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EXAMINATION OF THE LIMITING LAWS OF POLYELECTROLYTES AND COUNTERION CONDENSATION II

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The two phase model of polyelectrolyte solutions, which has been developed recently, is examined in a further detail. The binding free energy, which was introduced in the previous paper [J. Chem. Phys. 81 (1977) 1929], is replaced by the entropy of the condensed phase. This replacement leads to a detailed picture of the condensed phase. In a mixed system of mono- and divalent counterions, a couple of possibilities are examined in interpreting the condensation volume, which corresponds to the condensation entropy.

1. Introduction

In the previous paper [1], which will be referred to as paper I henceforth, we have examined the consistency of counterion condensation with Manning's limiting laws (MLL) [2] of polyelectrolytes based on the two phase model, which is recently being developed [3–5]. By introducing a binding free energy term we observed that the MLL's are not derived strictly. One of the possibilities is to assume counterion condensation takes place so as to satisfy the MLL in the salt free limit, i.e. for monovalent counterion systems an equation

$$n_u/n_p = \xi^{-1} \qquad (1)$$

is satisfied only in the salt free limit. Here n_u is the concentration of uncondensed counterions, n_p the concentration of the condensed counterions, and ξ the reduced charge density of the polyion $\xi = e^2/(\epsilon bkT)$, with e the elementary charge, ϵ the dielectric constant of the solvent, b the mean spacing of the charged groups along the polymer backbone, k the Boltzmann constant, and T the temperature. In assuming so, the deviation from the MLL in the excess salt condition is insignificant in terms of the activity coefficients in a system with single counterion species. In addition, we obtained a reasonable explanation of the mean activity coefficient of divalent salt measured in a mono- and divalent mixed counterion system [6], which the MLL can explain only partly, i.e. in the excess of divalent counterions. The physical picture of this two phase theory was, however, not clearly given.

On the other hand, Manning has developed a series of treatments [3–5] which prove counterion condensation takes place as given by eq. (1) under the excess salt conditions. While every term which appears in his theory bears a clear physical meaning, the relation to the MLL's is not yet clarified because his treatment is limited to the excess of salt condition, where the colligative quantities do not show the effects of polyelectrolytes. Furthermore, interpretations of NMR results have recently been given in connection with condensation (or binding). The discussions given there are significantly dependent on the comparison of the high salt (or excess salt) data with the low salt observation [7,8]. Moreover, it is necessary to examine the relation of NMR data with other observable quantities based on the same model.

In this paper, we will introduce the entropy term of the condensed phase instead of the binding free energy of paper I. This will enable us to clarify the assumptions made in paper I and give a detailed physical picture of this problem.

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2. Formalism

We consider a system of volume V, which consists of polyions, counterions, and coions. Let the equivalent polymer concentration be n_p and let all the small ions be monovalent, for simplicity. We denote the concentration of counterions and that of co-ions by n_+ and n_- respectively, assuming the charged groups of the polyions are monovalent and negative.

In this paper we are concerned only with the case that the charge density $\xi = \lambda/(4\pi b)$ is higher than unity, the critical value, since the other case, $\xi < 1$ has been considered in paper I. Here we have defined the Bjerrum length $\lambda/4\pi = e^2/(\epsilon kT)$ and b the mean spacing of the charged groups of the polymer, ϵ the dielectric constant of the solvent, e the elementary change, k the Boltzmann constant, and T the temperature. The conformation of the polymer is assumed to be fully extended and polymer–polymer interactions will be neglected on the ground that the polymer concentration is low, compared with the salt concentration. However, we will neglect those interactions also under the salt free condition, where justifications are not available except for the agreement of the result with experimental data.

