

## Donnan equilibria and the osmotic coefficients in polyelectrolyte solutions

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## 1. Introduction

Interactions of polyions with small ions have been reasonably understood on the basis of Manning's limiting law (LL)<sup>1</sup> or the Poisson-Boltzmann (P-B) approach.<sup>2-12</sup> According to the LL, thermodynamic properties, such as the osmotic coefficients in salt-free polyelectrolyte solutions and the salt exclusion parameter, could be estimated solely from a line charge density parameter in dilute solutions. Recently, however, it has been found that those thermodynamic properties were influenced by the chemical structures of polymers or the flexibility of polymer skeletons.<sup>13</sup> It is valuable to study the relation between those thermodynamic properties and chemical structures of polyelectrolytes.

To evaluate the Donnan osmotic pressure on the basis of the additivity, we need to know the distribution of salt across a semipermeable membrane and the osmotic coefficient in the salt-free polyelectrolyte solution. The Donnan distribution of salt has been studied over many years.<sup>14-22</sup> The distribution under the condition of excess salt has been rather well understood.<sup>1,3,4,22</sup> However, to understand the swelling of ionic gels at low ionic strengths, it is desirable to examine the salt distribution in the range of excess polyelectrolyte. Theoretical prediction in this range has not been developed.

The validity of the additivity rule for the osmotic pressures of the polyelectrolyte solutions with added salt was shown on the basis of the LL<sup>1</sup> and the Poisson-Boltzmann approach.<sup>2</sup> The Donnan osmotic pressure  $\pi_D$  based on the additivity rule is as follows

$$\pi_D / kT = n_p + \phi_p n_e + 2 ( n_s - n_s' ) \quad (1-1)$$



where  $n_p$  and  $n_e$  denote the polymer and the counterion concentrations, and  $n_s$  and  $n_s'$  represent the salt concentrations of the solutions with and without polyelectrolyte. Within the framework of the LL<sup>1</sup>, however, the sum of the second and the third terms on the rhs equals zero. That is to say, the counterion contribution and the Donnan salt distribution compensate each other. The extension of the LL to the excess salt condition has been done on the cylindrical Poisson-Boltzmann cell model and the correction terms to those of LL<sup>3,4</sup> have been given for both the osmotic coefficient and the Donnan salt distribution as follows.

$$\Gamma_0 = (2\xi^* - \xi^{*2} + \sigma) / (4\xi) \quad (\xi^* < 1) \quad \text{and} \quad \Gamma_0 = (1 + \sigma) / (4\xi) \quad (\xi^* > 1) \quad (1-2)$$

$$\phi_p = [(\xi^{-1} n_e / 2)(2\xi^* - \xi^{*2} + \sigma)] / n_e \quad (\xi^* < 1) \quad \text{and} \quad \phi_p = [(\xi^{-1} n_e / 2)(1 + \sigma)] / n_e \quad (\xi^* > 1) \quad (1-3)$$

where  $\Gamma_0$  is the Donnan salt exclusion factor defined as  $(m_s' - m_s) / m_e$  in the limit as  $m_e$  approaches 0,  $\xi$  is defined in terms of the Bjerrum length  $l_B$  and the separation of charges  $b$  along the polymer chain as  $l_B / b$ . The effective reduced axial charge density of the cylinder,  $\xi^*$ , is defined as  $\alpha^* \xi$ . A fraction  $(1 - \alpha^*)$  of the polyion charge may be compensated by closely associated counterions ( $0 < \alpha^* < 1$ ). A parameter  $\sigma$  is defined as follows,

$$\sigma \equiv S_a - \lim_{\lambda u \rightarrow 0} S_a \quad (1-4)$$

$$S_a \equiv (x_a^*)^2 / 4 [ \exp(y_a) + \exp(-y_a) ] \quad (1-5)$$

where  $x_a^*$  is defined as  $\kappa \alpha$ ,

$$\kappa^2 = 8\pi N_A e^2 n_s^R / (10^3 \epsilon kT) \quad (1-6)$$

and  $y_a$  is defined as  $|e\Psi/kT|$  at a distance from the polyion axis  $r = a$  (the polyion radius). The equality  $n_s' = n_s^R$  will hold at any electrolyte concentration if it can be assumed that the nonideality arising from interactions among small ions in the vicinity of the cell boundary is identical to that in a solution containing no polyions.

When eqns (1-2) and (1-3) are introduced into eqn (1-1), we have obtained again

$$\pi_D / kT = n_p \quad (1-7)$$

since the correction terms cancel out. It is obvious that the LL and its extension have enumerated the free energy up to the order of  $n_p$ . Actual osmotic pressures of polyelectrolyte solution always contain the contribution for the second virial term, i. e.  $n_p^2$ .

The osmotic coefficient in the salt-free polyelectrolyte solution is a significant measure of the polyion-counterion interaction. the osmotic coefficients have been reported and found to increase with the concentration.<sup>23-31</sup> In the dilute region, osmotic pressures of salt-free polyelectrolyte solutions have been understood due to the counterion contribution in terms of the LL<sup>1</sup> or the P-B approach.<sup>32</sup> On the other hand, the scaling theory in semidilute solution has been extended to polyelectrolyte,<sup>33-37</sup> and the osmotic pressures were sometimes explained due to polymer contribution.<sup>38,39</sup> Odijk's theory<sup>38</sup> evaluates only the polymer contribution. According to his theory, osmotic pressures without added salt were described as

$$\pi / kT \approx 1/\xi_{\text{cor}}^3 \approx 10b^{3/8}c^{9/8} \quad (1-8)$$

where  $\xi_{\text{cor}}$ ,  $b$ , and  $c$  represent the correlation length, the separation of charges along the polymer chain, and the monomer concentration, respectively. Equation (1-8) predicts



that osmotic pressures increase with  $c^{9/8}$ .

Generally, the osmotic pressures in semidilute polyelectrolyte solutions without added salt should be approximately described as follows.

$$\pi = \pi_i + \pi_p \quad (1-9)$$

Dubrynin et al. has proposed eqn (1-10)<sup>37</sup>

$$\pi / kT \approx c/A + 1/\xi_{\text{cor}}^3 \quad (1-10)$$

where  $A$  denotes the average number of monomers between effective charges. The term,  $c/A$ , corresponds to the uncondensed (free) counterion concentration. The correlation length  $\xi_{\text{cor}}$  is defined as  $(B/cd)^{1/2}$ , where parameters  $B$  and  $d$  represent the ratio of the chain contour length to the actual extended size and the monomer length. The first and the second terms on the rhs of eqn (1-10) represent the counterion contribution and the polymer contribution, respectively. Dubrynin et al.<sup>37</sup> have shown that the latter term in eqn (1-10) is negligible and hence the counterion contribution dominates over the polymer contribution. Thus osmotic pressures of polyelectrolyte solutions without added salt increase with  $c$  unless the term  $A$  depends on  $c$ . It is important to examine the concentration dependence of the osmotic coefficients in salt-free polyelectrolyte solutions.

In the present study, first, the Donnan salt distribution is examined in the range of excess polyelectrolyte for four polyelectrolytes, sodium polyacrylate (NaPA), sodium polystyrenesulfonate (NaPSS), poly(2-methacryloxyethyltrimethylammonium) chloride (PMETAC), and polyallylamine hydrochloride (PAAm) in the presence of NaCl or Na<sub>2</sub>SO<sub>4</sub> by equilibrium dialysis and non-equilibrium methods. The effect of NCS<sup>-</sup>

locating at the opposite positions to  $\text{SO}_4^{2-}$  in the Hofmeister's series was also examined for NaPSS and the result is compared with the results on  $\text{Cl}^-$  and  $\text{SO}_4^{2-}$ . For partially neutralized polyacrylate (PA), the Donnan distribution of NaCl was examined at differing polyelectrolyte charge densities.

Second, we evaluated the mean activity coefficients on the basis of these Donnan salt distribution data. Mean activity coefficients of salts in polyelectrolyte solutions are an important measure of the interactions of polyions with small ions. Observed mean activity coefficients were compared with predicted values from the LL. While small ion - small ion interactions are not taken into account in the LL, or these contributions are assumed to be approximately same in both the polyelectrolyte solution and the salt solution, their contribution is involved in the observed values. The excess free energy arising from the small ion-small ion interactions was added to that from polyion-small ion interaction to evaluate the activity coefficient of small ions. According to the treatment by Wells,<sup>40</sup> we approximated the contribution from small ion-small ion interaction with the mean activity coefficient in a pure salt solution at the salt concentration  $m_s$  found in the polyelectrolyte solution. The validity of this procedure was examined.

Finally, we reported the osmotic pressures of solutions of poly (2-methacryloxyethyltrimethylammonium) chloride (PMETAC), polyallylamine hydrochloride (PAAm), sodium polystyrenesulfonate (NaPSS), sodium polyacrylate (NaPA; the degree of ionization  $\alpha=1$ ), partially neutralized polyacrylic acid (PA;  $\alpha=0.9$ ), and partially neutralized polyvinylbenzoic acid (PVB;  $\alpha=0.9$ ). Polymer



samples other than PVB and PA ( $\alpha=0.9$ ) have the same charge densities  $\alpha=1.0$ . The polymer concentration dependence of the osmotic pressures in semidilute solutions is discussed in terms of both the scaling theory<sup>38</sup> and the Poisson–Boltzmann approach.<sup>32</sup>

In order to study the relation between the chemical structures of the ionic moiety and the osmotic coefficients in polyelectrolyte solutions, the osmotic coefficients were determined for some monomer analogues to the polymers examined, such as tetramethylammonium chloride (TMACl), methylamine hydrochloride (MAHCl), ethylamine hydrochloride (EAHCl), and sodium ethansulfonate (NaES).

## **2. Experimental**

### **2-1. Materials**

Polyacrylic acid (PA) was purchased from Toa Gosei Kagaku Co. and dialyzed against pure water. PA were neutralized with NaOH.

NaPSS was purchased from Polyscience, Inc. Low molecular weight materials were removed by ultrafiltration using a membrane (ADVANTEC Q2000).

2-methacryloxyethyltrimethylammonium chloride (METAC) in 50 % aqueous solution was purchased from Polyscience, Inc. Ammonium persulfate and sodium chloride were purchased from Nacalai Tesque, Inc. and Katayama Chemical Co., respectively. Polymer was prepared by free-radical solution polymerization. 70mmol of METAC, 40mmol of ammonium persulfate and 50mmol NaCl were dissolved in 100ml of water. The solution was degassed and polymerization was carried out in a container at 60 °C for 3 hours, followed by the precipitation of the polymer with

acetone. Precipitates were resolved in water. Low molecular weight materials were removed by ultrafiltration using a membrane (ADVANTEC Q0100).

Polyallylamine hydrochloride (PAAm) purchased from Nitto Boseki Co. Ltd. was purified by the same method as described.<sup>41</sup>

Sodium polyvinylbenzoate (NaPVB) was kindly supplied by Dr. M. Kawaguchi of Toyohashi University of Technology. Polyvinylbenzoic acids (PVB) were precipitated by adding HCl to NaPVB solution offered. The low molecular salts were removed from the polymer precipitates by repeated centrifugation, followed by drying under reduced pressure to constant weight. PVB was neutralized with NaOH.

The polymer concentrations were determined using Farjans method for PMETAC and pH titration for PAAm, PA and NaPSS.

Methylamine hydrochloride and tetramethylammonium chloride were from Kanto Chemical Co., Inc. Ethylamine hydrochloride and sodium ethansulfonate were from Tokyo Kasei and Aldrich Co., respectively. All salts were reagent grade and were used without further purification.

## **2-2. Procedure**

We have determined the Donnan salt distribution by the following two methods.

### **2-2-1. The equilibrium dialysis method**

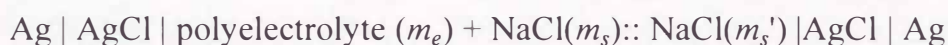
In the equilibrium dialysis, the two solutions under Donnan equilibrium separated by a semipermeable membrane (Viskase Sales Co.) were analyzed. The salt concentration of the inner solution  $m_s$  and the outer solution  $m_s'$  were determined by potentiometry



using a silver/silver chloride electrode for NaCl or by the electric conductance for Na<sub>2</sub>SO<sub>4</sub>. The calibration curves for the inner solution were obtained in the presence of the polyelectrolyte. The polyelectrolyte concentrations for calibration were same as in the dialysis experiments. Little or no difference in the calibration curves was observed in the presence or absence of polyelectrolyte in the potentiometry. Possible interaction of Ag<sup>+</sup> ions (or Ag/AgCl electrode) with polyions was thus shown to be negligible for both PA and PSS. For the conductimetry, a constant difference was observed between the two solutions.

### 2-2-2. The non-equilibrium method

In the non-equilibrium method introduced by Vink,<sup>20,21</sup> the following cell was constructed:



The emf of the cell  $E$  is given as follows in terms of the activities of NaCl in each compartment  $a_{\text{NaCl}}$  and the transference number  $t^+$  of Na<sup>+</sup> ions:

$$E = (RT/F) t^+ \ln [a_{\text{NaCl}}(m_s) / a_{\text{NaCl}}(m_s')] \quad (2-2-1)$$

The emf of the cell was measured as a function of  $m_s'$  at a constant composition ( $m_e$ ,  $m_s$ ) of the polyelectrolyte compartment. The activity which gave zero emf was obtained by interpolation as shown in Fig. 2-2-1. From the value of this activity  $m_s'$  was evaluated. This value of  $m_s'$  corresponded to the equilibrium value.

The emf was measured with an ADVANTEST R8240 digital electrometer. Determination of the salt concentrations in the equilibrium dialysis method was carried

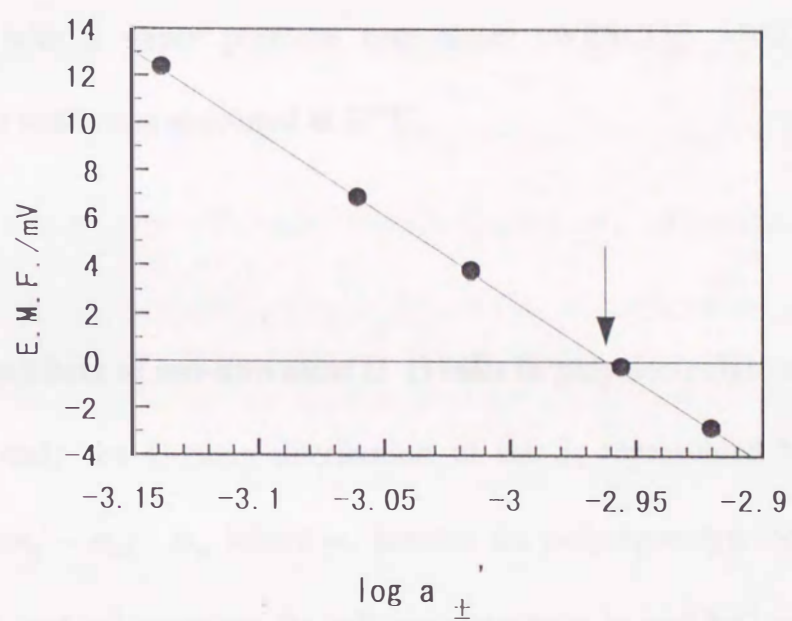


Figure 2-2-1. Example of dependence of the emf on the mean activity of the test solution.  $m_e = 0.01 \text{ mol kg}^{-1}$  (NaPSS),  $m_s = 0.001 \text{ mol kg}^{-1}$  (NaCl).



out with an Orion Research microprocessor ionalyzer/901. The conductivity was measured with a Toa conductivity meter CM-60V.

### 2-2-3. The osmotic pressure measurement

In dilute region, the osmotic pressures against water were measured at  $35.0 \pm 0.4^\circ\text{C}$  with a Knauer membrane osmometer using membranes (Knauer Y1244). At high concentrations, with a vapor pressure osmometer (WESCOR 5500) the osmotic pressures against water was measured at  $37^\circ\text{C}$ .

## 3. Results

### 3-1. Donnan equilibria of uni-univalent (1-1) salts in polyelectrolyte solutions

In the present study the Donnan distribution of salt is represented by  $\Gamma$  which is defined as  $\Gamma = (m_s' - m_s) / m_e$ , where  $m_e$  denotes the polyelectrolyte concentration in  $\text{mol kg}^{-1}$ , and  $m_s$  and  $m_s'$  represent the salt concentrations in  $\text{mol kg}^{-1}$  of the solutions with and without polyelectrolyte, respectively.

