-3} N_A (e^2/DkT) I \qquad (3b)$$

$$I = 1/2 \times \left(\nu_{1c}^2 C_{1c} + \nu_{2c}^2 C_{2c} + n_{1b}\nu_{1b}^2 C_1 + n_{2b}\nu_{2b}^2 C_2\right) \qquad (3c)$$

where ξ is the charge density parameter given as $e^2/DkTb$, e the electronic charge, D the dielectric constant of the bulk solvent, T the absolute temperature, and b the axial spacing of the charged groups. N represents the number of charges on a polyion, N_A Avogadro's number and I the ionic strength.

The activity coefficient, γ^{ii}, which represents small ion-small ion electrostatic interactions, is estimated by using the Debye-Hückel equation as modified by Kielland [15].

$$\log \gamma^{ii} = -0.5115\nu_i^2 I_0^{0.5}/(1 + 0.3291 r I_0^{0.5}) \tag{4}$$

where I_0 is the ionic strength of salt solution in the absence of polyelectrolyte and r the effective diameter of the ion determined by Kielland. It should be noted here that I_0 in eq. 4 is not equal to that in eq. 9 of our preceding paper. When a polyelectrolyte solution contains only one kind of counterion or different counterions of the same valence, I_0 is given by $\Sigma(n_{ic}\nu_{ic}^2 + n_{ib}\nu_{ib}^2)C_i/2$. In the present system, however, I_0 cannot be determined in an unequivocal manner, since counterions of different valences are present. Some assumption is necessary to assign the counterions to the polyelectrolyte and added salt. Here, counterions of ν_{2c} are preferentially assigned to polyelectrolyte because counterions of higher valence have higher affinity to polymer charges. Then, I_0 is given by the following equations:

(when $n_{2c}\nu_{2c}C_2 > C_p$)

$$I_0 = 1/2 \times \{(n_{1c}\nu_{1c}^2 + n_{1b}\nu_{1b}^2)C_1 + (n_{2c}\nu_{2c}^2 + n_{2b}\nu_{2b}^2)C_2 - (\nu_2 - \nu_1)C_p\} \tag{5a}$$

(when $n_{2c}\nu_{2c}C_2 \leqq C_p$)

$$I_0 = 1/2 \times \{(n_{1c}\nu_{1c}^2 + n_{1b}\nu_{1b}^2)C_1 + (n_{2c}\nu_{1c}\nu_{2c} + n_{2b}\nu_{2b}^2)C_2\} \tag{5b}$$

Although this is a rather arbitrary assignment, the estimation of θ values using eq. 1 is scarcely affected, the variation in θ values amounting at most to a few percent under the experimental conditions usually employed in this definition of I_0.

The activity coefficients for free counterions, γ_{1c} and γ_{2c}, are calculated from differentiation of F_{ex}/RT with the concentration of each species (eq. 5 of ref. 12). The stoichiometric activity coefficients, γ_{1c}^s and γ_{2c}^s, are given by the following equations.

$$\gamma_{1c}^s = \gamma_{1c}^{ii}\gamma_{1c}C_{1c}/(n_{1c}C_1 + C_p/\nu_{1c}) \tag{6a}$$

$$\gamma_{2c}^s = \gamma_{2c}^{ii}\gamma_{2c}C_{2c}/n_{2c}C_2 \tag{6b}$$

3. Experimental

The preparation and purification of sodium poly(styrenesulfonate)(PSSNa) and sodium poly(L-glutamate)(PLGNa) have been described in part I of this series [12]. $MgCl_2$ and $CaCl_2$ of analytical grade were used as the added salts and were purchased from Tokyo Kasei Co. Ltd. The ratio of divalent counterion to polymer, C_2/C_p, was adjusted to 0–0.8. All sample solutions were prepared with deionized and subsequently distilled water.

Counterion activities were measured at 25 ± 0.05 ° C with ion-selective electrodes, viz., an Orion 97-11 for Na^+ and an Orion 93-32 for the divalent ions in conjunction with an Orion 90-02 double-junction reference electrode. Electrode potential was measured using an Orion 901 ion analyser.