The excess free energy G of the system is given by $g = G/(VkT)$ with

$$g = g_0 + g_{DH} + g_S, \tag{2}$$

where g_0 is the contribution from small ion–small ion interactions and g_{DH} the effective Debye-Hückel term contribution of polyion–small ion interaction.

$$g_{DH} = -\xi(2n_p)^{-1}(n_p - n_c)^2 \ln[\lambda a^2(n_+ + n_- - n_c)], \tag{3}$$

where N_c is the number of condensed counterions, and $n_c = N_c/V$. The logarithmic dependence of eq. (2) arises either from the discrete charge model of the polymer or from the continuous charge model. In the former case it is $\ln(1 - e^{-\kappa b}) - \kappa b/2$, which is the ring term or the random phase approximation [10,11]. Here κ, the Debye-Hückel parameter, is defined by $\kappa^2 = \lambda(n_+ + n_- - n_c)$. Although this approximation is not equivalent to the Debye-Hückel approximation, the notation does not make confusions in our paper. In the latter case it is $\ln(\kappa a)$, where a is proportional to the radius of the polymer (see Appendix). The validity of eq. (2) is therefore limited by the condition either $3.05\ \kappa a \ll 1$ or $\kappa b \ll 1$. We allow both interpretations in this paper and denote both lengths by a. Although a finite value of the polymer radius has been argued to be inconsistent with counterion condensation, we keep the finite value of a on the ground that our formalism should be self-contained. Indeed, there is little difference whether we use a or b in eq. (3) qualitatively. Moreover, the finite value of a is justified when $\xi < 1$.

The other term that appears in eq. (2) is the entropy change due to the condensation,

$$g_S = (n_+ - n_c)\ln(n_+ - n_c) + n_c \ln(n_c/v_1) - n_+ \ln n_+. \tag{4}$$

The first term is the entropy contribution of the dilute phase and the second that of the condensed phase, with the ratio $v_1 = V'/V$, V' being the volume of the condensed phase. Because the ratio v_1 is unknown, it is simpler to regard the concentration n_c/v_1 as an unknown quantity. The third term of eq. (4) is the standard entropy.

The entropy term g_S corresponds to $\mathcal{F}_B + \mathcal{F}_S$ in paper I. In particular, we have a relation,

$$\mathcal{F}_B \sim n_c \ln(n_c/v_1). \tag{5}$$

Namely, we regard $\mathcal{F}_B$ as the entropy contribution to the free energy of the condensed phase. In eqs. (4) and (5) we omitted n_w, the number density of the solvent, which appeared in paper I, because it disappears automatically from the present formalism if it is included.

Next, we minimize the free energy g with respect to the condensed amount n_c of the counterions. This is equivalent to

$$\partial g/\partial n_c = 0. \tag{6}$$

Although g_0 is also dependent on n_c through the Debye-Hückel parameter, κ, it is insignificant in this minimization because the concentrations are low. Now eq. (6) is equivalent to Manning's equation [5] except for a minor constant.

Next, we will follow Manning's method [3] to derive two equations, one is related to the effective charge density and the other to the condensed entropy, from eq. (6). The two equations thus derived are, however, inconsistent with the MLL and also unable to explain experimental data, as we will see in the rest of this chapter. In the following chapter, we will return to eq. (6) and examine other possibilities.

In order to apply Manning's method, we have to keep a ratio X (= n_p/n_s) constant while we examine the dependence on n_p, because our system has two parameters n_p and X together with two unknown quantities n_c and n_c/v_1. Note that Manning's method has been originally applied only to the case that X is zero. If we assume that the condensed phase concentration n_c/v_1 and its n_c derivative are independent of n_p, the polymer concentration, we obtain

$$n_c/n_p = 1 - \xi^{-1}, \tag{7a}$$

$$(\partial/\partial n_c)[n_c \ln (n_c/v_1)]$$

$$= -(1/2)\xi^{-1} n_p [n_+ + n_- + (1-\xi^{-1})n_p]^{-1} + 1$$

$$- \ln\left(\frac{\lambda a^2(n_+ + n_- - (1-\xi^{-1})n_p}{n_+ - (1-\xi^{-1})n_p}\right) \tag{7b}$$

because eq. (6) remains to be valid for arbitrarily small values of n_p. Equation (7a) is identical to eq. (1) and eq. (7b) gives the entropy of the condensed phase.