In the limit as  $m_e$  approaches zero,  $\Gamma$  becomes  $\Gamma_0$ , the Donnan salt exclusion parameter frequently encountered in the literature. We define  $x$  and  $y$  as  $m_e/m_s$  and  $m_s'/m_s$ . For the ideal Donnan case,

$$\Gamma = 1 / \{1 + (x+1)^{1/2}\} \quad \text{and} \quad \Gamma_0 = 1/2 \quad (3-1-1)$$

According to the LL<sup>1</sup>, which is expected to hold when both  $m_e$  and  $m_s$  are small,

$$\Gamma_0 = 1/2 (1 - 1/2\xi) \quad (\xi < 1) \quad \text{or} \quad 1/(4\xi) \quad (\xi > 1) \quad \text{or equivalently} \quad \Gamma_0 = \phi_p/2 \quad (3-1-2)$$

where  $\phi_p$  is the osmotic coefficient in the salt-free polyelectrolyte solution. Parameter  $\xi$

is defined in terms of the Bjerrum length  $l_B$  and the separation of charges  $b$  along the polymer chain as  $\xi = l_B/b$ . In this study,  $\xi$  is taken as 2.85 for NaPA ( $\alpha=1$ ), NaPSS, PMETAC, and PAAm. Devore and Manning<sup>42</sup> presented an extended analysis for the Donnan salt exclusion as follows,

$$\Gamma = [(x+1)^{1/2} \exp \{-\xi x(x+2)^{-1/2}\} - 1] / x \quad (\xi < 1)$$

$$\text{and} \quad \Gamma = [(\xi^{-1}x+1)^{1/2} \exp \{-\xi^{-1}x(\xi^{-1}x+2)^{-1/2}\} - 1] / x \quad (\xi > 1) \quad (3-1-3)$$

Figure 3-1-1 shows the results predicted from the LL and from eqn (3-1-3). Devore and Manning (D-M) estimated the salt distribution in finite polymer concentrations, and the results were in agreement with the values in the limit as  $m_e$  approaches 0. The values calculated by the D-M treatment were smaller than the values predicted from the LL as shown in Fig. 3-1-1. Most experimental results for  $\xi=2.85$  were greater than the values from the LL as described in later sections. Thus, the result by the D-M treatment gives worse agreement with experimental data than the original simple limiting law in the case of  $\xi=2.85$ . Hence, this extended version was not considered in the analysis of the data for  $\xi=2.85$  in this study. However, the D-M treatment was examined for smaller  $\xi$  cases, since the experimental results in these cases were smaller than the values predicted from the LL.<sup>1</sup>

In the range that  $x \ll 1$ , the limiting law holds rather well unless  $m_s$  is too high. At high salt concentrations (and  $x \ll 1$ ), the P-B approach has given necessary corrections to the result of the LL.<sup>3,4</sup> For intermediate values of  $m_s$ , an empirical relation was proposed by Strauss and Ander.<sup>15</sup>



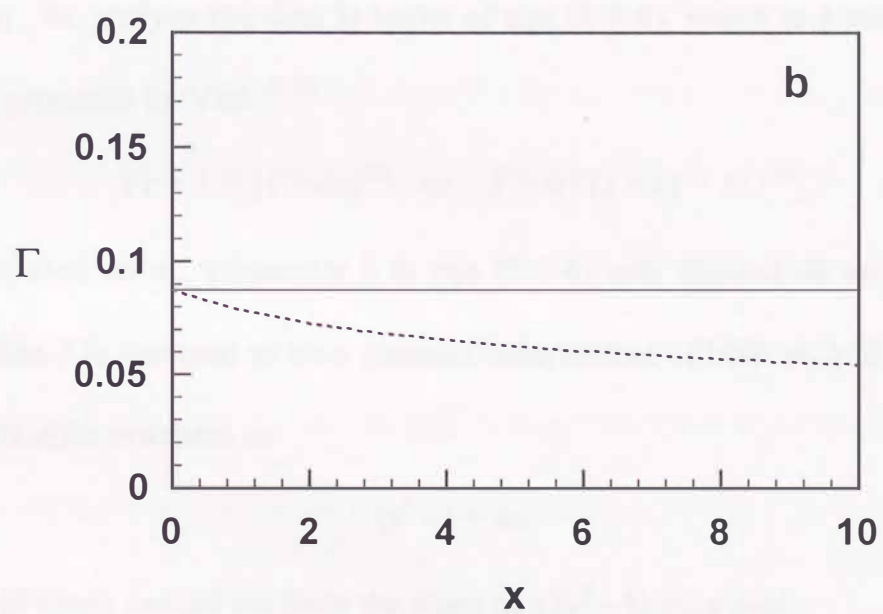
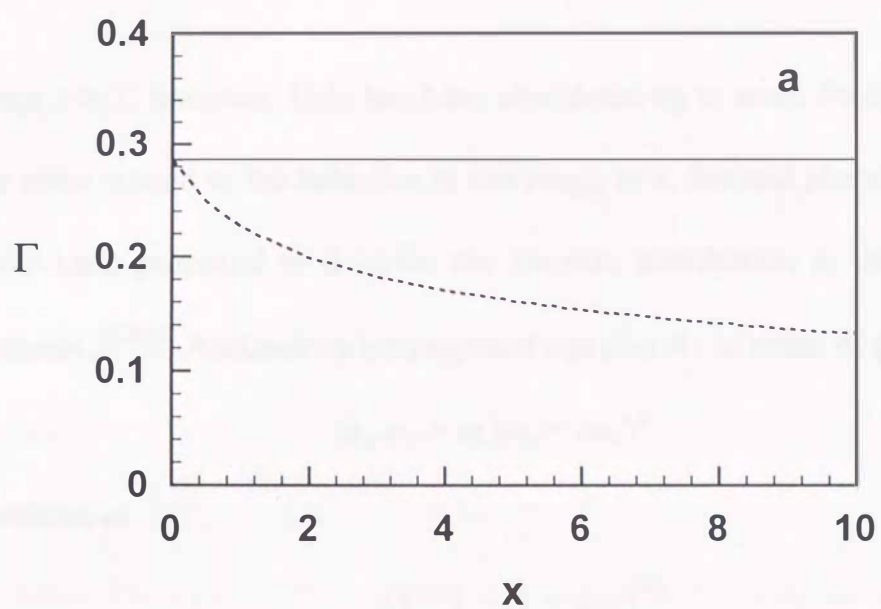


Figure 3-1-1. Comparison of eqn (3-1-2) (solid lines) and eqn (3-1-3) (dotted lines) for the Donnan salt exclusion parameter  $\Gamma$ . (a)  $\xi=0.855$ . (b)  $\xi=2.85$ .

In the range  $x > 1$ , however, little has been elucidated up to now. Swelling of ionic gels is quite often related to the behavior in this range of  $x$ . Several phenomenological relations have been proposed to describe the Donnan distribution in the range of  $x$  greater than unity.<sup>14,20,21</sup> Alexandrowicz proposed eqn (3-1-4) in terms of  $\phi_p$ .<sup>14</sup>

$$(\phi_p m_e + m_s)m_s = (m_s')^2 \quad (3-1-4)$$

which is rewritten as

$$\Gamma x + 1 = [1 + \phi_p x]^{1/2} \quad (3-1-5)$$

In the limit when  $x$  approaches zero, eqn (3-1-5) gives the limiting law result  $\Gamma_0 = \phi_p/2$ .

In this study, we analyze the data in terms of eqn (3-1-6), which is a modification of eqn (3-1-5) proposed by Vink.<sup>20,21</sup>

$$\Gamma x + 1 = [1 + kx]^{1/2} \quad \text{or} \quad \Gamma = k / [1 + (1 + kx)^{1/2}] \quad (3-1-6)$$

Since  $\phi_p$  depends on  $m_e$ , parameter  $k$  in eqn (3-1-6) may depend on  $m_e$ , although in Vink's relation  $k$  is assumed to be a constant independent of both  $m_e$  and  $m_s$ . In terms of  $y$ , eqn (3-1-6) is rewritten as

$$y^2 - 1 = kx \quad (3-1-7)$$

Evaluation of  $k$  was carried out from the slope of a  $(y^2 - 1)$  vs.  $x$  plot.

When  $kx \ll 1$ , eqn (3-1-6) reduces to eqn (3-1-8).

$$\Gamma = 2k / (4 + kx) \quad (3-1-8)$$

Equation (3-1-8) can be derived from the empirical formula for the osmotic pressure given by Dubrynin et al.<sup>37</sup> when combined with the additivity rule.

The excluded volume contribution  $\Gamma(\text{excl})$  has been given as  $B m_s'$ .<sup>43</sup> When the



contribution is added to eqn (3-1-6), we have

$$\Gamma = [(1 + kx)^{1/2} - 1] / x + B m_s' \quad (3-1-9)$$

### 3-2. Salt exclusion parameters for NaPA/NaCl, NaPSS/NaCl, PMETAC/NaCl, and PAAm/NaCl

#### 3-2-1. NaPA/NaCl

We have determined the Donnan distribution of NaCl in NaPA solutions at three polymer concentrations,  $m_e = 0.001, 0.01, \text{ and } 0.10 \text{ mol kg}^{-1}$ . Figure 3-2-1 shows  $\Gamma$  values as functions of  $x$ . In the experiments shown in Figs. 3-2-1(a)-(c),  $m_s$  was varied and  $m_e$  kept constant. Results obtained from the equilibrium dialysis and those from the non-equilibrium method are represented with open and filled circles, respectively. Consistent results were obtained between the two methods. At a low polymer concentration ( $m_e = 0.001$ ),  $\Gamma$  can be well approximated as a constant value of 0.088 which is the result from the LL. At  $m_e = 0.01$ , a slight deviation from the LL and at the same time a weak  $x$ -dependence are both significant. At  $m_e = 0.10$ ,  $\Gamma$  decreased from *ca.* 0.12 at  $x=1$  to *ca.* 0.09 at  $x=6.3$ .

The results at  $m_e = 0.001$  and 0.01 can be described by eqn (3-1-6) as shown in Fig. 3-2-1 with  $k$  ( $\pm 0.02$ ) values of 0.20 and 0.22, respectively. At  $m_e = 0.1$ , the observed  $x$ -dependence cannot be described by eqn (3-1-6), deviations occur for  $x > 5$  if  $k = 0.26$  and for  $x < 3$  if  $k = 0.22$ . The deviation of the observed  $x$ -dependence at  $m_e = 0.10$  can most likely be ascribed to the excluded volume effect. The contribution  $\Gamma(\text{excl})$  is proportional to  $m_s$ .

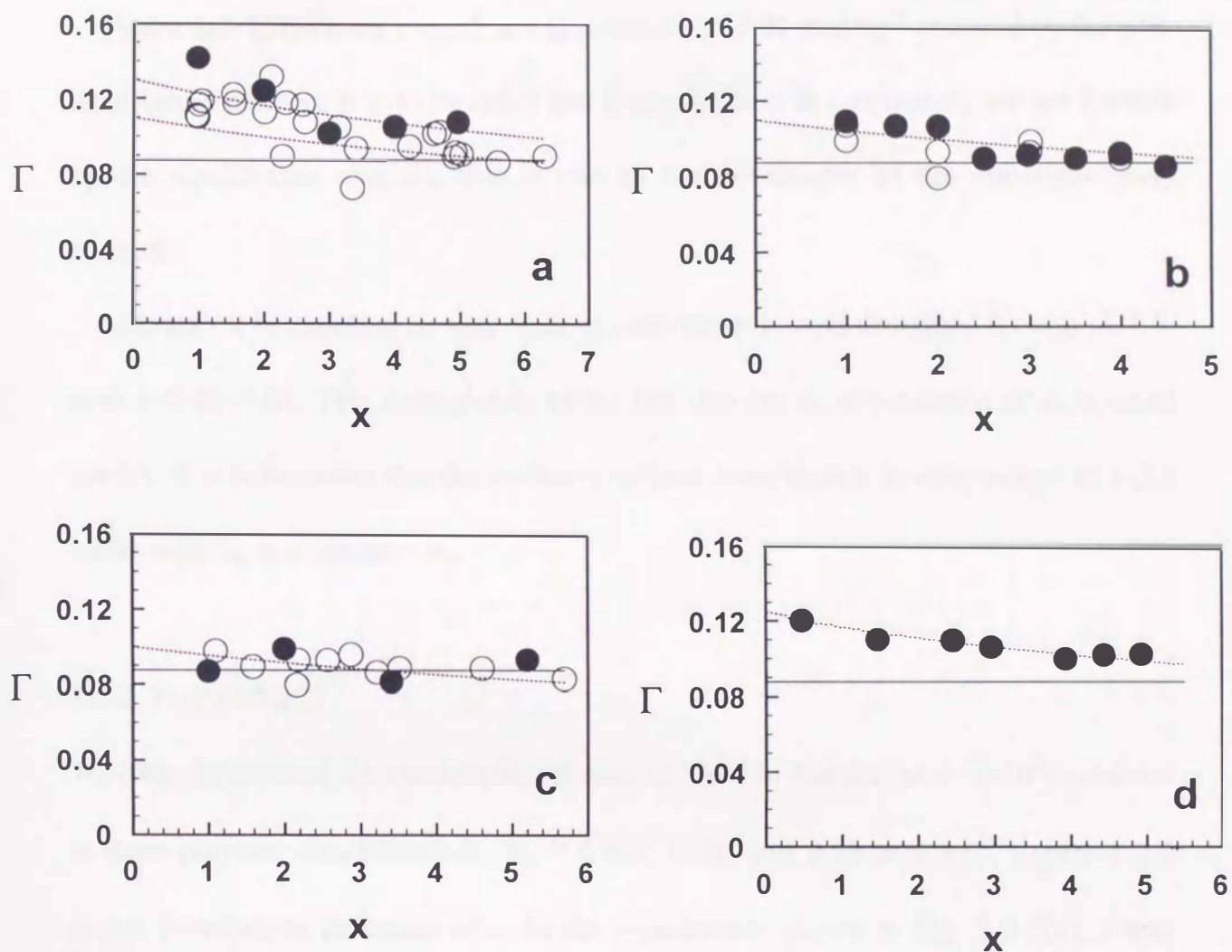


Figure 3-2-1. Donnan distribution of NaCl for NaPA at 25°C. Solid straight lines represent the result predicted from Manning's LL. (a)  $m_e = 0.10 \text{ mol kg}^{-1}$ . The upper and the lower dotted curves are calculated from eqn (3-1-6) with  $k = 0.26$  and  $0.22$ , respectively. (b)  $m_e = 0.01 \text{ mol kg}^{-1}$ . The dotted curve is calculated from eqn (3-1-6) with  $k = 0.22$ . (c)  $m_e = 0.001 \text{ mol kg}^{-1}$ . The dotted curve is calculated from eqn (3-1-6) with  $k = 0.20$ . (d)  $m_s = 0.01 \text{ mol kg}^{-1}$ ; The dotted curve is calculated from eqn (3-1-6) with  $k = 0.25$ . Open and filled symbols refer to the results from the equilibrium dialysis and the non-equilibrium method, respectively.



Figure 3-2-1(d) shows a result at a constant  $m_s$  of  $0.01 \text{ mol kg}^{-1}$  obtained by the non-equilibrium method. It is to be noted that measurements at constant  $m_s$  are not feasible by the equilibrium dialysis; this is one of the advantages of the non-equilibrium method.

Although  $k$  is expected to vary with  $m_e$ , the result is well described by eqn (3-1-6) with  $k=0.25\pm0.01$ . This corresponds to the fact that the  $m_e$  dependence of  $\phi_p$  is small for PA. It is to be noted that the excluded volume contribution is independent of  $x$  if  $x$  varies with  $m_e$  at a constant  $m_s$ .

### 3-2-2. NaPSS/NaCl

We have determined the Donnan distribution of NaCl in NaPSS ( $M_w=7\times10^4$ ) solutions at three polymer concentrations,  $m_e = 0.001, 0.01, \text{ and } 0.10 \text{ mol kg}^{-1}$ . Figure 3-2-2 shows  $\Gamma$  values as functions of  $x$ . In the experiments shown in Fig. 3-2-2(a),  $x$  was varied and  $m_e$  kept constant. The results obtained from the equilibrium dialysis and the non-equilibrium method are represented by open and filled circles, respectively. Consistent results were obtained by the two methods. At a low polymer concentration ( $m_e=0.001$ ),  $\Gamma$  values depended weakly on  $x$  but they were significantly greater than the result (0.088) from the LL. At  $m_e=0.01$ , the  $x$ -dependence became more significant. At  $m_e=0.10$ ,  $\Gamma$  decreased from *ca.* 0.18 at  $x=1$  to *ca.* 0.13 at  $x=5$ .

The results can be described by eqn (3-1-6) as shown in Fig. 3-2-2 (a) with  $k$  values of 0.25, 0.29, and 0.38 for  $m_e = 0.001, 0.01, \text{ and } 0.10$ , respectively. The dependence of  $k$  on  $m_e$  was more than double that observed for NaPA as shown in Table 1.