4. Comparison with Manning theory

Manning [11] has extended his limiting law for counterion condensation to general cases. According to his study, the degrees of condensation of any kind of counterion present in any ratio and at any concentration can be estimated if the condensed phase volume V_p can be properly evaluated. Manning has suggested two models for the calculation of V_p: the 'independent condensation' model and a modified 'monolayer condensation' model. These were originally proposed by Iwasa [16]. In the former model, V_p for each counterion species is estimated by neglecting the presence of the other counterion species, resulting in multiple V_p values. In the latter model, a single V_p value is used for calculation of counterion condensation; it is assumed that V_p values for different counterions take a mean value given by the weighted average, $\Sigma z_i V_{pi} \exp(-\delta\mu_i^o/RT)$. Here, z_i is the weight for the i-th counterion, V_{pi} the condensed phase volume, and $\delta\mu_i^o$ the difference of the chemical potential in the reference state including the activity coefficients of the condensed and free counterions. If z_i is taken as the ratio of the number of counterion i to the total number of all the counterions, this estimation procedure for V_p reduces to that of the two-variable theory of Manning when one counterion species is present in excess.

In fig. 1a–c we compare θ_1 and θ_2 values for mono- and divalent counterion systems estimated according to eq. 1 and by the later model of Manning. The theoretical θ_i values from Manning theory were obtained numerically as a combination of θ_1 and θ_2 which minimizes the free energy given by eq. 6 of ref. 11. Fig. 1a–c shows the