Having determined the two unknown quantities, we are ready to proceed to thermodynamic quantities. First, we will evaluate osmotic pressure. The excess osmotic pressure π^{ex} is given by

$$-\pi^{ex}/kT = (\partial/\partial V)(gV)_{T,\xi,\text{no. of ions}}.$$

Since eq. (7) is independent of the volume V, we are immediately led to

$$-\pi^{ex}/kT = n_p[1 + (2\xi)^{-1}],$$

which is Manning's limiting law for osmotic pressure, and which is also equivalent to the additivity rule for that quantity. An important observation is that the osmotic pressure is quite an insensitive quantity in a theoretical sense. Not only is the additivity rule for osmotic pressure identical with MLL, but it is also the same as a new limiting law [12].

The activity coefficients for counterions and coions are given by

$$\ln \gamma_+ = (\partial g/\partial n_+)_{T,\xi,V,n_-,n_p},$$

$$\ln \gamma_- = (\partial g/\partial n_-)_{T,\xi,V,n_+,n_p}. \tag{9}$$

We thus obtain

$$\ln(\gamma_-/\gamma_0) = -[2\xi(\xi^{-1} + 2X^{-1})]^{-1} + f_-, \tag{10a}$$

$$\ln(\gamma_+/\gamma_0) = -[2\xi(\xi^{-1} + 2X^{-1})]^{-1}$$

$$+ \ln[(\xi^{-1} + X^{-1})/(1 + X^{-1})] + f_+, \tag{10b}$$

with

$$f_- = (1-\xi^{-1})(\xi^{-1} + 2X^{-1})^{-1}[(2 + 4\xi X^{-1})^{-1} - 1],$$

$$f_+ = f_- + (1-\xi^{-1})/(\xi^{-1} + X^{-1}). \tag{11}$$

The terms f_+ and f_- arise because the condensation entropy is dependent on the concentrations n_+ and n_-. These terms are indeed important. In the salt free limit, we have $f_- \to -(1/2)(\xi - 1)$ and $f_+ \to (1/2)(\xi - 1)$. These values should be compared with the rest, i.e. MLL values, namely $\ln \gamma_-(\text{MLL}) \to 1/2$ and $\ln \gamma_+(\text{MLL}) \to -1/2 - \ln \xi$. For example, if we put $\xi = 2.8$, a value corresponds to polystyrenesulfonate, we have higher values for counterion activity coefficient than that for coion activity coefficient. Although we have $\gamma_\pm \approx \gamma_\pm(\text{MLL})$ at the salt free limit, eq. (10) is therefore unphysical, indicating we made a wrong assumption.

If the counterion concentration in the condensed phase is independent of n_+ and n_-, we have $f_+ = f_- = 0$ and MLL for activity coefficients is obtained. In other words, a condition

$$\ln(n_c/v_1) = \text{constant} \tag{12}$$

accompanied by eq. (6) is equivalent to MLL.

3. Entropy term of the condensed phase

We now return to eq. (6). This equation contains two unknown quantities, n_c and n_c/v_1, and an additional condition is required to determine those quantities. As we have seen, eq. (7a), one of the necessary conditions for MLL, is not appropriate. Instead, we will assume eq. (12), the other necessary condition for MLL, should hold. In doing so, we can satisfy eq. (7a) approximately, as we will see in the following.

Before going further, we need to make a remark. Since we introduced two undetermined quantities n_c and V', it is logical that a condition

$$\partial g/\partial V' = 0 \tag{12'}$$

be coupled with eq. (6) to determine n_c and V'. In this sense, eq. (12) is a replacement of eq. (12′). Applied to our free energy, however, eq. (12′) does not yield a meaningful relation, because V' dependence appears only in the entropy term of the condensed phase. Although we may regard a as a function of V', we have ambiguity relating them. In addition, the derivation of V' dependent electrostatic free energy term, which could replace eq. (19), requests a much more detailed picture of the condensed phase. For this reason, we do not discuss this problem any further in the present paper.