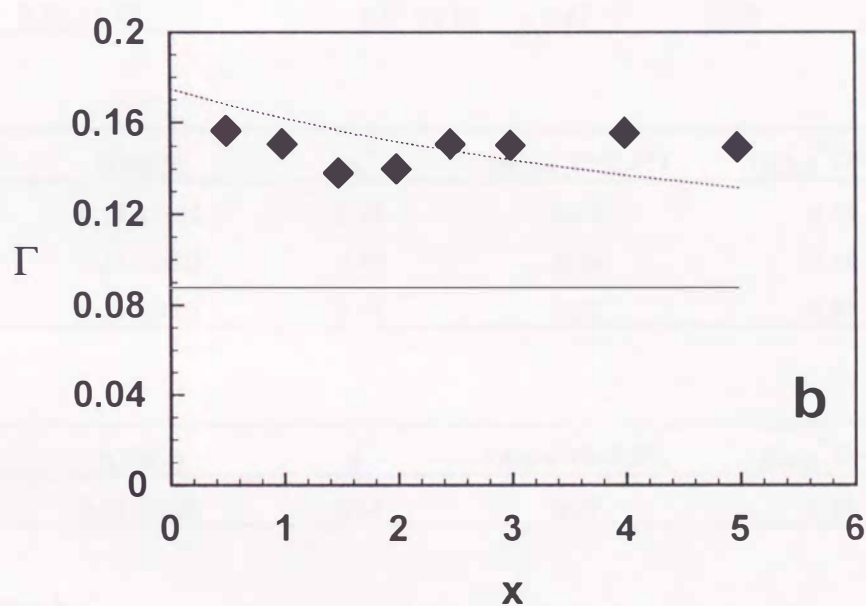
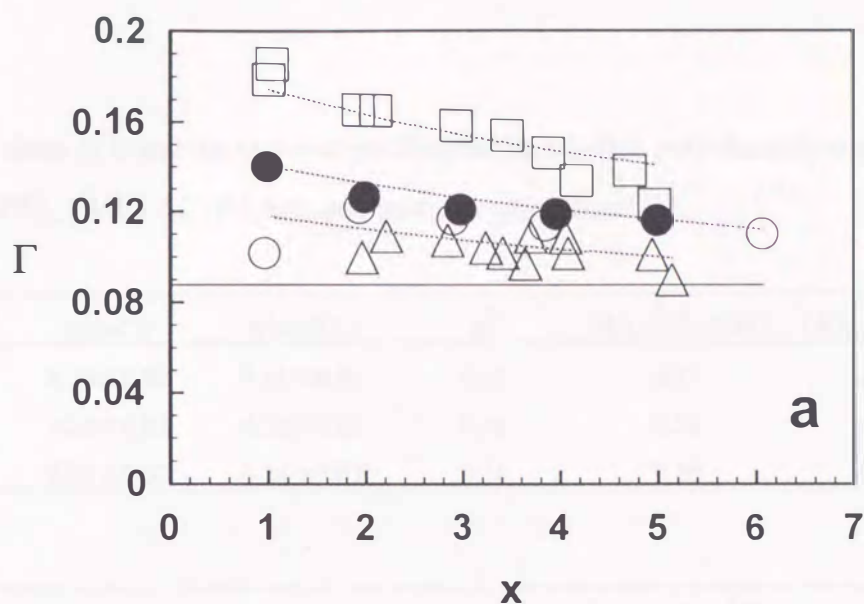


Figure 3-2-2. Donnan distribution of NaCl for NaPSS at 25°C. The solid straight lines represent the result predicted from the LL. (a) ( $\triangle$ )  $m_e = 0.001 \text{ mol kg}^{-1}$  (equilibrium dialysis method); ( $\circ$ )  $m_e = 0.01 \text{ mol kg}^{-1}$  (equilibrium dialysis method); ( $\bullet$ )  $m_e = 0.01 \text{ mol kg}^{-1}$  (non-equilibrium method); ( $\square$ )  $m_e = 0.10 \text{ mol kg}^{-1}$  (equilibrium dialysis method). The three curves are calculated from eqn (3-1-6) with  $k = 0.38, 0.29$  and  $0.25$ , from top to bottom, respectively. (b)  $m_s = 0.01 \text{ mol kg}^{-1}$ ; the dotted curve is calculated from eqn (3-1-6) with  $k = 0.35$ .



Table 1. Values of  $k$  and the osmotic coefficients in salt-free polyelectrolyte solutions  $\phi_p$  for NaPA, NaPSS, PMETAC, PAAm, and partially neutralized PA.

| NaPA                               |                  |                             |                             |                                          |                                          |                                         |
|------------------------------------|------------------|-----------------------------|-----------------------------|------------------------------------------|------------------------------------------|-----------------------------------------|
| $m_e/\text{mol kg}^{-1}$           | $k(\text{NaCl})$ | $k(\text{Na}_2\text{SO}_4)$ | $\phi_p^c$                  | $(\phi_p)_{\text{P-B}}^b (\lambda=2.85)$ | $(\phi_p)_{\text{P-B}}^b (\lambda=4.5)$  |                                         |
| 0.001                              | $0.20 \pm 0.02$  | $0.21 \pm 0.02$             | 0.13                        | 0.21                                     |                                          | 0.14                                    |
| 0.01                               | $0.22 \pm 0.02$  | $0.23 \pm 0.03$             | 0.14                        | 0.23                                     |                                          | 0.15                                    |
| 0.10                               | $0.25 \pm 0.03$  | $0.24 \pm 0.03$             | 0.18                        | 0.26                                     |                                          | 0.17                                    |
|                                    |                  |                             |                             |                                          |                                          |                                         |
| NaPSS                              |                  |                             |                             |                                          |                                          |                                         |
| $m_e/\text{mol kg}^{-1}$           | $k(\text{NaCl})$ | $k(\text{NaNCS})$           | $k(\text{Na}_2\text{SO}_4)$ | $\phi_p^a$                               | $(\phi_p)_{\text{P-B}}^b (\lambda=2.85)$ | $(\phi_p)_{\text{P-B}}^b (\lambda=4.5)$ |
| 0.001                              | $0.25 \pm 0.05$  |                             | $0.22 \pm 0.02$             | 0.12                                     | 0.23                                     | 0.15                                    |
| 0.01                               | $0.29 \pm 0.02$  | $0.30 \pm 0.02$             | $0.28 \pm 0.02$             | 0.19                                     | 0.27                                     | 0.17                                    |
| 0.10                               | $0.38 \pm 0.03$  |                             | $0.37 \pm 0.03$             | 0.27                                     | 0.35                                     | 0.23                                    |
|                                    |                  |                             |                             |                                          |                                          |                                         |
| PMETAC                             |                  |                             |                             |                                          |                                          |                                         |
| $m_e/\text{mol kg}^{-1}$           | $k(\text{NaCl})$ |                             | $\phi_p^a$                  | $(\phi_p)_{\text{P-B}}^b (\lambda=2.85)$ | $(\phi_p)_{\text{P-B}}^b (\lambda=4.5)$  |                                         |
| 0.001                              | $0.18 \pm 0.02$  |                             | 0.10                        | 0.23                                     |                                          | 0.14                                    |
| 0.01                               | $0.22 \pm 0.02$  |                             | 0.12                        | 0.26                                     |                                          | 0.16                                    |
| 0.10                               | $0.25 \pm 0.03$  |                             | 0.17                        | 0.32                                     |                                          | 0.21                                    |
|                                    |                  |                             |                             |                                          |                                          |                                         |
| PAAm                               |                  |                             |                             |                                          |                                          |                                         |
| $m_e/\text{mol kg}^{-1}$           | $k(\text{NaCl})$ |                             | $\phi_p^a$                  | $(\phi_p)_{\text{P-B}}^b (\lambda=2.85)$ | $(\phi_p)_{\text{P-B}}^b (\lambda=4.5)$  |                                         |
| 0.10                               | $0.23 \pm 0.03$  |                             | 0.14                        | 0.27                                     |                                          | 0.18                                    |
|                                    |                  |                             |                             |                                          |                                          |                                         |
| PA at $m_e=0.01\text{mol kg}^{-1}$ |                  |                             |                             |                                          |                                          |                                         |
| $\alpha$                           | $k(\text{NaCl})$ |                             | $\phi_p^c$                  | $(\phi_p)_{\text{P-B}}^b (\lambda=2.85)$ | $(\phi_p)_{\text{P-B}}^b (\lambda=4.5)$  |                                         |
| 0.3                                | $0.54 \pm 0.01$  |                             | 0.37                        | 0.61                                     |                                          | 0.45                                    |
| 0.5                                | $0.36 \pm 0.01$  |                             | 0.25                        | 0.43                                     |                                          | 0.29                                    |
| 0.8                                | $0.24 \pm 0.01$  |                             | 0.16                        | 0.29                                     |                                          | 0.18                                    |

<sup>a</sup> Interpolated values from our unpublished data.

<sup>b</sup>  $(\phi_p)_{P-B}$  represents the calculated values of  $\phi_p$  according to eqns (3-7-2)-(3-7-4) .

<sup>c</sup> From ref. 23 and 29

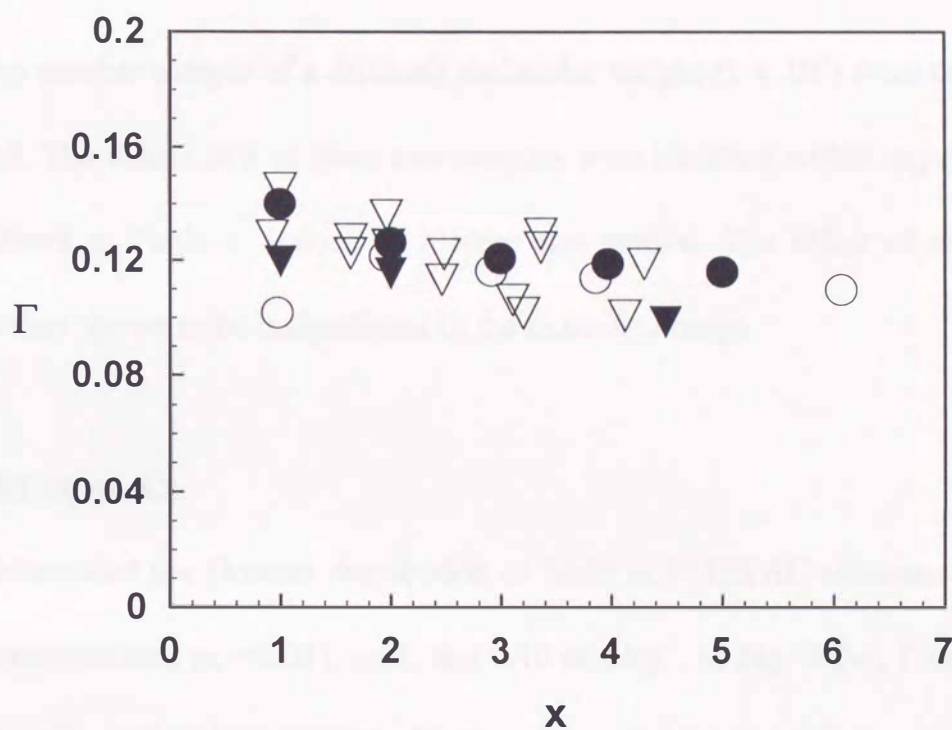


Figure 3-2-3. Dependence of the Donnan distribution of NaCl on the molecular weight of NaPSS.  $m_e = 0.01 \text{ mol kg}^{-1}$ . Open symbols: equilibrium dialysis method; filled symbols: non-equilibrium method. Molecular weights: (○, ●)  $7 \times 10^4$  and (▽, ▼)  $5 \times 10^5$ .



A result at a constant  $m_s$  of  $0.01 \text{ mol kg}^{-1}$  obtained by the non-equilibrium method is also shown in Fig. 3-2-2(b). The result is approximately independent of  $x$ . For PSS,  $k$  is expected to increase with  $m_e$  just as  $\phi_p$  does. This gives a positive  $x$ -dependence of  $\Gamma$  and compensates to a considerable extent the negative  $x$  dependence inherent to eqn (3-1-6).

Results on another sample of a different molecular weight ( $5 \times 10^5$ ) were compared in Fig. 3-2-3. The values of  $k$  of these two samples were identical within experimental errors as shown in Table 1. Values of  $\Gamma$  were also similar. The effect of molecular weight was thus shown to be insignificant in the examined range.

### 3-2-3. PMETAC/NaCl

We have determined the Donnan distribution of NaCl in PMETAC solutions at three polymer concentrations,  $m_e = 0.001, 0.01$ , and  $0.10 \text{ mol kg}^{-1}$ . In Fig. 3-2-4,  $\Gamma$  values are shown as functions of  $x$ . At  $m_e = 0.001$ ,  $\Gamma$  values depended on  $x$  and they were smaller than the result from the LL for  $x > 4$ . At  $m_e = 0.01$ , though the  $x$ -dependence was similar to  $m_e = 0.001$ ,  $\Gamma$  values were significantly greater than the result from the LL for  $x < 4$ . The results at  $m_e = 0.001$  and  $0.01$  for PMETAC can be described by eqn (3-1-6) with single  $k$  values as shown in Fig. 3-2-4.

At  $m_e = 0.1$ ,  $\Gamma$  values are similar to those at  $m_e = 0.01$  in the range  $x > 2$ . At  $x = 1$ , however,  $\Gamma$  values are significantly greater than those at  $m_e = 0.01$ . The observed  $x$ -dependence at  $m_e = 0.1$  cannot be described by eqn (3-1-6). Parameter  $k$  increased with  $m_e$  for PMETAC, similar to those of anionic polyelectrolyte NaPA and NaPSS.

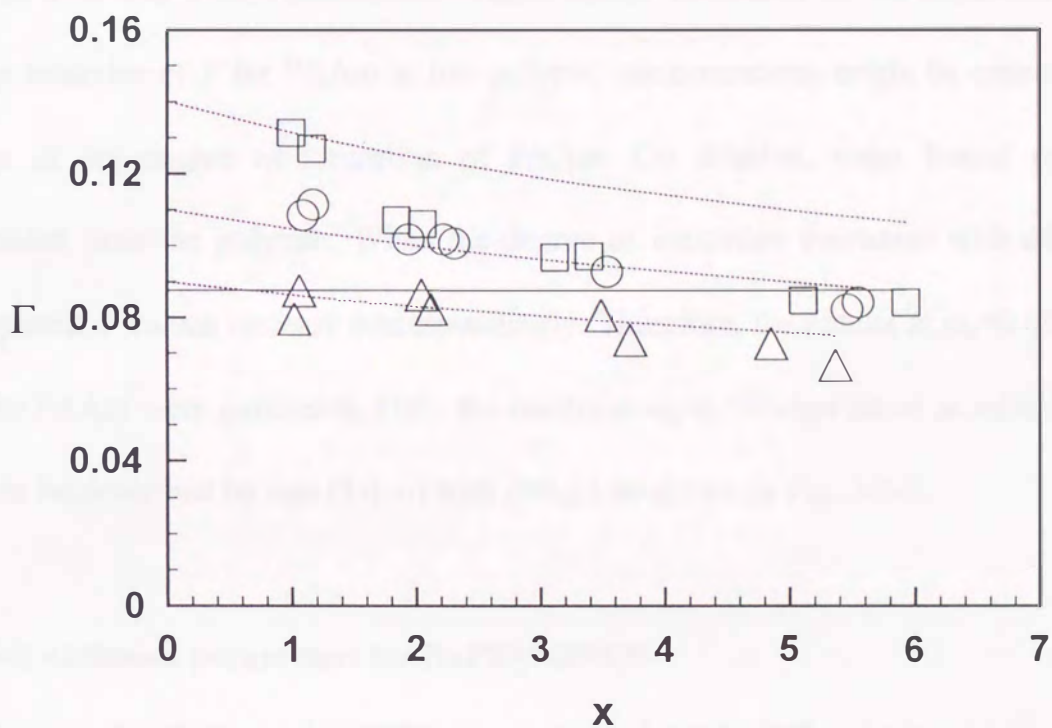


Figure 3-2-4. Donnan distribution of NaCl for PMETAC at 25°C. The solid straight line represents the result predicted from the LL.  $m_e = (\triangle) 0.001 \text{ mol kg}^{-1}$ ;  $(\circ) 0.01 \text{ mol kg}^{-1}$  and  $(\square) 0.10 \text{ mol kg}^{-1}$ . Dotted curves are calculated from eqn (3-1-6) with  $k=0.28, 0.22$  and  $0.18$ , from top to bottom, respectively.



#### 3-2-4. PAAm/NaCl

The Donnan distribution of NaCl in PAAm solutions were determined only at  $m_e=0.10$  mol kg<sup>-1</sup>. At  $m_e=0.001$  and  $0.01$ , the observed  $\Gamma$  values were almost constant and were *ca.* 0.14-0.20 and 0.10, respectively. These values decreased as  $m_e$  increased. This strange behavior of  $\Gamma$  for PAAm at low polymer concentrations might be caused by a change of the degree of ionization of PAAm. On dilution, some bound protons dissociated from the polymer. When the degree of ionization decreases with dilution, the apparent  $\Gamma$  values increase correspondingly. Therefore, the results at  $m_e=0.001$  and  $0.01$  for PAAm were unreliable. Only the results at  $m_e=0.10$  were taken as reliable and they can be described by eqn (3-1-6) with  $k=0.23$  as shown in Fig. 3-2-5.

#### 3-3. Salt exclusion parameters for NaPSS/NaNCS

The Donnan distribution of NaNCS was examined for NaPSS solutions at  $m_e=0.01$ . NCS<sup>-</sup> ion is located at one end of the Hofmeister series. The result is shown in Fig. 3-3-1.  $\Gamma$  values decrease with  $x$  and they are significantly greater than the result from the LL. The results can be described by eqn (3-1-6) as shown in Fig. 3-3-1 with  $k=0.30 \pm 0.03$ .