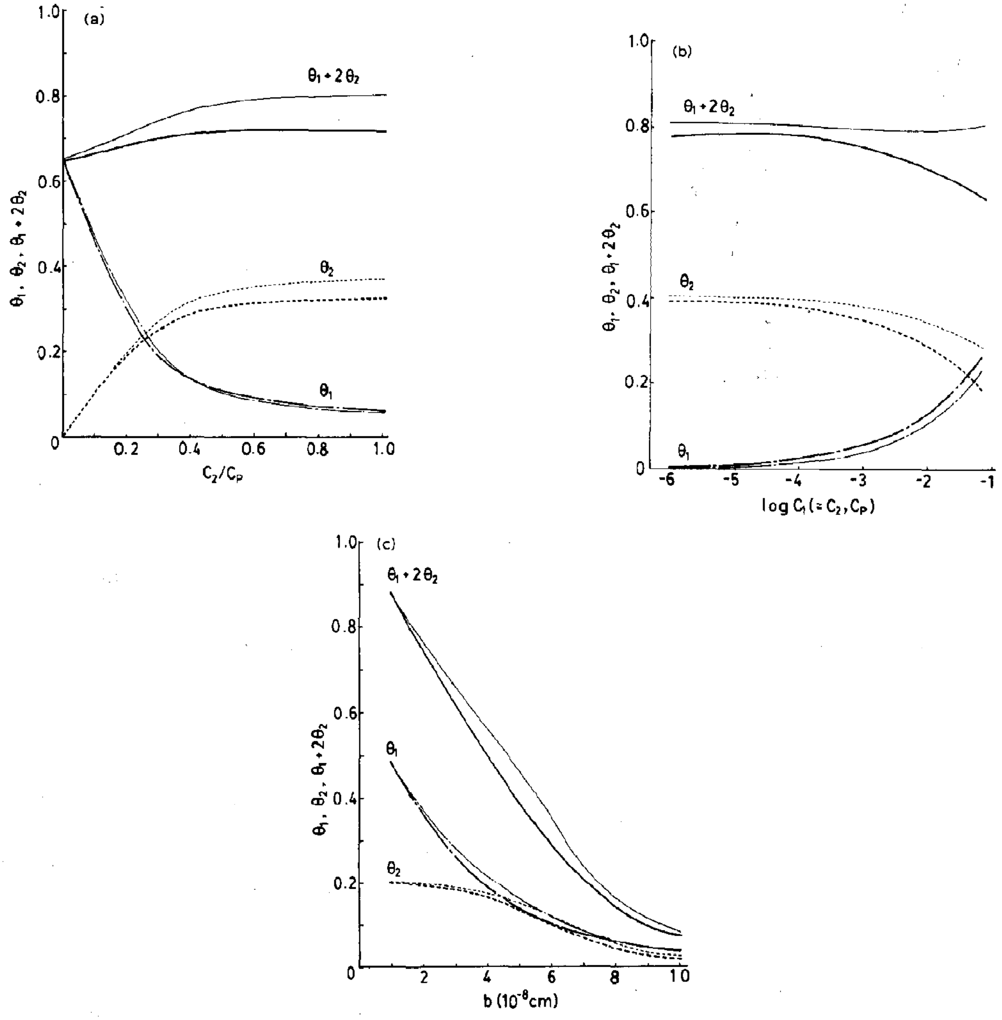

Fig. 1. Comparison of theoretical θ_i values for the intermediate model and Manning theory. Thick curves, intermediate model; thin curves, Manning theory. (a) Dependence on divalent counterion ratio, C_2/C_p. $N = 1000$, $b = 2.5 \times 10^{-8}$ cm, $C_1 = 0$, $C_p = 1.0 \times 10^{-2}$ eq./l. (b) Dependence on ionic strength, I. $N = 1000$, $b = 2.5 \times 10^{-8}$ cm, $C_1 = C_2 = C_p$. (c) Dependence on charge spacing, b. $N = 1000$, $C_1 = 0$, $C_2 = 2.0 \times 10^{-3}$ mol/l, $C_p = 1.0 \times 10^{-2}$ eq./l.

dependences of θ_i values on the molar ratio of divalent counterion to polyelectrolyte, C_2/C_p, ionic strength, I, and charge density, b (the charge spacing), respectively. In each case, one observes that the two theoretical estimations for θ_i are similar in a qualitative sense. For example, both theories predict that θ_1 increases and θ_2 decreases with increasing ionic strength, as shown in fig. 1b. These predictions are reasonable because at lower ionic strengths, counterions of higher valence are preferred by the polyelectrolyte to reduce effectively the electrostatic interaction between polymer charges. With increasing ionic strength, such a preference becomes less significant. In fact, the decreasing trend in θ_2 values has been demonstrated experimentally [4].

Although not apparent from fig. 1b, which covers the usual range of ionic strengths, an essential difference between the two estimations can be found concerning their predictions on the ionic strength dependence of θ_i values. The intermediate model predicts that θ_i decreases to zero with decreasing ionic strength tending toward infinite dilution, whereas according to Manning theory, the θ_i values remain constant in the limit of dilution. The latter originates from an unrealistic polymer model, i.e., the infinitely long polymer model adopted in the Manning theory, as discussed in our preceding paper. The prediction of the present model as regards the ionic strength dependence of counterion condensation is consistent with those of Mayer's cluster integral [17], statistical mechanics [18] and the Poisson-Boltzmann cell model [19], and also with the experimental observations on the ionic strength dependence of counterion activity coefficients, especially at lower ionic strengths [12].

Another difference demonstrated in fig. 1a–c is that the values of θ_2 and $\theta_1 + 2\theta_2$ estimated by the intermediate model are lower than those of the Manning theory. It may be worthwhile comparing these theoretical estimations with experimental data on the degree of condensation for mixed-counterion systems. Joshi and Kwak [4] measured θ_2 for Mg^{2+} and Ca^{2+} in solutions of sodium and potassium dextran sulfates by using a two-wavelength dye spectrophotometric method. The authors found that the θ_2 values for combinations of M^{2+}/K^+ at a given C_2, C_p and I are lower than those of M^{2+}/Na^+. This was attributed to the smaller hydrated radius and the resultant greater affinity of K^+ to the polyion. In fig. 2, θ_2 values for dextran sulfate/$CaCl_2$/NaCl and /KCl systems are compared with the two theoretical curves. It is observed that the agreement between the curves from the Manning theory and intermediate model with the experimental results is satisfactory for both Ca^{2+}/Na^+ and Ca^{2+}/K^+ systems, respectively. In a region of greater ionic strength, Manning theory overestimates θ_2 for the Mg^{2+}/Na^+ system as shown by the lower dashed curve in fig. 2. It can be stated that both the intermediate model and the Manning theory, in spite of not being applicable in dealing with ion-specific counterion binding, provide fairly good estimates. However, it should be noted again that V_p values in the Manning theory have to be determined rather arbitrarily for the relevant systems.

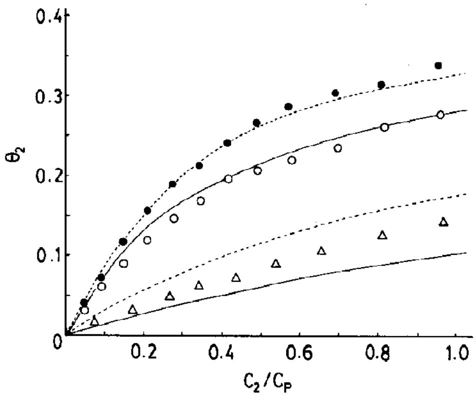

Fig. 2. Experimental θ_2 values for dextran sulfate [4] and theoretical estimations according to the intermediate model and Manning theory. $N = 2775$, $b = 2.5 \times 10^{-8}$ cm. Solid curves, intermediate model; dashed curves, Manning theory. (●) DSNa/NaCl/$CaCl_2$, $I = 0.01$, $C_p = 1 \times 10^{-3}$ eq./l. (○) DSK/KCl/$CaCl_2$, $I = 0.01$, $C_p = 1 \times 10^{-3}$ eq./l. (▵) DSNa/NaCl/$MgCl_2$, $I = 0.06$, $C_p = 2 \times 10^{-3}$ eq./l.