There are two simple possibilities to determine the constant on the right-hand-side of eq. (12). One is to choose the value of eq. (7b) at the excess salt condition,

$$\ln(n_c/v_1) = 1 - \ln(2\lambda a^2). \tag{13}$$

In this case the charge density condition eq. (7a) is exact at the excess salt condition, and increasing deviations are expected with decreasing salt. The rhs of eq. (13) is greater than Manning's theory by a factor two [5].

The other choice is to expect the charge density condition eq. (7a) is exact at the salt free limit, i.e. putting $X \to \infty$ in eq. (7b),

$$\ln(n_c/v_1) = 1/2 - \ln(\lambda a^2). \tag{14}$$

This is identical with paper I. Inevitably an increasing deviation from eq. (6) is to be observed with increasing salt. It gives the best agreement with experimental data of activity coefficients and MLL in the salt free limit, and numerically no significant difference is found elsewhere as shown in paper I. The difference of eq. (13) and (14) in terms of the activity coefficients is however, also not so important.

Recently a number of papers on the NMR measurement of ^{23}Na in polyelectrolytes have been reported [7,8,13–16]. Among these, papers of Reuben et al. [7] and Anderson et al. [8] are of particular interest, because they observed the effect of the added salt. This corresponds to changing X at constant n_p, the polymer concentration. The expected condensed (or bound) ratio r_c ($= n_c/n_p$) is given in fig. 1. To compare with the data of Anderson et al. we put $n_p = 0.02$ and $\xi = 4.2$. Because of this high n_p value eq. (3) is no longer justified at small X, and the logarithmic term is replaced by $\ln(1 - e^{-\kappa b}) - \kappa b/2$. Eqs. (13) and (14) yield quite similar result (fig. 1). Moreover, the deviation from eq. (7a) is small, as to make a clear conclusion by comparing experimental data. However, Anderson group's data on Bu$_4$N DNA [8] may be regarded as supporting the present theory, because r_c is higher for higher X values. If the polymer concentration n_p is lower, the deviation from eq. (7a) is even smaller.

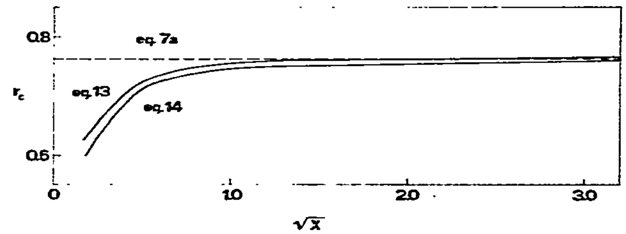

Fig. 1. Ratio r_c of condensed counterions versus $X^{1/2}$: Equation (13) (upper full line), eq. (14) (lower full line), and eq. (7a) (broken line).

In order to clarify the physical picture of counterion condensation, it is worthwhile to evaluate the order of magnitude of the counterion concentration in the condensed phase. As mentioned earlier, we allowed two interpretations for the length a, and we cannot determine it uniquely. At 25°C, $\lambda = 0.874 \times 10^{-6}$ cm, and if $a = 3$Å, we obtain $n_c/v = 2.87$ mol/l according to eq. (13), and $n_c/v_1 = 3.48$ mol/l according to eq. (14). The former interpretation yields higher density for a higher polymer charge density, and latter gives a higher value of condensed counterion density for a higher value of the polymer radius. Manning's corresponding value is lower a factor three.

A similar argument is easily applied to a divalent counterion system [1]. The resulting entropy term of the condensed phase is then given by either

$$\ln(n_{2c}/v_2) = 1 - \ln(8\lambda a^2), \tag{15}$$

or

$$\ln(n_{2c}/v_2) = 1/2 - \ln(4\lambda a^2), \tag{16}$$

where v_2 is the ratio of the condensation volume for divalent counterions to the volume V of the system. The former, eq. (15), corresponds to eq. (13), and the latter, eq. (16), to eq. (14). The quantity n_{2c} is defined by $n_{2c} = N_{2c}/V$, N_{2c} being the number of condensed divalent counterions.