#### 3-4. Salt exclusion parameters for PA ( $\alpha=0.3, 0.5, 0.8$ , and $1$ )/NaCl

Figure 3-4-1 shows the Donnan distribution of NaCl in partially neutralized PA ( $\alpha=0.3, 0.5, 0.8$ , and  $1.0$ ) solutions at  $m_e=0.01$ . It is to be noted that chain concentrations increased as  $\alpha$  decreased to keep  $m_e$  constant. At  $\alpha=0.3$ ,  $\Gamma$  values decreased with

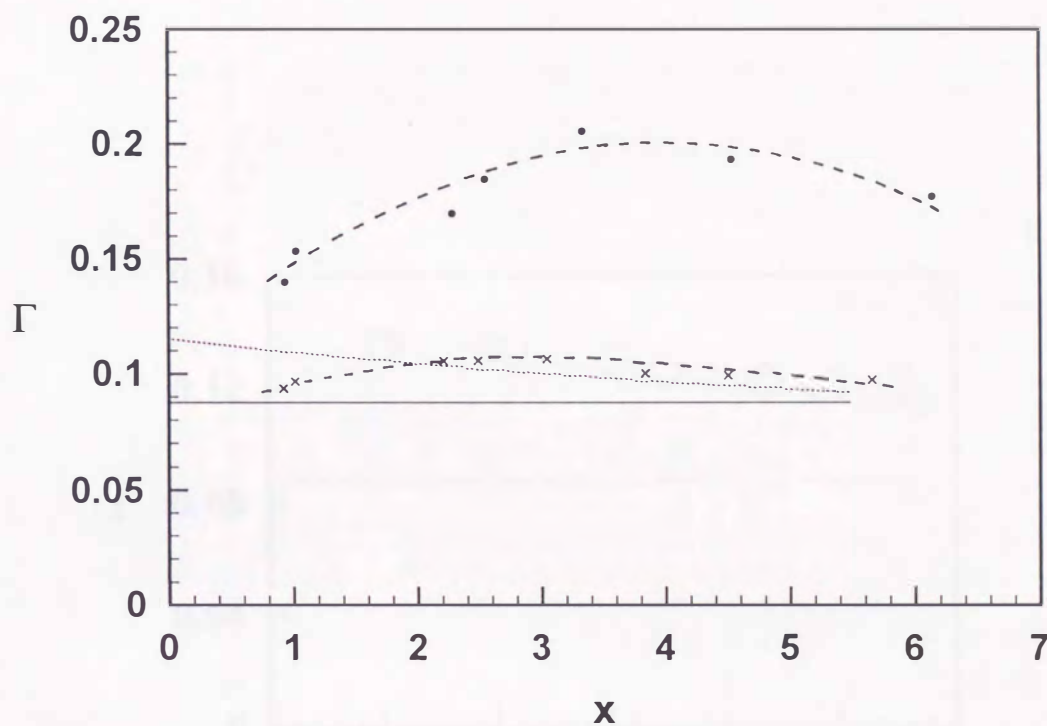


Figure 3-2-5. Donnan distribution of NaCl for PAAm at  $m_e = 0.10 \text{ mol kg}^{-1}$  at  $25^\circ\text{C}$ . The solid straight line represents the result predicted from the LL. The dotted curves are calculated from eqn (3-1-6) with  $k = 0.23$ . (---) drawn through experimental results represented with crosses and dots at  $m_e = 0.001$  and  $0.01$ , from top to bottom, respectively.



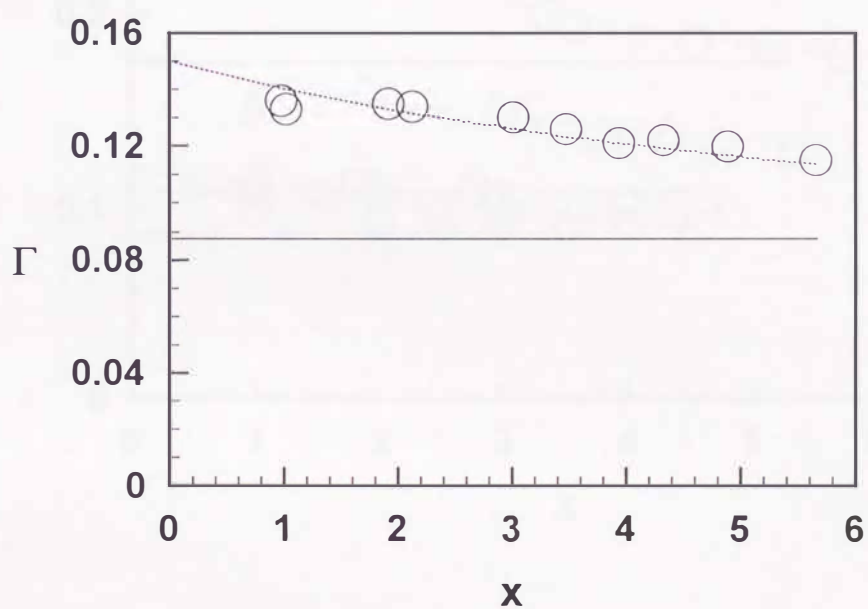


Figure 3-3-1. Donnan distribution of NaNCS for NaPSS at  $m_e = 0.01 \text{ mol kg}^{-1}$  at  $25^\circ\text{C}$ . The solid straight line represents the result predicted from the LL. The dotted curve is calculated from eqn (3-1-6) with  $k = 0.30$ .

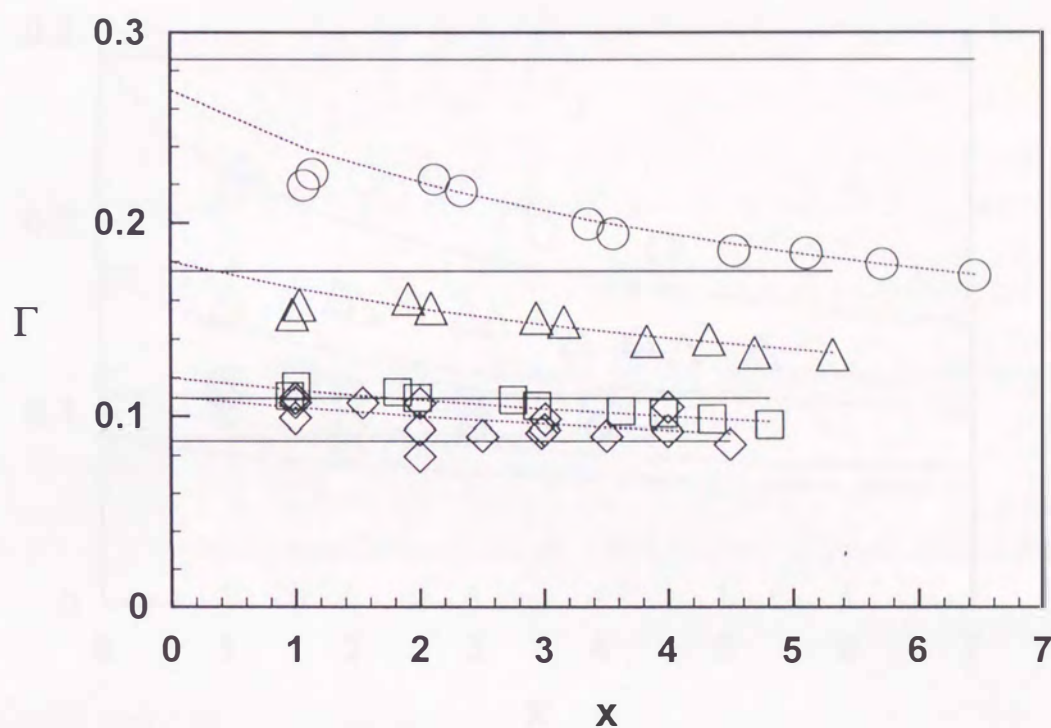


Figure 3-4-1. Donnan distribution of NaCl for partially neutralized PA at  $m_e = 0.01$  mol kg<sup>-1</sup> at 25°C. Solid straight lines represent the results from the LL for  $\alpha = 0.3, 0.5, 0.8$  and  $1.0$ , from top to bottom, respectively.  $\alpha = (\bigcirc) 0.3; (\triangle) 0.5; (\square) 0.8; (\diamond) 1$ . The dotted curves are calculated from eqn (3-1-6) with  $k = 0.54, 0.36, 0.24$  and  $0.22$ , from top to bottom, respectively.



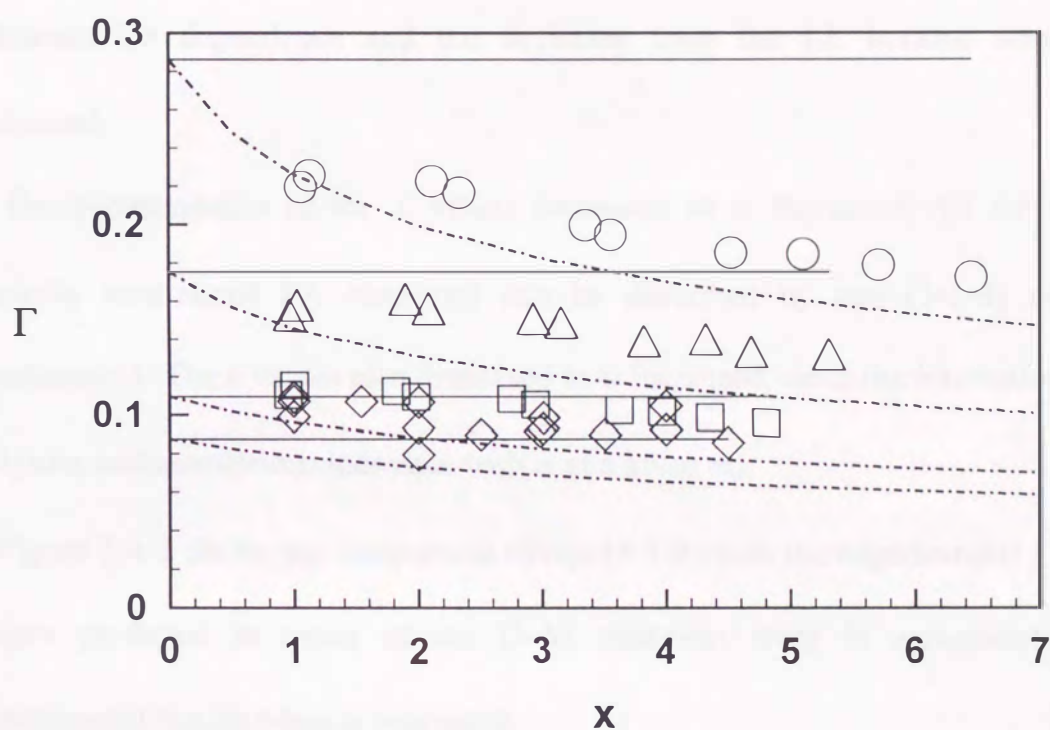


Figure 3-4-2. Donnan distribution of NaCl for partially neutralized PA at  $m_e = 0.01$  mol kg<sup>-1</sup> at 25°C. Solid straight lines represent the results from the LL for  $\alpha = 0.3, 0.5, 0.8$  and  $1.0$ , from top to bottom, respectively.  $\alpha = (\bigcirc) 0.3; (\triangle) 0.5; (\square) 0.8; (\diamond) 1$ . The chain curves are calculated from eqn (3-1-3) with  $\xi = 0.855, 1.43, 2.28$  and  $2.85$ , from top to bottom, respectively.

increasing  $x$  and they were much smaller than the result from the LL. In the present study  $x \rightarrow 0$  corresponds to large excess salt. The limiting law behavior is expected for large  $x$ , that is, small  $m_s$ . But deviation becomes more significant as  $x$  increases. At  $\alpha=0.8$ ,  $\Gamma$  values can be approximated with the LL, as in the case for  $\alpha=1.0$ . Both the concentration dependence and the deviation from the LL became smaller as  $\alpha$  increased.

The  $x$ -dependence of the  $\Gamma$  values decreased as  $\alpha$  increased. All the results on partially neutralized PA examined can be described by eqn (3-1-6) with single parameters  $k$ . The  $k$  values also decreased as  $\alpha$  increased, since the interaction between polyions and counterions increases with  $\alpha$  at a given  $m_e$ .

Figure 3-4-2 shows the comparison of eqn (3-1-3) with the experimental  $\Gamma$  data. The values predicted in terms of the D-M treatment were in agreement with the experimental results when  $\alpha$  was small.

### 3-5. Donnan equilibria of a 1-2 salt in polyelectrolyte solutions (NaPA/Na<sub>2</sub>SO<sub>4</sub> and NaPSS/Na<sub>2</sub>SO<sub>4</sub>)

For 1-2 salts, the preceding relation eqn (3-1-1) for 1-1 salts in the ideal Donnan case becomes eqn (3-5-1).

$$\Gamma = [(1 + x/2)^{2/3} - 1] / x \quad (3-5-1)$$

The value of  $\Gamma_0$  is 1/3 rather than 1/2 for the 1-1 salt. The decrease in  $\Gamma_0$  is a manifestation that uneven salt distribution is less favored on entropic ground for a 1-2



salt. According to the LL,<sup>1</sup>

$$\Gamma_0 = 1/3 (1 - 1/2\xi) \quad (\xi < 1) \text{ or } 1/(6\xi) \quad (\xi > 1) \text{ or equivalently } \Gamma_0 = \phi_p / 3 \quad (3-5-2)$$

The Alexandrowicz relation is extended to 1-2 salts as follows.

$$(\phi_p m_e + 2m_s)^2 m_s = (2m_s')^2 m_s' \quad (3-5-3)$$

This is rewritten as

$$\Gamma = \phi_p [1 + \phi_p x/4] / (y^2 + y + 1) \quad (3-5-4)$$

In the present study, we employ eqn (3-5-5) with a parameter  $k$  in place of  $\phi_p$ .

$$\Gamma = k [1 + kx/4] / (y^2 + y + 1) = [(1 + kx/2)^{2/3} - 1] / x \quad (3-5-5)$$

The last expression is obtained since  $y - 1 = \Gamma x$ . Values of  $k$  were determined from  $(y^{3/2} - 1)$  vs.  $x$  plot, since

$$y^{3/2} = 1 + kx/2 \quad (3-5-6)$$

Once  $k$  is determined,  $\Gamma$  is calculated according to eqn (3-5-5). It is interesting to examine whether or not  $k$  is identical for NaCl and Na<sub>2</sub>SO<sub>4</sub> for a given polymer at the same  $m_e$ .

We have determined the Donnan distribution of Na<sub>2</sub>SO<sub>4</sub> for both NaPA and NaPSS (Mw =  $5 \times 10^5$ ) at three polymer concentrations,  $m_e = 0.001, 0.01$ , and  $0.10 \text{ mol kg}^{-1}$ . In Fig. 3-5-1 and 3-5-2, values of  $\Gamma$  are shown as functions of  $x$ , for NaPA and NaPSS, respectively. In these experiments  $x$  was varied while  $m_e$  was kept constant. At a low polymer concentration ( $m_e = 0.001$ ),  $\Gamma$  values of both polyelectrolytes were slightly, but significantly, greater than 0.058 which is the result from the LL. At  $m_e = 0.01$  for both polymers, a slight deviation from the LL and a weak  $x$ -dependence are both significant.

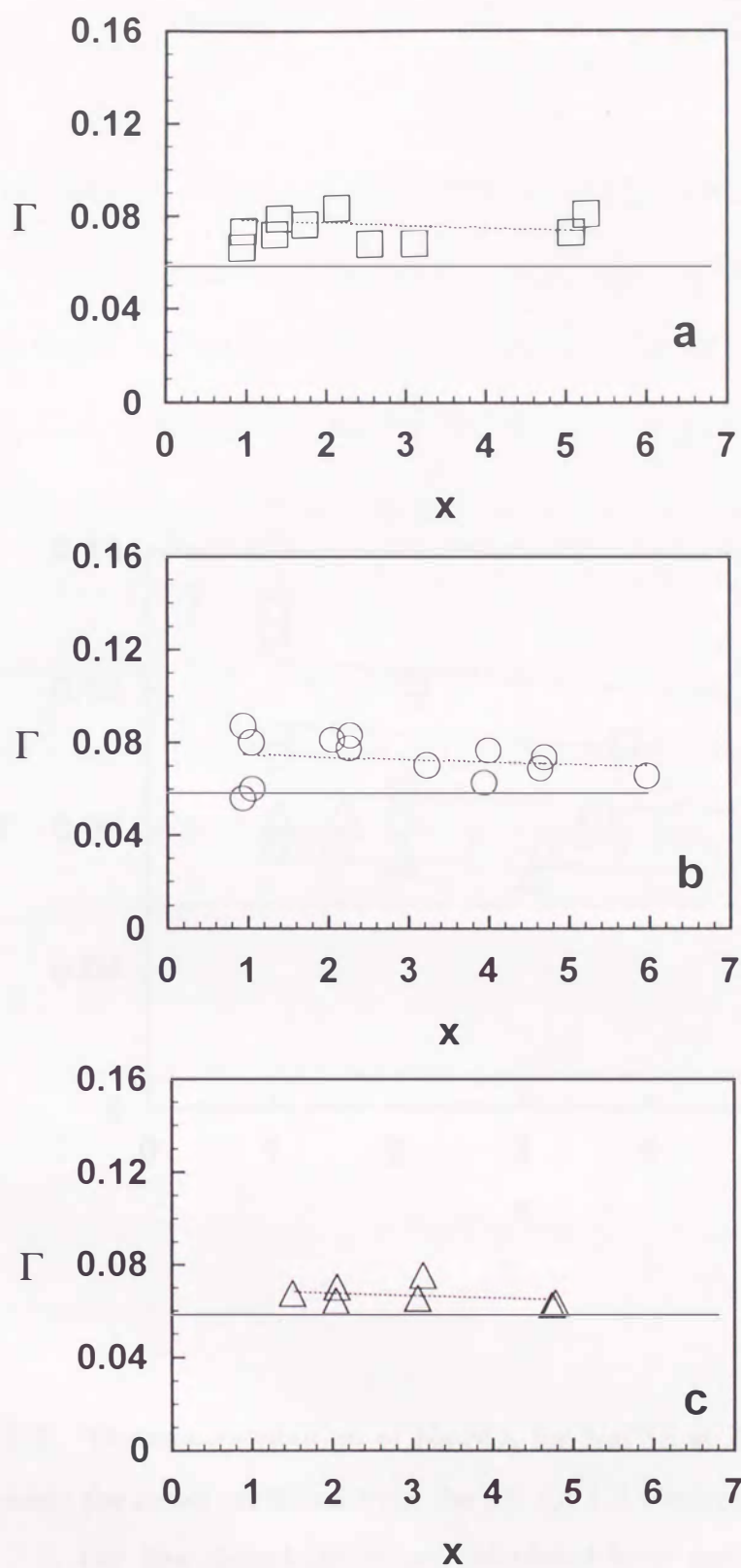


Figure 3-5-1. Donnan distribution of  $\text{Na}_2\text{SO}_4$  for NaPA at  $25^\circ\text{C}$ . The solid straight lines represent the result predicted from the LL for 1-2 electrolytes. (a)  $m_e = 0.10 \text{ mol kg}^{-1}$ . The dotted curve is calculated from eqn (3-5-5) with  $k = 0.24$ . (b)  $m_e = 0.01 \text{ mol kg}^{-1}$ . The dotted curve is calculated from eqn (3-5-5) with  $k = 0.23$ . (c)  $m_e = 0.001 \text{ mol kg}^{-1}$ . The dotted curve is calculated from eqn (3-5-5) with  $k = 0.21$ .