5. Counterion activities and the theoretical estimation of the intermediate model

In figs. 3 and 4, the activity coefficients a_{Na}/C_{Na} $(= \gamma_{1cs})$ and a_2/C_2 $(= \gamma_{2cs})$ for PSSNa/

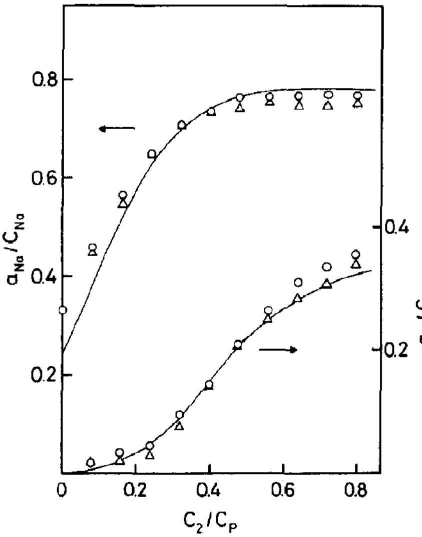

Fig. 3. Experimental activity coefficient for PSSNa/$MgCl_2$, $CaCl_2$ systems and theoretical estimations from the intermediate model. $N = 452$, $b = 2.5 \times 10^{-8}$ cm, $C_1 = 0$, $C_p = 1 \times 10^{-2}$ eq./l.

$MgCl_2$ or $CaCl_2$ and PLGNa/$MgCl_2$ or $CaCl_2$ systems are plotted as a function of C_2/C_p. For these polyions, the results obtained with the $MgCl_2$ systems agree with those of $CaCl_2$ within the limits of experimental error.

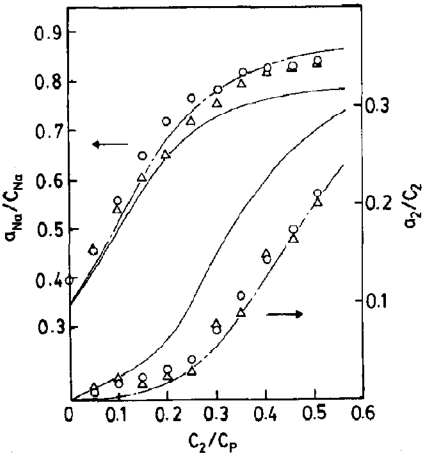

Fig. 4. Experimental activity coefficients for PLGNa/$MgCl_2$, $CaCl_2$ systems and theoretical estimations from the intermediate model. $N = 457$, $b = 3.6 \times 10^{-8}$ cm, $C_1 = 0$, $C_p = 1 \times 10^{-2}$ eq./l. Solid curves, intermediate model; dashed-dotted curves, intermediate model with $\Delta E_{ex} = -1.5$ kcal/mol.