It should be emphasized that the number density and the charge density of the counterions in the condensed phase is lower in the divalent counterion system than that in the monovalent system. This is just contrary to what one would naively conceive: the counterion concentration in the neighborhood of a polyion should be higher when the counterion valence is higher. This may be attributed to the two phase model, and to the definition of the condensed phase [‡1] in particular. The charge density condition corresponding to eq. (7a) is

$$2n_{2c}/n_p = 1 - (2\xi)^{-1}. \qquad (17)$$

4. Mixed counterion system

As shown in previous papers [1,6], a mixed counterion system of mono- and divalent counterions is particularly sensitive to test counterion condensation and MLL. Indeed we will encounter a new problem in dealing with this system, as we shall see later.

The excess free energy of this system is

$$g = g_0 + g_{DH} + g_s(1) + g_s(2), \qquad (18)$$

where g_0 is the small ion-small ion interaction term, g_{DH} the Debye-Hückel contribution from the polyion-small ion interaction given by

$$-g_{DH} = (1/2)\xi n_p^{-1}(n_p - n_c - 2n_{2c})^2$$
$$\times \ln[(\lambda a^2(n_+ + 4n_{2+} + n_- - n_c - 4n_{2c})], \qquad (19)$$

$g_s(1)$ the entropy contribution of monovalent counterions given by eq. (4) and $g_s(2)$ that of divalent counterions. Note we have to replace v_1 by v_1' in eq. (4). Here n_{2+} represents the mean concentration of the divalent counterions in the system. The meaning of v_1' is discussed later. The term $g_s(2)$ is given by

$$g_s(2) = (n_{2+} - n_{2c})\ln(n_{2+} - n_{2c})$$
$$+ n_{2c}\ln(n_{2c}/v_2') - n_{2+}\ln n_{2+}. \qquad (20)$$

In paper I, the expression corresponding to eq. (18) was an additional assumption in the mixed counterion system, i.e. we neglected the interference of the two binding free energy terms. In the present treatment eq. (18) is not the result of such an assumption. However, there are evidently two possibilities in interpreting the ratio v_1' and v_2', which appear in eq. (18).

One interpretation is to regard these two ratios v_1' and v_2' as identical, i.e. $v = v_1' = v_2'$. We will call this picture as monolayer condensation, in comparison with the other to be mentioned later. In this picture we have three undetermined quantities, n_c, n_{2c}, and v, which should satisfy a set of equations,

$$\partial g/\partial n_c = \partial g/\partial n_{2c} = 0. \qquad (21)$$

Here we can try an attempt to reduce the number of unknown quantities by assuming n_p independence as given in section 2. However, we only obtain two mutually exclusive equations for the effective charge density. Again, such an idea seems to be unsound.

The other interpretation is to regard the ratios v_1' and v_2' independent. The concentrations n_c/v_1' and n_{2c}/v_2' are determined separately by the system with single counterion species only, i.e. $v_1' = v_1$ and $v_2' = v_2$. This is equivalent to what we assumed in paper I, where the combination of eqs. (14) and (16) give rather successful explanation of the mean activity coefficients of the mixed counterion system in some extent. However, we now adopt a definition of the distance a different from that used in paper I, and the results given there should be reviewed. If we put $a = \hat{a}$, the concentrations should be lowered by a factor 9.30 (= 3.05^2) than that given in paper I. This yields lower values for $\gamma_\pm(CaCl_2)$ making the agreement with experimental data poorer.