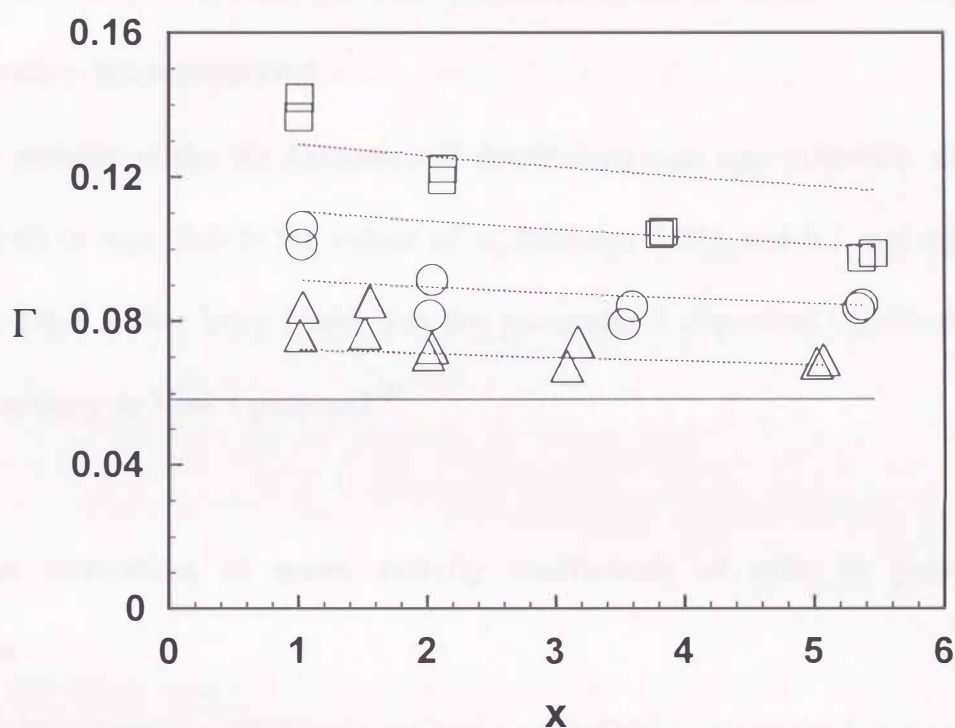


Figure 3-5-2. Donnan distribution of  $\text{Na}_2\text{SO}_4$  for NaPSS at  $25^\circ\text{C}$ . The solid straight line represents the result predicted from the LL for 1-2 electrolytes. Symbols as given in Fig. 3-2-2. The four dotted curves are calculated from eqn (3-5-5) with  $k = 0.40$ ,  $0.34$ ,  $0.28$  and  $0.22$ , from top to bottom, respectively.

At  $m_e=0.10$ , the  $x$ -dependence of  $\Gamma$  was weak for NaPA, while  $\Gamma$  decreased from *ca.* 0.14 at  $x=1$  to *ca.* 0.10 at  $x=5.4$  for NaPSS. The results can be described by with eqn (3-5-5), as shown in Figs. 3-5-1 and 3-5-2, with  $k$  values of 0.21, 0.23, and 0.24 for NaPA and 0.22, 0.28, and 0.37 for NaPSS. These  $k$  values are in good coincidence with those obtained on NaCl for both polyelectrolytes. In Table 1,  $k$  values together with  $\phi_p$  values are summarized.

In the present study, the Donnan salt distribution was approximately described by eqn (3-1-6) or eqn (3-5-5) for values of  $m_e$  between 0.001 and 0.1 mol kg<sup>-1</sup> and of  $x$  between 1 and 5. We have found that the parameter  $k$  depended significantly on  $m_e$ . This is contrary to Vink's proposal.<sup>20</sup>

### 3-6. The estimation of mean activity coefficients of salts in polyelectrolyte solutions

Mean molal activity coefficients  $\gamma_{\pm}$  of NaCl or NaNCS in the polyelectrolyte solutions were calculated from the following equation.

$$(\gamma_{\pm})^2 (m_s + m_e) m_s = (\gamma_{\pm}' m_s')^2 \quad (3-6-1)$$

For Na<sub>2</sub>SO<sub>4</sub>, eqn (3-6-2) was used in place of eqn (3-6-1).

$$(\gamma_{\pm})^3 (2m_s + m_e)^2 m_s = 4(\gamma_{\pm}' m_s')^3 \quad (3-6-2)$$

For NaCl, mean rational activity coefficients of polyelectrolyte-free salt solutions  $f_{\pm}'$  were calculated as<sup>44</sup>

$$\log f_{\pm}' = -A(m_s')^{1/2} / [1 + (m_s')^{1/2}] + b m_s' \quad (A=0.5115 \text{ and } b=0.16) \quad (3-6-3)$$



Here,  $\gamma_{\pm}'$  were calculated as  $f_{\pm}' / (1 + 0.001\nu W_A m)$ , where  $\nu$ ,  $W_A$  and  $m$  represent, respectively, the number of moles of ions formed by the ionization of one mole of solute (NaCl), the molecular weight of the solvent (water), and moles of solute per kilogram of solvent.<sup>44</sup>

For NaNCS<sup>45</sup>

$$\log \gamma_{\text{Na}}' = -A (m_s')^{1/2} / [1 + B a^* (m_s')^{1/2}] \quad (3-6-4)$$

$$\log \gamma_{\text{NCS}}' = -A (m_s')^{1/2} / [1 + B a^* (m_s')^{1/2}] \quad (3-6-5)$$

where  $A=0.5114$ ,  $B=0.3291 \times 10^8$ ,  $a^*=4.5$  and  $3.5$  for  $\text{Na}^+$  and  $\text{NCS}^-$ , respectively.

$$\gamma_{\pm}' = (\gamma_{\text{Na}}' \gamma_{\text{NCS}}')^{1/2} \quad (3-6-6)$$

For  $\text{Na}_2\text{SO}_4$ <sup>46</sup>

$$\log \gamma_{\pm}' = -0.708(6m_s')^{1/2} / \{1 + A (6m_s')^{1/2}\} + B (6m_s') - \log (1 + 0.054m_s') \quad (3-6-7)$$

where  $A=0.719$  and  $B=-0.0053$ .

The activity coefficient is related to the salt exclusion parameter  $\Gamma$  as

$$(\gamma_{\pm} / \gamma_{\pm}')^2 = (\Gamma x + 1)^2 / (x + 1) \quad \text{for NaCl and NaNCS} \quad (3-6-8)$$

$$(\gamma_{\pm} / \gamma_{\pm}')^3 = 4 (\Gamma x + 1)^3 / (x + 2)^2 \quad \text{for Na}_2\text{SO}_4 \quad (3-6-9)$$

Mean activity coefficients predicted from the LL,  $(\gamma_{\pm})_{\text{LL}}$ , are given as follows.

For 1-1 electrolyte,<sup>1</sup> such as NaCl and NaNCS,

$$\ln (\gamma_{\pm})_{\text{LL}} = -\xi x / \{2(x + 2)\} \quad (\xi < 1)$$

$$\text{and } (\gamma_{\pm})_{\text{LL}} = \{(\xi^{-1}x + 1)/(x + 1)\}^{1/2} \exp[-\xi^{-1}x / \{2(\xi^{-1}x + 2)\}] \quad (\xi > 1) \quad (3-6-10)$$

For 1-2 electrolyte, such as  $\text{Na}_2\text{SO}_4$ ,

$$\ln (\gamma_{\pm})_{\text{LL}} = -\xi x / (x + 6) \quad (\xi < 1)$$

$$\text{and } (\gamma_{\pm})_{LL} = \{(\xi^{-1}x + 2)/(x + 2)\}^{2/3} \exp\{-\xi^{-1}x/(\xi^{-1}x + 6)\} \quad (\xi > 1) \quad (3-6-11)$$

The charge density parameter  $\xi$  is estimated to be 2.85 for NaPA, NaPSS, PAAm, and PMETAC. For partially neutralized PA,  $\xi$  is taken as  $\alpha \times 2.85$  in terms of  $\alpha$ , the degree of ionization. The values of  $(\gamma_{\pm})_{LL}$  are shown with dotted lines in all figures.

The activity coefficients of NaCl and Na<sub>2</sub>SO<sub>4</sub> for NaPA are shown in Figs. 3-6-1 and 3-6-2, respectively. Activity coefficients decreased as  $m_e$  or  $m_s$  increased. At  $m_e=0.001$ , the observed values agree with  $(\gamma_{\pm})_{LL}$ . When  $m_e$  is large, however, the observed values are smaller than  $(\gamma_{\pm})_{LL}$  in the small  $x$  region, that is, the large  $m_s$  region. In particular, they are considerably smaller than  $(\gamma_{\pm})_{LL}$  for Na<sub>2</sub>SO<sub>4</sub> over the entire range of  $x$  examined. While small ion - small ion interactions are not taken into account in the LL, or their contributions are assumed to be approximately same to both  $\gamma_{\pm}$  and  $\gamma'_{\pm}$ , their contribution  $\gamma_{\pm}^{ss}$  is involved in the observed  $\gamma_{\pm}$  values. The difference between observed values and  $(\gamma_{\pm})_{LL}$  will be reduced if the contribution  $\gamma_{\pm}^{ss}$  is taken into account.

When the electrostatic free energy is assumed to be the sum of two interactions, polyion - small ion and small ion - small ion, we have,  $\gamma_{\pm} = \gamma_{\pm}^{ps} \gamma_{\pm}^{ss}$ , where  $\gamma_{\pm}^{ps}$  represents the contribution from the polyion - small ion interaction. When accounts were taken of interactions between small ions, the LL would become applicable to finite concentrations of simple salt under low polyelectrolyte concentrations. Observed activity coefficients should be compared with  $(\gamma_{\pm}^{ss})(\gamma_{\pm})_{LL}$  rather than  $(\gamma_{\pm})_{LL}$ .

Wells<sup>40</sup> approximated  $\gamma_{\pm}^{ss}$  with  $\gamma'_{\pm}(m_s)$ , the mean activity coefficient in a salt solution at the salt concentration  $m_s$ . It is to be noted that the external salt concentration in the



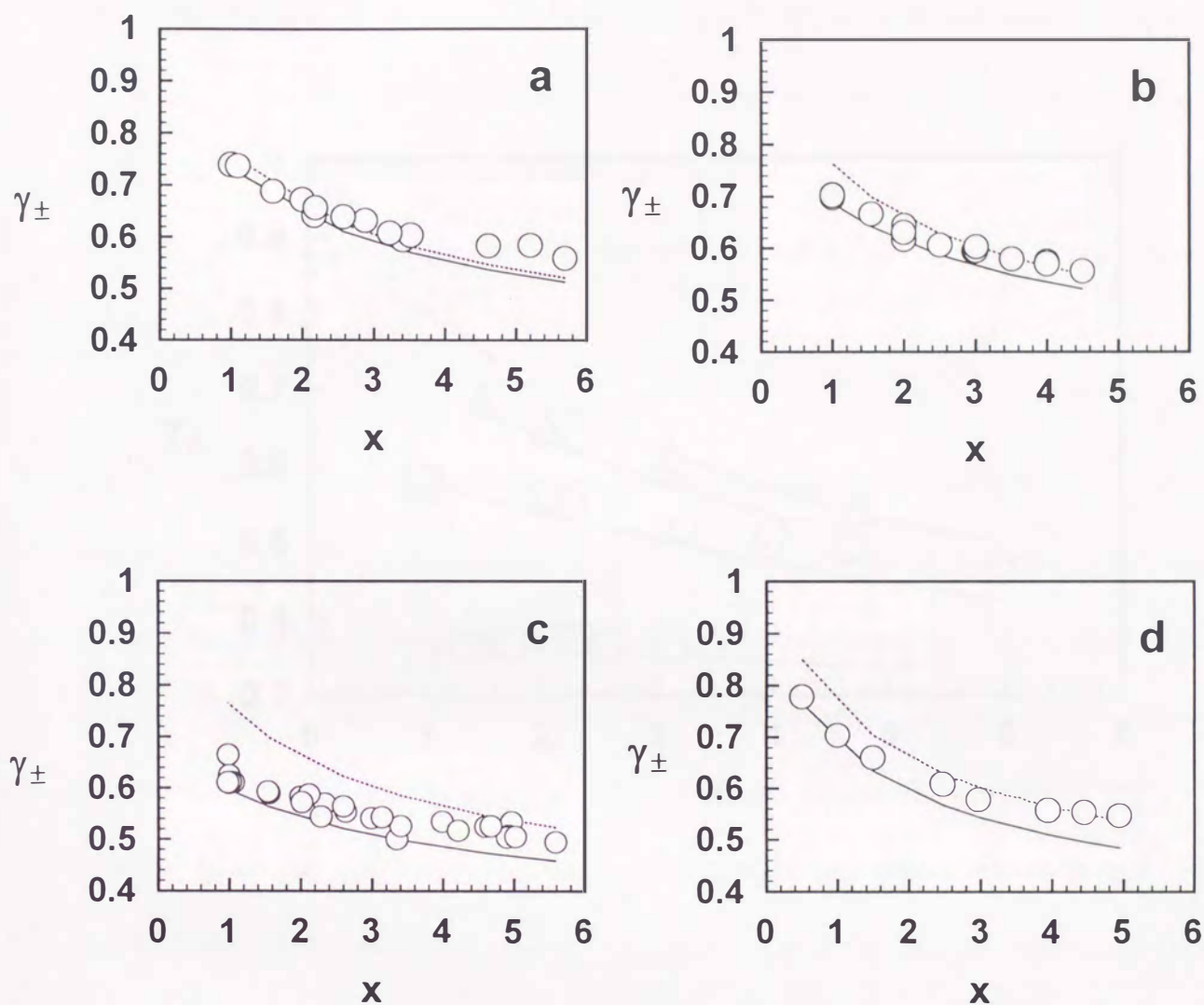


Figure 3-6-1. Mean activity coefficients of NaCl as a function of  $x$  in NaPA solutions. (a)  $m_e = 0.001 \text{ mol kg}^{-1}$ . (b)  $m_e = 0.01 \text{ mol kg}^{-1}$ . (c)  $m_e = 0.10 \text{ mol kg}^{-1}$ . (d)  $m_s = 0.01 \text{ mol kg}^{-1}$ . Dotted curves,  $(\gamma_{\pm})_{LL}$ , are predicted from eqn (3-6-10). Solid curves represent  $(\gamma_{\pm})_{LL}\gamma_{\pm}'(m_s)$ .

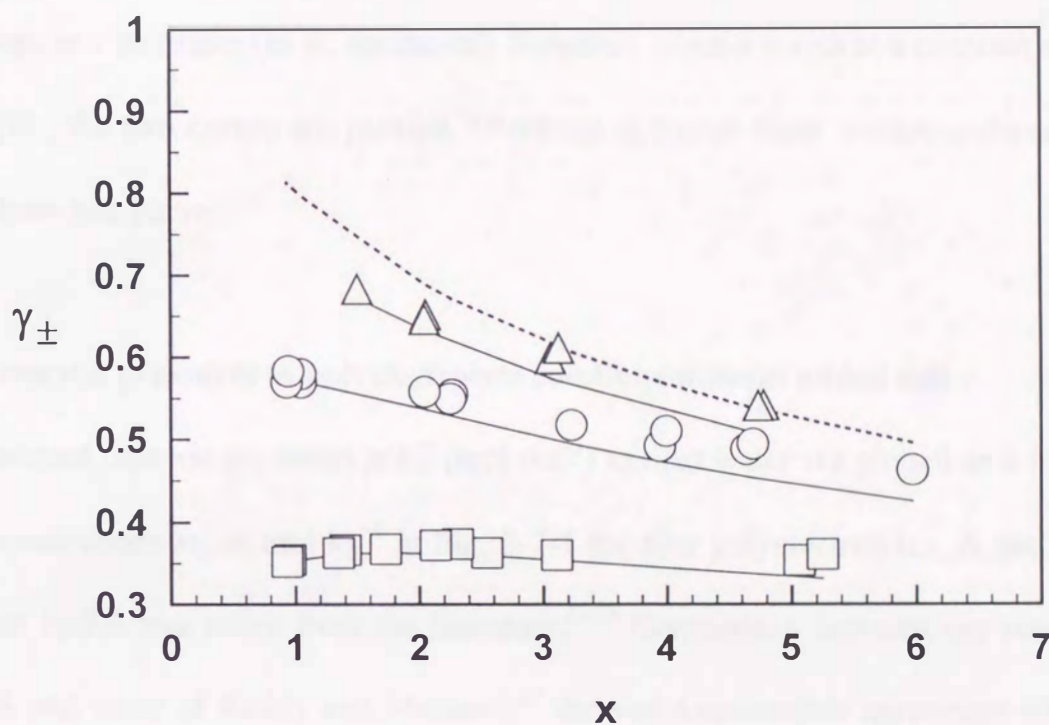


Figure 3-6-2. Mean activity coefficients of  $\text{Na}_2\text{SO}_4$  as a function of  $x$  in NaPA solutions. ( $\Delta$ )  $m_e = 0.001 \text{ mol kg}^{-1}$ ; ( $\circ$ )  $m_e = 0.01 \text{ mol kg}^{-1}$ ; ( $\square$ )  $m_e = 0.10 \text{ mol kg}^{-1}$ . The dotted curve,  $(\gamma_{\pm})_{LL}$ , is predicted from eqn (3-6-11). Solid curves represent  $(\gamma_{\pm})_{LL}\gamma_{\pm}'(m_s)$  for  $m_e = 0.001, 0.01$ , and  $0.10 \text{ mol kg}^{-1}$ , from top to bottom, respectively.