The increase in and saturation of a_{Na}/C_{Na} with increasing C_2/C_p are due to the exchange of condensed Na^+ with added M^{2+}. The increase in a_2/C_2 becomes noticeable concomitantly with saturation of Na^+ activity. These forms of behavior of the change in activity are explained by the intermediate model. The theoretical curves for PSSNa/M^{2+} systems exhibit quantitative agreement with experimental data on the respective activity coefficients. However, the activity coefficients of M^{2+} and Na^+ for PLGNa/M^{2+} systems are over- and underestimated, respectively, by the intermediate model. The discrepancy, converted into the degree of counterion binding, between the estimation of the intermediate model and the experimental results for divalent counterions is 2-fold greater than that found in the sodium dextran sulfate/$CaCl_2$ system. Such a marked disagreement may be attributed to differences in binding mode. The counterion binding of polystyrenesulfonate is classified as being of the 'atmospheric binding' mode, in which counterions are least dehydrated upon binding [20]. On the other hand, it is known that divalent counterions interact with those polyelectrolytes having carboxylate groups in a specific mode close to the site binding; counterions are substantially dehydrated [20]. According to Mattai and Kwak [21], divalent counterion binding to polyelectrolytes having sulfonate or sulfate groups (e.g., PSS, dextran sulfate) can be correlated with the two-variable theory of Manning, which, however, largely underestimates the counterion binding for carboxylated polyanions (e.g., polypectate and carboxymethylcellulose). If Mg^{2+} and Ca^{2+} are attracted to the charged groups of PLG more strongly than is predicted by the intermediate model, then the activities of M^{2+} and Na^+ should be lower and higher, respectively, than in the theoretical estimations. This is actually observed. In order to estimate the extra interaction energy, ΔE_{ex}, for condensed divalent ions, we incorporated an additional term, $\Delta E_{ex}/RT \times \theta_2 \times C_p$, into eq. 1. The dashed-dotted lines in fig. 4 were obtained by assuming a value of -1.5 kcal/mol for ΔE_{ex}. It should be noted that not only the theoretical curve for a_2/C_2 but also that for a_{Na}/C_{Na} can be fitted to the experimental results by assuming a single extra interaction energy for divalent counterion binding. The ΔE_{ex} value contains contributions from the short-range electrostatic energy (favorable) between polymer charges and a counterion, and the dehydration energy (unfavorable). In the case of small ion association (divalent cation-divalent anion; e.g., Ca^{2+}-malonate anion), the free energies are of the order of a few (negative) kcal/mol [22]. Therefore, the value estimated for ΔE_{ex} seems reasonable. Further discussion of the correlation of the hydration (and dehydration) behavior of divalent counterions and ion specificity in counterion condensation phenomena will be presented in a forthcoming paper.

The present study has reported as extension of the intermediate model to multi-counterion systems. The θ values estimated according to this extended version show dependences on the ionic strength which are qualitatively different from those obtained using the Manning theory for finite ionic strength. The intermediate model quantitatively explains mono- and divalent counterion activity coefficients in PSSNa/$MgCl_2$, $CaCl_2$ systems. This model is also applicable to polyion systems, such as PLGNa/$MgCl_2$, $CaCl_2$, in which dehydration is supposed to occur with counterion binding, if the effects of the hydration changes upon counterion binding are taken into account in terms of the extra interaction energy.

References

1 M.T. Record, Jr, Biopolymers 14 (1975) 2137.
2 M. Satoh, J. Komiyama and T. Iijima, Biopolymers 21 (1982) 1927.
3 J.C.T. Kwak and Y.M. Joshi, Biophys. Chem. 13 (1981) 55.
4 Y.M. Joshi and J.C.T. Kwak, Biophys. Chem. 13 (1981) 65.
5 J. Mattai and J.C.T. Kwak, Biophys. Chem. 14 (1981) 55.
6 J. Mattai and J.C.T. Kwak, J. Phys. Chem. 86 (1982) 1026.
7 G.S. Manning, Q. Rev. Biophys. 11 (1978) 179.
8 S. Miyamoto and N. Imai, Biophys. Chem. 11 (1980) 345.
9 S. Miyamoto, Biophys. Chem. 14 (1981) 341.
10 T. Shimizu, A. Minakata and N. Imai, Biophys. Chem. 14 (1981) 333.
11 G.S. Manning, J. Phys. Chem. 88 (1984) 6654.
12 M. Satoh, T. Kawashima, J. Komiyama and T. Iijima, Polym. J. 19 (1987) 1191.
13 G.S. Manning, J. Chem. Phys. 51 (1969) 924.
14 K. Iwasa and J.C.T. Kwak, J. Phys. Chem. 81 (1977) 408.
15 J. Kielland, J. Am. Chem. Soc. 59 (1937) 1675.
16 K. Iwasa, Biophys. Chem. 9 (1979) 397.
17 C.P. Woodbury, Jr and G.V. Ramanathan, Macromolecules 15 (1982) 82.
18 G.V. Ramanathan and C.P. Woodbury, Jr, J. Chem. Phys. 77 (1982) 4133.
19 D. Bratko and D. Dolar, J. Chem. Phys. 80 (1984) 5782.
20 U.P. Strauss and Y.P. Leung, J. Am. Chem. Soc. 87 (1965) 1476.
21 J. Mattai and J.C.T. Kwak, Macromolecules 19 (1986) 1663.
22 A.E. Martell and M. Calvin, Chemistry of the metal chelate compounds (Prentice-Hall, New York, 1952).