Moreover, we must be careful in using this interpretation. By assuming that the condensation volume of the mono- and divalent counterions are independent, we essentially admit the existence of three phases, i.e. a dilute (or uncondensed) phase, a condensed phase for the monovalent counterions, and one for divalent counterions, although the two condensed phases are likely to overlap, if partly. The NMR result for ^{23}Na by van der Klink et al. [13] seems to suggest that the condensed phase of the divalent counterions is not located closer to the polyion than that of the monovalent counterions. The multilayer condensation picture seems to have a difficulty in explaining it if the composition ratio of the

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[‡1] This seems, however, to be in agreement with Bjerrum's treatment [17], of ion association. A higher valence yields a larger radius of the association volume.

divalent counterions is small. In this case the electric field affecting ^{23}Na will be influenced by the number of the condensed divalent counterions, unless the divalent ion layer is outside of the monovalent ion layer. In addition, this picture gives a minimum of $\gamma_{\pm}(\mathrm{CaCl_2})$ plotted against composition ratio w_1 of counterions (figs. 1–3 of paper I.) This minimum corresponds to a maximum in Scatchard plot of divalent ion binding (or condensation) to polyions. This kind of behavior is only observed when a conformational change of the polymer is likely to occur [18,19]. Therefore this phenomenon should be regarded as an artifact due to an improper modeling.

On the other hand, the monolayer condensation picture has no such difficulties. It needs, however, an dditional condition to determine one of the unknown quantities. We can provide such a condition as follows. By rewriting eq. (14) and (16), we have

$$v_1 = \lambda a^2 n_c \exp(-1/2), \tag{22a}$$

$$v_2 = 4\lambda a^2 n_{2c} \exp(-1/2). \tag{22b}$$

Since both extremes of the composition ratio of counterions should coincide with single counterion systems, we have $v(w_1 = 1) = v_1$ at the excess of monovalent counterions, and $v(w_1 = 0) = v_2$ at the excess of divalent counterions. The simplest functional form of v satisfying these conditions is

$$v = v_1' = v_2' = v_1 + v_2. \tag{23}$$

Replacing v_1' and v_2' of eq. (14) and (16) by v, we have

$$\ln(n_c/v) = 1/2 - \ln \lambda a^2 + \ln[n_c/(n_c + 4n_{2c})], \tag{24a}$$

$$\ln(n_{2c}/v) = 1/2 - \ln \lambda a^2 + \ln[n_{2c}/(n_c + 4n_{2c})]. \tag{24b}$$

With equation (24) we will eliminate the undetermined ratio v, and we can readily solve eq. (21). Also we observe that the functional dependence of eq. (24) does not yield an additional term to the osmotic coefficient or the activity coefficients. Again, we should notice that eq. (23) is only the simplest choice to eliminate v, and alternative, though more complicated, relations are also possible [‡2].

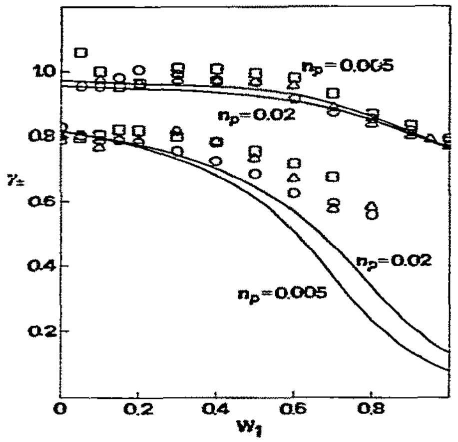

Fig. 2. Corrected $\gamma_{\pm}$ values for monovalent salt (upper lines) and divalent salt (lower lines) at $X = 1$: Experimental points are adopted from ref. [6]. Values for NaCl (upper points) and $\mathrm{CaCl_2}$ (lower points) at $n_p = 0.02$ (○), $n_p = 0.01$ (□), and $n_p = 0.005$ (△). Calculation is based on $\xi = 2.8$ and polymer radius 1.0 nm.