Donnan equilibrium is  $m_s'$ . The values  $(\gamma_{\pm})_{LL} \gamma'_{\pm}(m_s)$  are shown in Figs. 3-6-1 and 3-6-2 with solid lines. It is to be noted that the agreement between the observed  $\gamma_{\pm}$  and  $(\gamma_{\pm}^{ss})(\gamma_{\pm})_{LL}$  is greatly improved for  $\text{Na}_2\text{SO}_4$ . The two curves  $(\gamma_{\pm})_{LL}$  and  $(\gamma_{\pm})_{LL} \gamma'_{\pm}(m_s)$  tend to merge as  $x$  increases (as  $m_s$  decreases). However, when  $x$  varies at a constant  $m_s$ , Fig. 3-6-1(d), the two curves are parallel. Observed  $\gamma_{\pm}$  values show weaker  $x$ -dependence than those two curves.

### 3-7. Osmotic pressures in polyelectrolyte solutions without added salt

The reduced osmotic pressures  $\pi/RT$  ( $\text{mol dm}^{-3}$ ) against water are plotted as a function of concentrations  $m_e$  in  $\text{mol kg}^{-1}$  in Fig. 3-7-1 for four polyelectrolytes. A part of the data for NaPA was taken from the literature.<sup>23,29</sup> Comparison between our results on NaPSS and those of Reddy and Marinsky<sup>27</sup> showed a reasonable agreement although both the molecular weights of samples and the measuring method were different. The result evaluated by the LL is shown with a solid straight line of unit slope. The comparison between the observed values and the results from the LL shows that the counterion contribution is dominant in the osmotic pressures of polyelectrolyte solutions. The slopes of the plot of  $\log \pi/RT$  vs.  $\log m_e$  are around  $1.2 \pm 0.1$  in the semidilute range ( $0.2$ – $1.9 \text{ mol kg}^{-1}$ ) and about  $1.0 \pm 0.1$  in the dilute range ( $m_e < 0.03 \text{ mol kg}^{-1}$ ). The slope value in the semidilute regime is significantly greater than unity, which indicates that the osmotic coefficient increases with the concentration.

The practical osmotic coefficient,  $\phi_p$ , was calculated from the measured osmotic

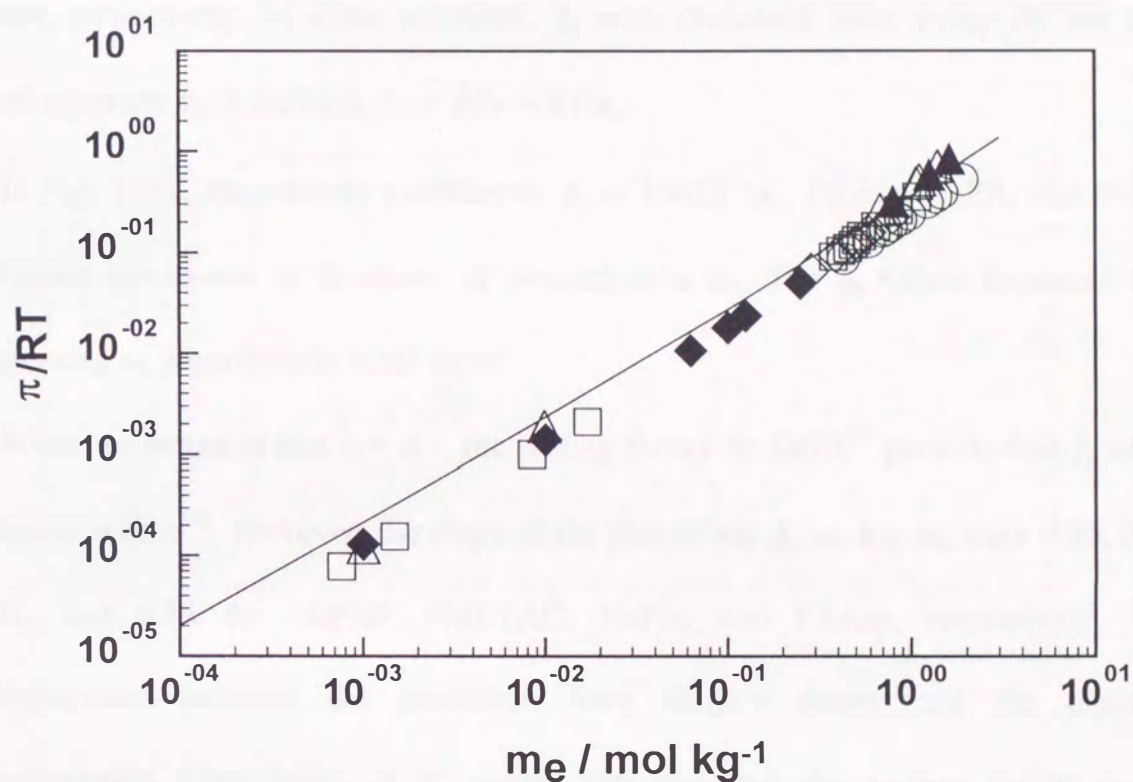


Figure 3-7-1. Reduced osmotic pressures  $\pi/RT$  in  $\text{mol dm}^{-3}$  of aqueous solutions for PAAm, PMETAC, NaPA, and NaPSS as a function of counterion concentrations  $m_e$  in  $\text{mol kg}^{-1}$ .  $\circ$ : PAAm;  $\square$ : PMETAC;  $\diamond$ : NaPA;  $\triangle$ : NaPSS;  $\blacklozenge$ : NaPA taken from the literature<sup>23,29</sup>;  $\blacktriangle$ : NaPSS taken from the literature<sup>27</sup>. The solid straight line represents the results from the LL.



pressures  $\pi$  according to the relation<sup>44</sup>

$$\phi_p = \frac{1000 \overline{V}_w^0}{m_e M_w} \frac{\pi}{RT} \quad (3-7-1)$$

where  $\overline{V}_w^0$  and  $M_w$  represent the partial molal volume of water and molecular weight of water, respectively. In dilute solutions,  $\phi_p$  were evaluated from  $\pi / \pi_{id}$ . By the van't Hoff equation  $\pi_{id}$  is defined,  $\pi_{id} = RTc \approx RTm_e$ .

In Fig. 3-7-2, the osmotic coefficients  $\phi_p$  of PMETAC, PAAm, NaPA, and NaPSS solutions are shown as functions of concentration  $m_e$ . The  $\phi_p$  values increased with increasing  $m_e$  significantly in all cases.

When we assumed that  $\pi = \phi_p c$ , the scaling theory by Odijk<sup>34</sup> predicts that  $\phi_p$  values increase with  $c^{1/8}$ . However, the slope of the plot of  $\log \phi_p$  vs.  $\log m_e$  were 0.36, 0.30, 0.21, and 0.18 for NaPSS, PMETAC, NaPA, and PAAm, respectively. This disagreement between the prediction from Odijk's theory and the observed concentration dependence of  $\phi_p$  values indicates that the scaling theory is not applicable to the osmotic pressures of polyelectrolyte solutions without added salt.

We can evaluate  $\phi_p$  on the basis of the P-B equation<sup>32</sup> modified by Marcus<sup>47</sup> as follows.

$$\phi_p = (1 - \beta^2) (1 - e^{-2\gamma}) / (2\xi) \quad (3-7-2)$$

where  $\beta$  is a constant defined by

$$\xi = (1 - \beta^2) / (1 + \beta \coth \beta \gamma) \quad (3-7-3)$$

The concentration parameter  $\gamma$  is connected with the polymer concentrations  $c$  in molarity.

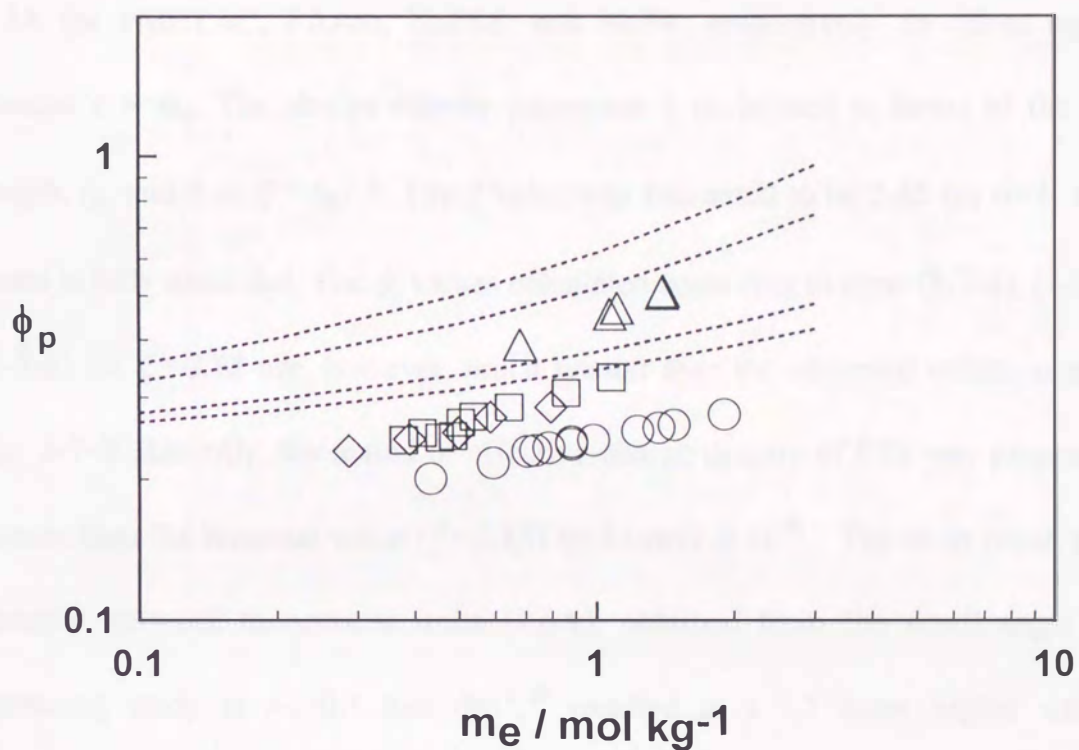


Figure 3-7-2. Osmotic coefficients,  $\phi_p$ , of aqueous solutions for PAAm, PMETAC, NaPA, and NaPSS as a function of counterion concentrations,  $m_e$ . Symbols are given in Fig. 3-7-1. Dotted curves represent osmotic coefficients estimated from eqns (3-7-2), (3-7-3), and (3-7-4) for  $\xi=2.85$  with  $\alpha=8$ , 6, 3 and 2.3, from top to bottom, respectively.



$$\gamma = (1/2) \ln (10^3 / \pi a^2 b N_A c) \quad (3-7-4)$$

where  $a$  and  $N_A$  are the radius of the polyion and Avogadro's number. Parameter  $a$  was estimated from the chemical structure of polymers and the values were 6, 3, 8, and 2.3 Å for PMETAC, PAAm, NaPSS, and NaPA, respectively. In dilute region, we assume  $c \approx m_e$ . The charge density parameter  $\xi$  is defined in terms of the Bjerrum length,  $l_B$ , and  $b$  as  $\xi = l_B / b$ . The  $\xi$  value was estimated to be 2.85 for  $\alpha=1$ , when the chain is fully extended. The  $\phi_p$  values calculated according to eqns (3-7-2), (3-7-3), and (3-7-4) for  $\xi=2.85$  are, however, much greater than the observed values as shown in Fig. 3-7-2. Recently, the actual or effective charge density of PSS was proposed to be greater than the nominal value ( $\xi=2.85$ ) by Maarel et al.<sup>48</sup> The short mean projected distance between monomeric units (1.6 Å), obtained from the small angle neutron scattering study at  $m_e=0.1 \text{ mol dm}^{-3}$ ,<sup>48</sup> resulted in a 1.7 times higher value of  $\xi$  compared to the value corresponding to a fully stretched chain conformation. From this result,  $\xi$  was estimated to be 4.5. The  $\phi_p$  values were calculated according to eqns (3-7-2), (3-7-3), and (3-7-4) for  $\xi=4.5$ .

The results from the Poisson-Boltzmann cylindrical cell model theory<sup>32</sup> with  $\xi=4.5$  are in fair agreement with the experimental results over the low and semidilute concentration regime, as shown in Fig. 3-7-3, except for NaPA.

The scaling theory predicts only the concentration dependence of osmotic pressures, that is, the slope of the plot of  $\log \pi/RT$  vs.  $\log m_e$ . On the other hand, the P-B approach has predicted the absolute values of the measured osmotic pressures. Judged

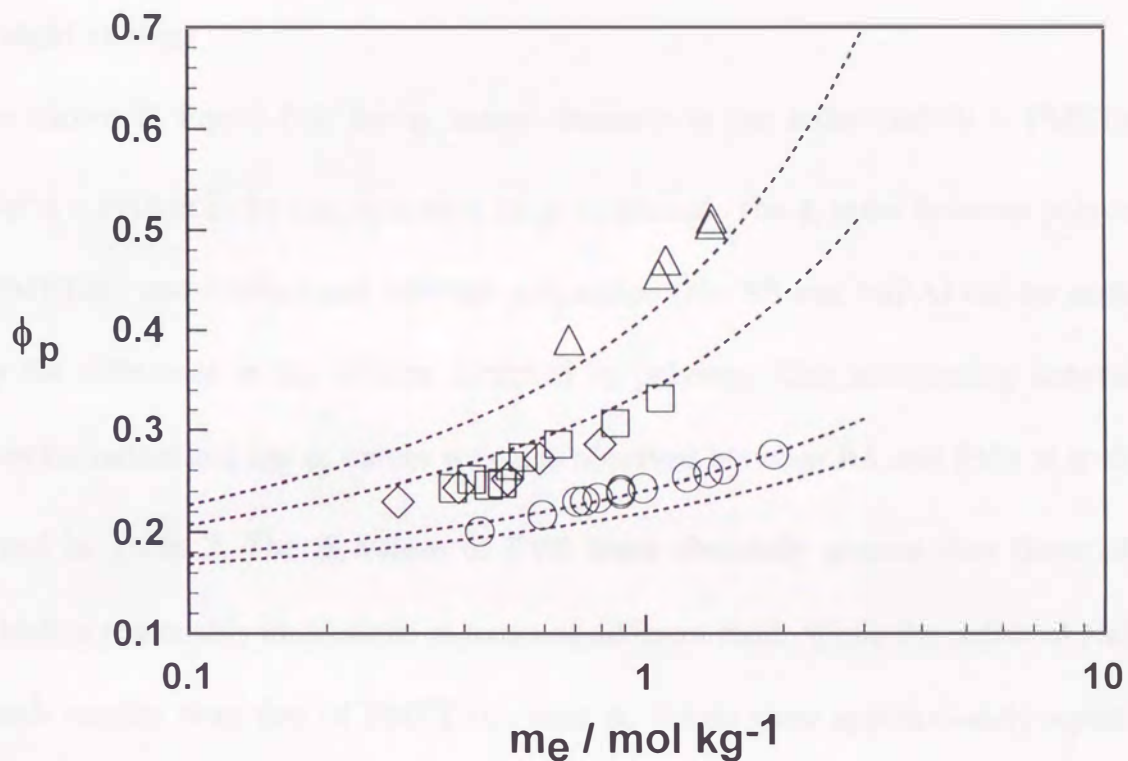


Figure 3-7-3. Osmotic coefficients,  $\phi_p$ , of aqueous solutions for PAAm, PMETAC, NaPA and NaPSS as a function of counterion concentrations,  $m_e$ . Symbols are given in Fig. 3-7-1. Dotted curves represent osmotic coefficients estimated from eqns (3-7-2), (3-7-3), and (3-7-4) for  $\zeta=4.5$  with  $\alpha=8, 6, 3$  and  $2.3$ , from top to bottom, respectively.



from this finding, we concluded that the osmotic pressures could be mainly estimated in terms of the counterion contribution.

### 3-8. Osmotic coefficients of polyelectrolyte solutions and their low-molecular weight analogs

As shown in Fig. 3-7-2, the  $\phi_p$  values decrease in the order NaPSS > PMETAC  $\approx$  NaPA > PAAm in the concentration range examined. The  $\phi_p$  order between polycations (PMETAC and PAAm) and between polyanions (NaPSS and NaPA) can be explained by the difference in the volume occupied by polyions. This relationship between the polyion radius and the  $\phi_p$  values was also observed between PA and PVB at  $\alpha=0.9$ , as listed in Table 2. The  $\phi_p$  values of PVB were obviously greater than those of PA, which is reasonably understood in terms of different radii. While the radius of NaPA is much smaller than that of PMETAC, their  $\phi_p$  values were approximately equal. The result might be attributed to the hydrated radii of counterions ( $\text{Cl}^- > \text{Na}^+$ ) and the degree of the interaction between ionic moiety and counterions.

In order to investigate the relation between the  $\phi_p$  values and the ionic moiety of the polyelectrolytes, the osmotic coefficients  $\phi$  were determined for some low-molecular weight electrolytes, such as methylamine hydrochloride (MAHCl), ethylamine hydrochloride (EAHCl), tetramethylammonium chloride (TMACl) and sodium ethansulfonate (NaES), which were chosen as monomer analogues to polyelectrolytes examined. Figure 3-8-1 shows the results. The molal osmotic coefficient for 1-1 electrolytes is related to the osmotic pressure by<sup>44</sup>

Table 2. Osmotic coefficients in polyelectrolyte solutions without added salt,  $\phi_p$ , at counterion concentrations,  $m_e$ , for partially neutralized polyvinylbenzoic acid (PVB) and polyacrylic acid (PA).

| PVB ( $\alpha=0.88$ )      |          | PA ( $\alpha=0.84$ )       |          |
|----------------------------|----------|----------------------------|----------|
| $m_e / \text{mol kg}^{-1}$ | $\phi_p$ | $m_e / \text{mol kg}^{-1}$ | $\phi_p$ |
| 0.316                      | 0.318    | 0.297                      | 0.270    |
| 0.363                      | 0.318    | 0.350                      | 0.276    |
| 0.435                      | 0.336    | 0.436                      | 0.282    |
| 0.453                      | 0.347    | 0.521                      | 0.293    |
| 0.527                      | 0.352    | 0.612                      | 0.299    |
| 0.555                      | 0.353    | 0.705                      | 0.308    |
| 0.622                      | 0.356    |                            |          |
| 0.766                      | 0.359    |                            |          |



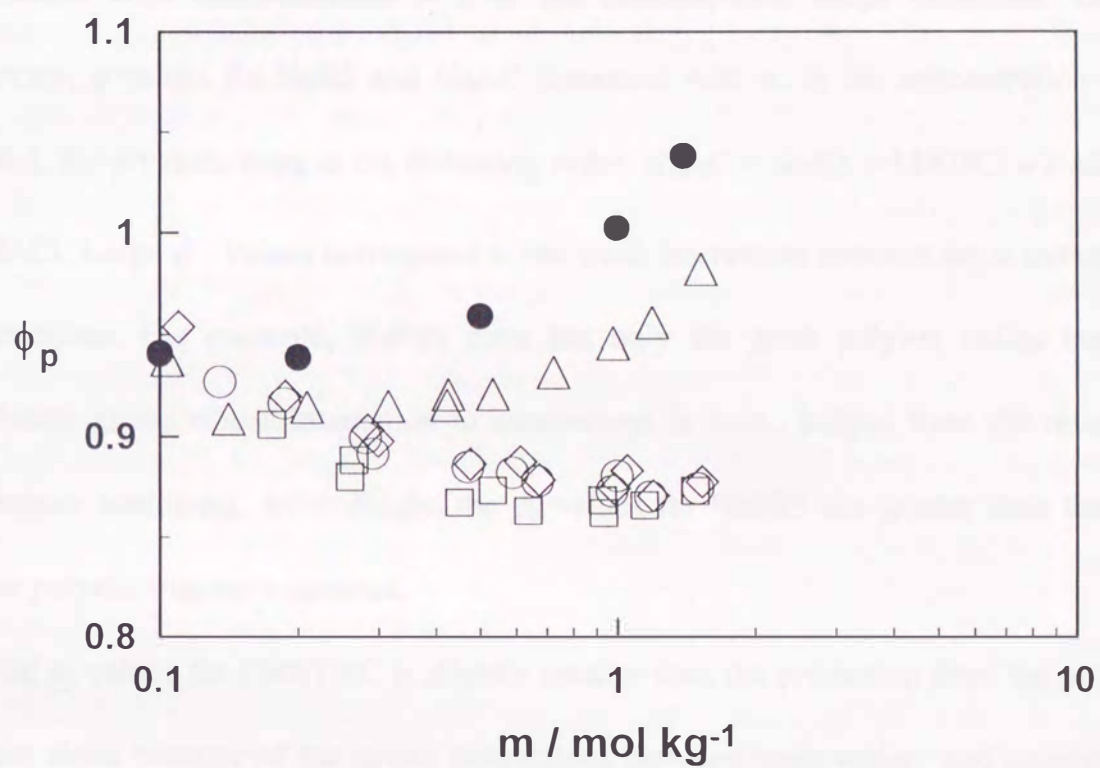


Figure 3-8-1. Osmotic coefficients of low molecular electrolytes for TMACl, MAHCl, EAHCl, NaES, and NaAC,  $\phi$ , as a function of concentrations  $m$  in mol kg<sup>-1</sup>. ○: TMACl; □: MAHCl; ◇: EAHCl; △: NaES; ●: NaAC taken from the literature<sup>49</sup>.

$$\phi = \frac{1000 \overline{V}_w^0}{2mM_w} \frac{\pi}{RT} \quad (3-8-1)$$

For sodium acetate (NaAC), the value in the literature<sup>49</sup> was used. For MAHCl, EAHCl and TMACl,  $\phi$  values were identical within the experimental error and decreased with concentrations  $m$  over the concentration range examined. On the contrary,  $\phi$  values for NaES and NaAC increased with  $m$ . In the concentration range  $m > 0.2$ , the  $\phi$  values were in the following order: NaAC > NaES > MAHCl  $\approx$  EAHCl  $\approx$  TMACl. Large  $\phi$  values correspond to the weak interaction between ionic moiety and counterions. For example, NaPSS have not only the great polyion radius but also sulfonate group whose interaction to counterions is weak, judged from the results of monomer analogues. Accordingly, the  $\phi_p$  values for NaPSS are greater than those of other polyelectrolytes examined.

The  $\phi_p$  values for PMETAC is slightly smaller than the prediction from the polymer radius alone because of the strong interactions between ionic moiety and counterions. On the other hand, the  $\phi_p$  values for NaPA is much greater than the prediction from the polymer radius alone due to weak interactions between carboxylate groups and sodium ions.



## 4. Discussion

### 4-1. Donnan equilibria in polyelectrolyte solutions

#### 4-1-1. Polyion species dependence of the parameter $k$

The agreement of  $\Gamma$  values between the observed and the predicted values from the LL was fair for NaPA–NaCl at a low  $m_e$  of 0.001 mol kg<sup>-1</sup>. For NaPSS and for NaPA at higher concentrations, deviations were observed from the LL. The following differences were found between NaPA and NaPSS. (i)  $\Gamma$  is greater for NaPSS than NaPA by *ca.* 1.2 - 1.6 times. This arises partly from the fact that  $\phi_p$  is greater for NaPSS than for NaPA. (ii) The concentration dependence of  $k$  and that of  $\phi_p$  for NaPSS are significantly greater than those for NaPA. However, these  $\Gamma$  values were well described by eqn (3-1-6) for 1-1 electrolytes in almost all cases examined, when  $k$  was allowed to vary with  $m_e$ . similarly, both  $k$  and  $\phi_p$  values on PMETAC were greater than those on PAAm at  $m_e=0.10$  mol kg<sup>-1</sup>.

The results for the Donnan equilibrium are agreement with those for the osmotic pressures of polyelectrolyte solutions without added salt. The Donnan distribution is also closely related to the polyion structures and the interaction between ionic groups and counterions.

#### 4-1-2. Co-ion species dependence of the parameter $k$

It is to be noted that  $k$  values were nearly identical for NaCl and Na<sub>2</sub>SO<sub>4</sub>, as found in the present study on both NaPA and NaPSS. The parameter  $k$  is mainly related to the interaction of counterions with polyion and this interaction is scarcely affected by the

presence of co-ions. Hence, this interaction is expected to be similar to that in salt-free solutions. The effect of different valences between the two kinds of co-ions only shows up in different expressions of  $\Gamma$  [eqns (3-1-6) and (3-5-5)], which essentially originate from the entropic effect associated with producing an uneven distribution of the neutral salt component.

The  $k$  value on NaNCS is also in good coincidence with those obtained for NaPSS at the same  $m_e$  on NaCl ( $k=0.28 \pm 0.03$ ) and Na<sub>2</sub>SO<sub>4</sub> ( $k=0.28 \pm 0.03$ ) within the experimental error. Thus, it is shown that  $k$  remains constant when the coion species varies from the one end to the other end of the Hofmeister series. This suggests that  $k$  is determined by the interaction of the polyelectrolyte with its counterions.

#### 4-1-3. The charge density dependence of the parameter $k$

The influence of the charge density on the Donnan equilibrium was previously studied by Vink<sup>21</sup> on hydroxyethyl cellulose substituted with carboxymethyl groups (HEC) and partially neutralized PA for a limited range. As to HEC, the deviation from the LL at the range  $1 < \xi < 5$  is smaller as the charge density becomes higher. This tendency is similar to our results on partially neutralized PA. The effect of decreasing  $\alpha$  is similar to but more accentuated than the effect of  $m_e$ : increase of  $\Gamma$  and its dependence on  $x$ .

The  $k$  values at  $m_e=0.01$  are plotted against the linear charge density  $\xi$  from the chemical structure in Fig. 4-1-1. An open circle represents the data by Vink for  $\xi=0.1$  ( $m_e=0.0027$ ). Figure 4-1-1 shows  $(\phi_p)_{LL}$  and  $(\phi_p)_{P-B}$  calculated by the P-B approach at



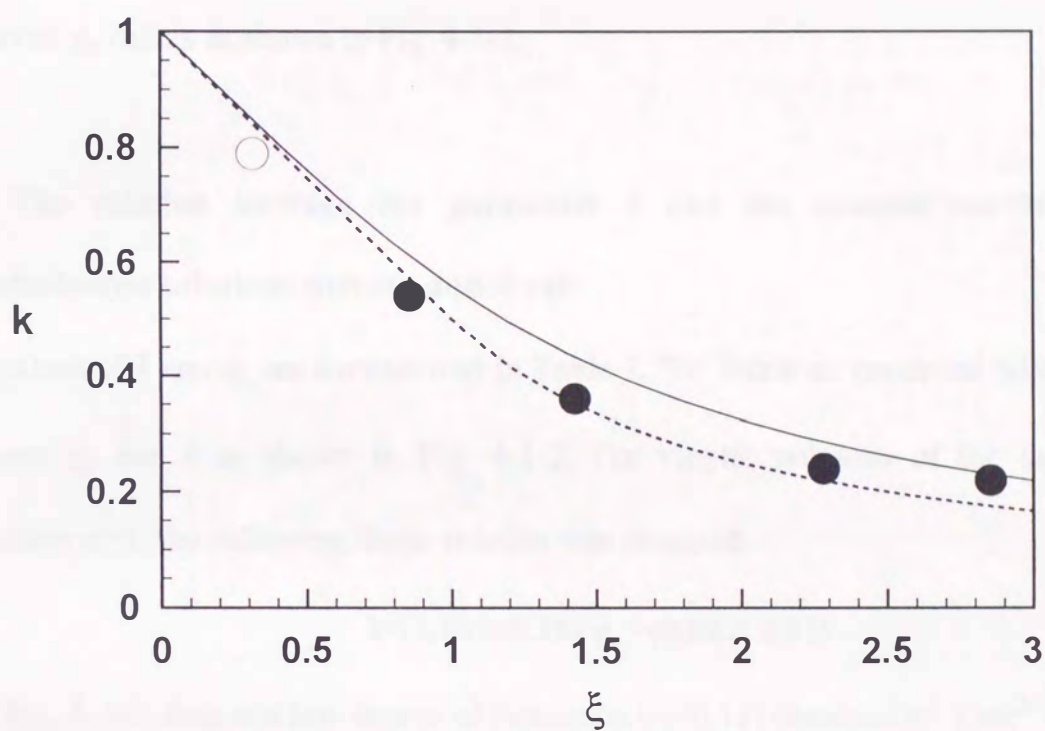


Figure 4-1-1. Relation between  $k$  and  $\xi$  for PA. The solid curve represents  $(\phi_p)_{P-B}$  and is calculated from eqns (3-7-2), (3-7-3), and (3-7-4) with  $\alpha=2.3\text{\AA}$ . The dotted curve represents  $(\phi_p)_{I.L.}$ . (○) work by Vink.<sup>21</sup> (●) this study.

$m_e=0.01$  as described in a later section. At this  $m_e$ , the  $k$  values are in fair agreements with  $(\phi_p)_{LL}$  except for  $\xi=2.85$  corresponding to  $\alpha=1.0$ . The agreement between  $(\phi_p)_{LL}$  and  $k$  becomes worse at high  $m_e$ , since  $(\phi_p)_{LL}$  is dependent of  $m_e$ . Although values of  $k$  are close to calculated values of  $\phi_p$ ,  $(\phi_p)_{LL}$  or  $(\phi_p)_{P-B}$ , they are considerably greater than observed  $\phi_p$  values as shown in Fig. 4-1-2.

#### 4-2. The relation between the parameter $k$ and the osmotic coefficient in polyelectrolyte solutions without added salt

The values of  $k$  and  $\phi_p$  are summarized in Table 1. We found an empirical relationship between  $\phi_p$  and  $k$  as shown in Fig. 4-1-2. For vinylic polyions of the degree of ionization  $\alpha=1$ , the following linear relation was obtained.

$$k=(1.09 \pm 0.18) \phi_p + (0.08 \pm 0.03) \quad (4-2-1)$$

In Fig. 4-1-2, data at a low degree of ionization ( $\alpha=0.11$ ) obtained by Vink<sup>21</sup> are also shown with filled diamonds. Clearly, the above linear relation cannot be extended to the range  $\phi_p > 0.3$ . For the range including larger  $\phi_p$  values, a quadratic relation is more appropriate. The following empirical relation was obtained in the range of  $\phi_p$  0.1-0.5.

$$k = 1.88 \phi_p^2 + 0.37 \phi_p + 0.14 \quad (4-2-2)$$

Above empirical equations, eqns (4-2-1) and (4-2-2), could be universally applied for different polymer concentrations, polymer species and coion species. We are able to estimate the  $k$  value satisfactorily if we know the  $\phi_p$  value and vice versa.

When both  $m_e$  and  $x$  approach zero, the additivity rule for the osmotic pressure is set



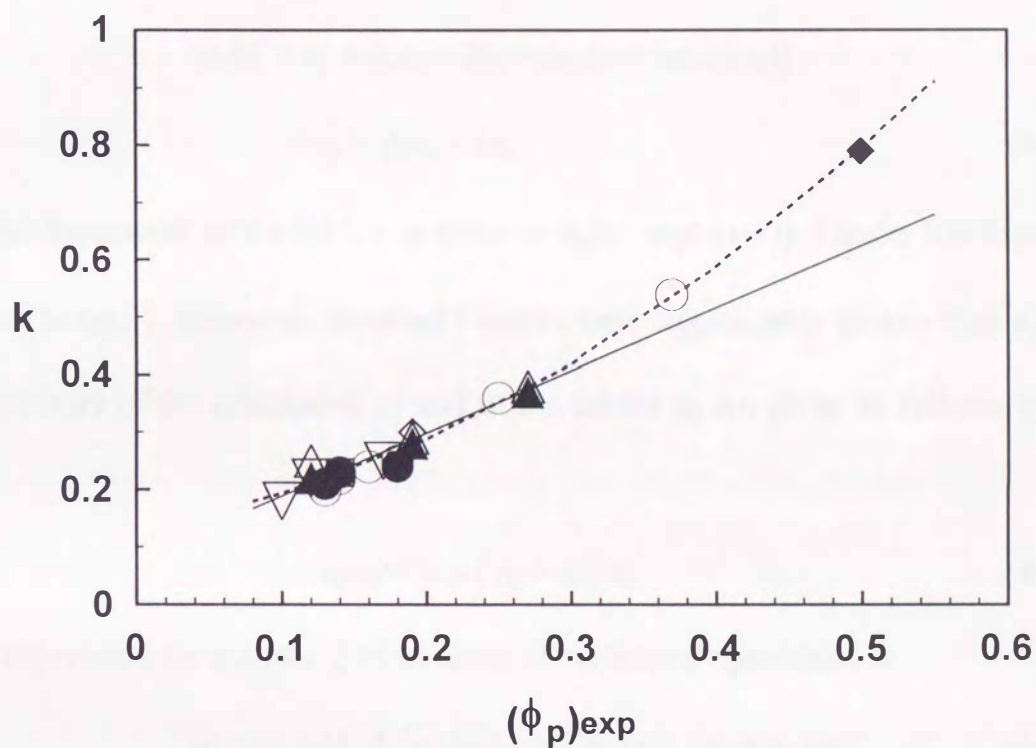


Figure 4-1-2. Relation between  $k$  and  $\phi_p$ . Some values of  $k$  and  $\phi_p$  are taken from the literature.<sup>23,27,29</sup> ( $\circ$ ) NaPA ( $\alpha=0.3, 0.5, 0.8, 1.0$ ) - NaCl; ( $\bullet$ ) NaPA ( $\alpha=1$ ) - Na<sub>2</sub>SO<sub>4</sub>; ( $\triangle$ ) NaPSS - NaCl; ( $\blacktriangle$ ) NaPSS - Na<sub>2</sub>SO<sub>4</sub>; ( $\nabla$ ) PMETAC - NaCl; ( $\square$ ) PAAm - NaCl; ( $\diamond$ ) NaPSS - NaNCS; ( $\blacklozenge$ ) NaPA ( $\alpha=0.1$ ) - NaCl.<sup>21</sup> The solid straight line represents eqn (4-2-1). The dotted curve represents eqn (4-2-2).

up. According to the additivity, the osmotic pressure were described by eqn (1-1).