The numerical calculation is carried out minimizing the excess free energy with respect to two quantities, n_c and n_{2c}. The results are shown in figs. 2, 3, and 4. These calculations are based on eq. (24). First, we do not have a maximum or a minimum in our theoretical curves, in agreement with experimental observation. However, we still have a polymer concentration dependence in the mean activity coefficient, which is not confirmed experimentally. In the excess of monovalent counterions the mean activity coefficient $\gamma_{\pm}(\mathrm{CaCl_2})$ for the divalent salt is lower than the experimental data. Indeed the ratio of the condensed divalent counterions to the total divalent counterions increase monotonically almost up to unity with increasing composition ratio w_1 of the monovalent counterions (fig. 3). The reason for this behavior is that the concentration of the divalent counterions in the condensed phase is very low when the ratio w_1 is close to unity, the condensation volume being solely determined by n_c, the amount of condensed monovalent counterions. The difference due to the choice between eqs. (13) and (14) is small.

In the figures we put $a = \hat{a}$, i.e. we regarded the length a related to the polymer radius. If we put $a = b$, i.e. if we regard a as the mean spacing of the charged

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[‡2] However, every monolayer condensation picture does not necessarily lead to a good result. For example, $v = \max(v_1, v_2)$ yields a similar maximum and minimum as the multilayer model does.

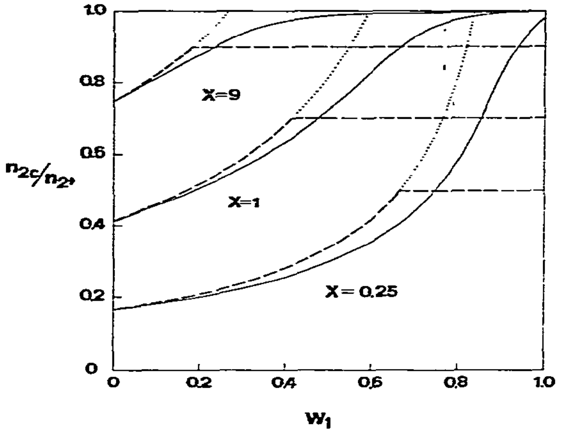

Fig. 3. Ratio of condensed divalent counterions versus composition ratio w_1. Present theory (full line), extended MLL (dotted line), and empirically modified MLL (broken line) of ref. [6]. Calculation is based on $\xi = 2.8$ and polymer radius 1.0 nm. $w_1 = n_+/(n_+ + 2n_{2+})$.

groups, the length a is smaller and the agreement with the experimental data is poorer. Yet, we still need a careful examination to make a judgement as to which is superior.

Although there can be other relations which replace eq. (23), the monolayer condensation picture is very successful. This may suggest that the entropy of the condensed phase, which is first introduced by Manning [5], is superior to the binding free energy of paper I. The former provides a clearer picture as well as more consistent result with experimental data.

A different approach to the mixed counterion system has been reported by Dolar and Peterlin [21] in the salt free condition. These authors used Poisson-Boltzmann equation together with the cell model, and the counterion activity coefficients show a gradual and monotonic change against the composition ratio w_1 of the counterions. This kind of treatment, however, does not allow for example to evaluate the effect of small ion–small ion interactions consistently. It encounters serious difficulties in dealing with salt added systems. In this sense our two phase model is so far the only consistent way to explain salt added systems, in spite of the theoretical difficulty in justifying counterion condensation [22–24] ‡3.

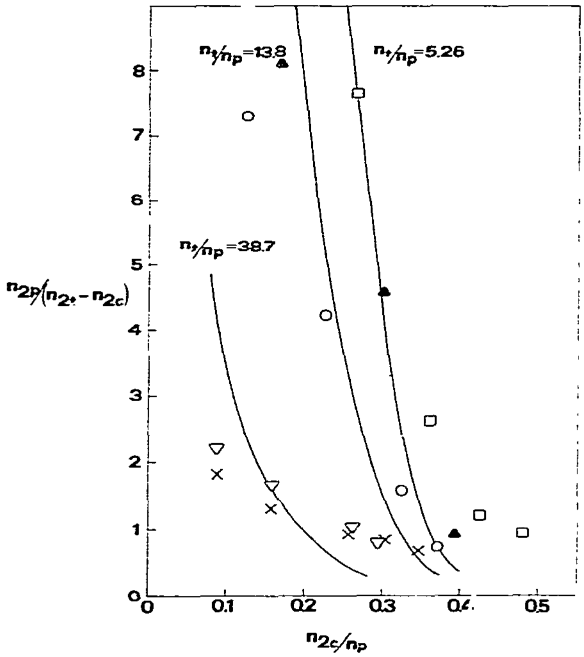

Fig. 4. Scatchard plot of divalent counterion binding (or condensation) to poly (A+2U): Experimental points are adopted from ref. [20]. n_+/n_p = 5.26 (▲), 6.67 (□), 13.8 (○), 38.7 (▽), and 33.3 (×). Calculation is based on $\xi = 4.2$ and polymer radius 1.0 nm.

Finally we will summarize our result. Of the necessary conditions for MLL, the charge density condition, eq. (7a), cannot be satisfied rigorously, because it leads to an unphysical result for the activity coefficients. It can be, however, approximately satisfied by assuming eq. (12), that the concentration of the condensed phase is independent of the coion or counterion concentration. In mixed counterion systems the condensation volume for the divalent counterions should be identical with that of the monovalent counterions. This model gives the best explanation of experimental data. The importance of the higher order cluster terms has recently been shown [21,22]. The inclusion of these terms should affect the result. This problem will be reported elsewhere [25].

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‡3 For experimental assessment, see ref. [24]

Acknowledgement

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Appendix

Evaluation of the excess free energy in the Debye-Hückel approximation

We consider a system without counterion condensation.

The electrostatic potential ψ is determined in the Debye-Hückel approximation by

$$r^{-1}\partial/\partial r(r\partial/\partial r)\psi = \kappa^2\psi$$

because the system is treated two-dimensionally. We have a solution

$$\psi(r) = (2\nu/\epsilon)K_0(\kappa r)[\kappa A K_1(\kappa A)]^{-1},$$

satisfying the boundary condition that the polymer radius is A and the linear charge density of the polymer is ν. Here K_0 and K_1 are modified Bessel functions. The excess free energy f^{ex} per length along the polymer is obtained by the Debye charging process,

$$f^{\mathrm{ex}} = \int_0^1 \mathrm{d}\lambda\, \nu\psi_\lambda(A), \tag{A.1}$$

where λ is the charging parameter and $\psi_\lambda(A)$ is the electrostatic potential at the polymer surface when every charge has a value λe instead of e. Namely, we have

$$\psi_\lambda(A) = (2\lambda/\nu\epsilon)K_0(\lambda\kappa A)[\lambda\kappa A K_1(\lambda\kappa A)]^{-1}.$$

The excess free energy F^{ex} of the system is given by $F^{\mathrm{ex}}/VkT = bn_\mathrm{p}Vf^{\mathrm{ex}}$. Thus we obtain

$$F^{\mathrm{ex}}/VkT = -2\xi n_\mathrm{p}(\kappa A)^{-1}\ln[\kappa A K_1(\kappa A)].$$

If the concentrations are so low as to satisfy $\kappa A \ll 1$, we have

$$F^{\mathrm{ex}}/VkT = -\xi n_\mathrm{p}[\ln(\kappa A/2) + \gamma - 1], \tag{A.2}$$

where γ is Euler's constant, i.e. $\gamma = 0.5772$ ... We can replace the square bracket on the right-hand-side of the above equation by $\ln(\kappa\bar{a})$ with $\bar{a} \approx A/3.052$. This is equation (3) in the text. In paper I, we put $a = A$.

The charging process given above does not yield different result for thermodynamic quantities as that given by Manning's charging process [2]

$$f^{\mathrm{ex}} = \int_0^1 \mathrm{d}\lambda\, \nu\psi_{\lambda=1}(A) \tag{A.3}$$

provided that $\kappa A \ll 1$, because a constant term in the square bracket of eq. (A.2) does not contribute to those directly observable quantities. If we replace eq. (A.1) by eq. (A.3), we obtain a relation $a = A/1.123$.

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