Equation (1-1), in terms of parameter  $k$ , reduces to

$$\pi/RT = n_p + \phi_p n_e + 2n_s - 2[(kn_e + n_s)n_s]^{1/2} \quad (4-2-3)$$

When the fourth term on the rhs was expanded in powers of  $kn_e/n_s$ , eqn (4-2-3) is transformed as follows,

$$\begin{aligned} \pi/RT &= n_p + \phi_p n_e + 2n_s - 2n_s[1 + kn_e/(2n_s)] \\ &= n_p + \phi_p n_e - kn_e \end{aligned} \quad (4-2-4)$$

Within the framework of the LL<sup>1</sup>,  $\pi$  is given as  $n_p RT$  [eqn (1-7)]. Hence,  $k$  is expected to be equal to  $(\phi_p)_{LL}$ . However, obtained  $k$  values were significantly greater than  $\phi_p$ .

The activities of the counterion  $a_1$  and of the co-ion  $a_2$  are given as follows by the LL<sup>1</sup>

$$a_1 a_2 = \gamma_1 \gamma_2 (n_e + n_s) n_s \quad (4-2-5)$$

Another expression for  $a_1 a_2$  for  $\xi > 1$  in terms of "effective" quantities is

$$a_1 a_2 = \gamma_1(1, \xi^{-1} n_e) \gamma_2(1, \xi^{-1} n_e) (\xi^{-1} n_e + n_s) n_s \quad (4-2-6)$$

where  $\gamma_1(1, \xi^{-1} n_e)$  and  $\gamma_2(1, \xi^{-1} n_e)$  mean the activity coefficients for "effective" small ions (uncondensed counterion and co-ion) in polyelectrolyte solutions.

When the product  $\gamma_1(1, \xi^{-1} n_e) \gamma_2(1, \xi^{-1} n_e)$  is assumed to be unity for  $\xi > 1$ , we obtained that  $k = \xi^{-1}$ . Then, eqn (3-1-3) was reduced to the eqn (3-1-6). Obtained  $k$  values were, however, smaller than  $\xi^{-1}$  [ $=2(\phi_p)_{LL}$ ]. We might predict that  $(\phi_p)_{LL} < k < 2(\phi_p)_{LL}$ , from the above argument. The value of  $(\phi_p)_{LL}$  is 0.175 for  $\xi = 2.85$ , thus  $k$  values were between 0.175 and 0.35 in most cases.



Since  $k$  value is introduced as an empirical parameter, it is not easy to estimate it theoretically. The  $k$  values imply the fraction of unbound counterions, and they are expected to be greater than  $\phi_p$  due to the shielding with salts of electrostatic repulsion. In the LL, the Donnan salt distribution can be treated in the limit of negligible  $m_e$  and  $m_s'$ . Extension to finite or excess salt has been achieved by the P-B approach.<sup>3,4</sup> However, it is not easy to evaluate the Donnan distribution of salts under the excess polyelectrolyte condition by the P-B approach.

Contrary to the salt distribution problem, we can evaluate  $\phi_p$  on the basis of the P-B approach by eqn (3-7-2), (3-7-3), and (3-7-4), as described in section 3-7. Parameter  $a$  in eqn (3-7-4) was estimated from the chemical structure of polymers and the values were 2.3, 8, 6 and 3 Å for NaPA, NaPSS, PMETAC and PAAm, respectively. Charge density parameter  $\xi$  was estimated to be 2.85.

Values of  $k$  are plotted against  $(\phi_p)_{P-B}$  for  $\xi=2.85$  as shown in Fig. 4-2-1, where a straight line of unit slope is also shown. The  $k$  values are in good agreement with the  $(\phi_p)_{P-B}$  for NaPA and NaPSS. However, the agreement is not good for PMETAC, PAAm and partially neutralized PA. For PMETAC and PAAm, the  $(\phi_p)_{P-B}$  values coincided with  $k$  values when the parameters  $a$  were taken as 1.4 and 0.8, respectively, which are unrealistic. In the case of partially neutralized PA, the deviation from the relation  $k = (\phi_p)_{P-B}$  is already evident in Fig. 4-1-1. When the charge density is small, the chain might easily bend. Therefore, the effective charge density might be higher than that from the chemical structure.<sup>48</sup>

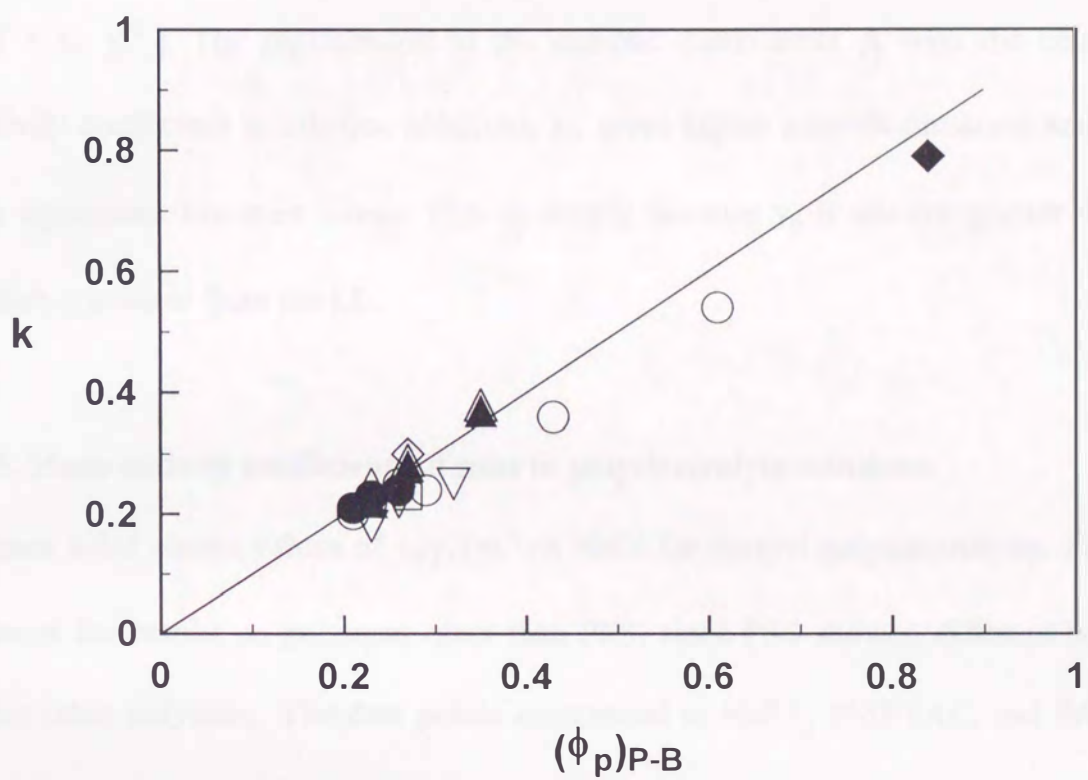


Figure 4-2-1. Relation between  $k$  and  $(\phi_p)_{P-B}$ . Symbols as given in Fig. 4-1-2. The solid straight line with a slope equal to unity is shown.



The above results provide us with an empirical way to estimate the Donnan osmotic pressure  $\pi_D$  by the following procedures under the condition  $1 < x < 6$ . [1] Set  $k = (\phi_p)_{P-B}$  or  $(\phi_p)_{LL}$ . [2]  $\phi_p$  is evaluated from eqn (4-2-1) or (4-2-2) and the  $k$  value obtained by procedure [1]. [3] From the additivity of the osmotic pressure,  $\pi_D = \phi_p m_e - 2km_e / [1 + (1 + kx)^{1/2}]$ . The replacement of the osmotic coefficients  $\phi_p$  with the counterion activity coefficient in salt-free solutions,  $\gamma_p$ , gives higher osmotic pressures and hence the agreement becomes worse. This is simply because  $\gamma_p$  is always greater than  $\phi_p$ , which is evident from the LL.

#### 4-3. Mean activity coefficients of salts in polyelectrolyte solutions

Figure 4-3-1 shows values of  $\gamma_{\pm}/\gamma'_{\pm}(m_s)$  of NaCl for several polyelectrolytes. First, we discuss the results on polymers other than PSS, since PSS showed different behavior from other polymers. The data points correspond to NaPA, PMETAC, and PAAm at different  $m_e$  and  $m_s$ . Although scattered, different values of  $\gamma_{\pm}$  obtained at different  $m_e$  converge to values within a narrow width after corrected for  $\gamma_{\pm}^{ss}$ . The value  $\gamma_{\pm}/\gamma'_{\pm}(m_s)$  is regarded as a good approximation to  $\gamma_{\pm}^{ps}$  and hence compared with  $(\gamma_{\pm})_{LL}$  given by a dotted curve. The values  $\gamma_{\pm}/\gamma'_{\pm}(m_s)$  show systematic upward deviation from  $(\gamma_{\pm})_{LL}$  by ca. 0.02 at small  $x$ , and the upward deviation is more significant at  $x$  greater than 5. Large  $x$  values correspond to small  $m_s$  except for the data represented with filled symbols. (The latter was obtained at constant  $m_s$ .) The upward deviation indicates  $\gamma_{\pm}^{ss} > \gamma'_{\pm}$ . It is reasonable that at small  $m_s$ ,  $\gamma_{\pm}^{ss}$  is closer to unity and hence greater than  $\gamma'_{\pm}(m_s)$  because

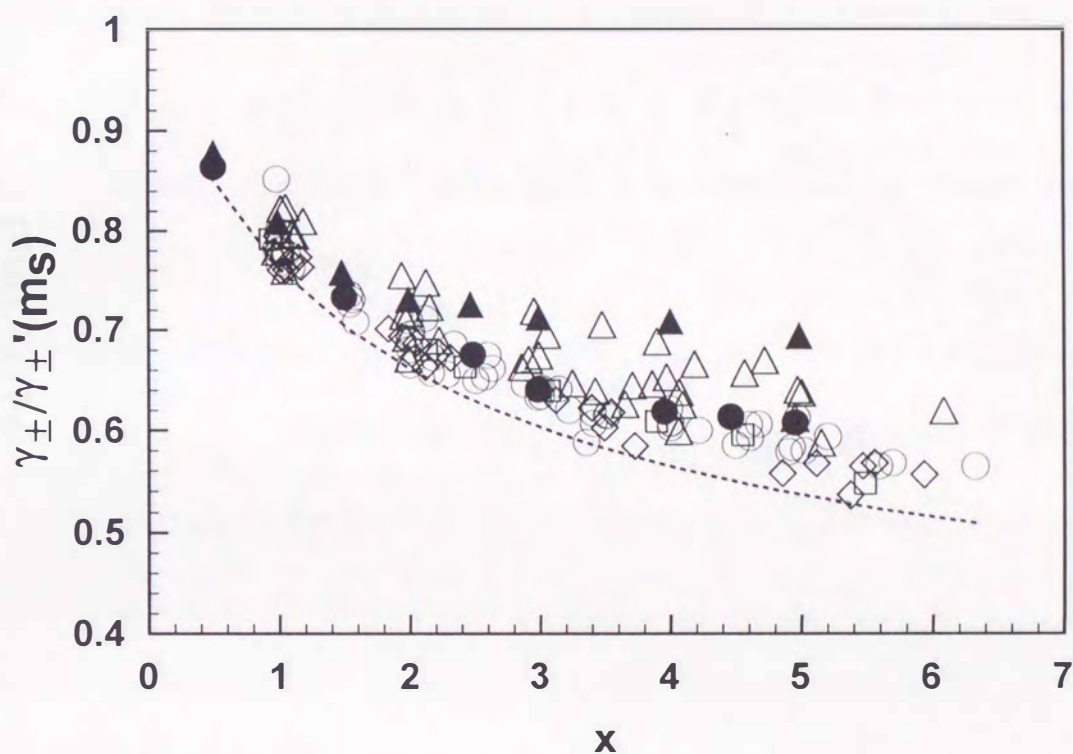


Figure 4-3-1. Plots of  $\gamma_{\pm} / \gamma'_{\pm} (m_s)$  of NaCl against  $x$  for NaPA, NaPSS, PMETAC, and PAAm. ( $\circ$ ) NaPA at constant  $m_e$ ; ( $\bullet$ ) NaPA at constant  $m_s$ ; ( $\triangle$ ) NaPSS at constant  $m_e$ ; ( $\blacktriangle$ ) NaPSS at constant  $m_s$ ; ( $\square$ ) PMETAC at constant  $m_e$ ; ( $\diamond$ ) PAAm at constant  $m_e$ . The dotted curve,  $(\gamma_{\pm})_{LL}$ , is predicted from eqn (3-6-10).



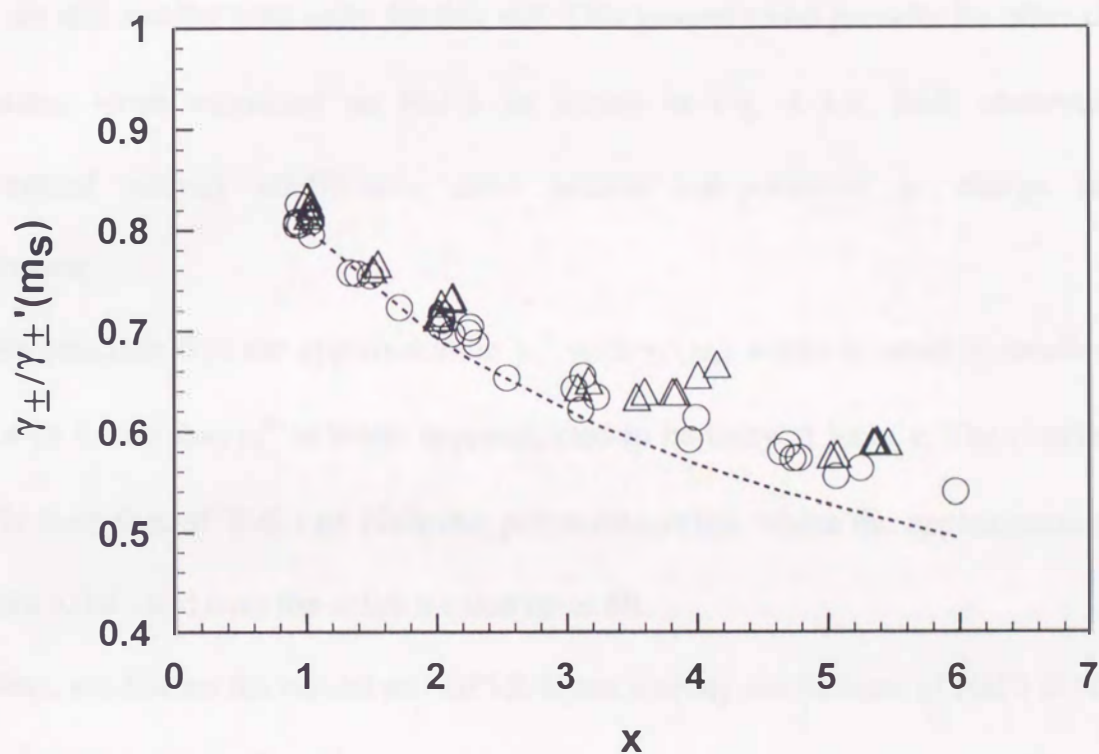


Figure 4-3-2. Plots of  $\gamma_{\pm} / \gamma'_{\pm} (m_s)$  of  $\text{Na}_2\text{SO}_4$  against  $x$  for NaPA and NaPSS.  $\circ$ : NaPA at constant  $m_e$ ;  $\triangle$ : NaPSS at constant  $m_e$ . The dotted curve,  $(\gamma_{\pm})_{LL}$ , is predicted from eqn (3-6-11).

of the strong influence of the polyion electric field. In other words, the superposition approximation is not good at small  $m_s$ . In the case of  $\text{Na}_2\text{SO}_4$  shown in Fig. 4-3-2, the agreement is fair over the entire range of  $x$  for both NaPA and NaPSS, suggesting that  $\gamma_{\pm}^{\text{ss}}$  are still smaller than unity for this salt. This general trend prevails for other charge densities when examined on NaPA as shown in Fig. 4-3-3. Both observed and theoretical activity coefficients show weaker  $x$ -dependence as charge density decreases.

We conclude that the approximation  $\gamma_{\pm}^{\text{ss}}$  with  $\gamma_{\pm}'(m_s)$  works at small  $x$ , smaller than *ca.* 4 or 5, and that  $\gamma_{\pm}^{\text{ss}}$  is better approximated to be unity at large  $x$ . The conclusions differ from that of Wells on NaBr-Na polymethacrylate where the approximation was shown to be valid over the entire  $x$  value up to 60.

Next, we discuss the results on NaPSS. Mean activity coefficients of NaCl in NaPSS solutions are greater than those of other polyelectrolytes examined as judged from Fig. 4-3-1. Similar results were obtained for both NaNCS and NaCl as shown in Fig. 4-3-4. Activity coefficients of  $\text{Na}_2\text{SO}_4$  are also slightly greater than those of NaPA (Fig. 4-3-2). The peculiar behavior of PSS is thus commonly seen with different co-ions extending over a wide range of the Hofmeister series. This behavior of  $\gamma_{\pm}$  is a consequence of the previous result that the salt exclusion in NaPSS solution is significantly greater than those of other polyelectrolytes examined. Also, osmotic coefficients for NaPSS in salt-free polyelectrolyte solution have been known to be greater than those for other polyelectrolytes. These imply that the interaction between  $\text{PSS}^-$  ion with counterions is weaker than those of other polymers examined. A



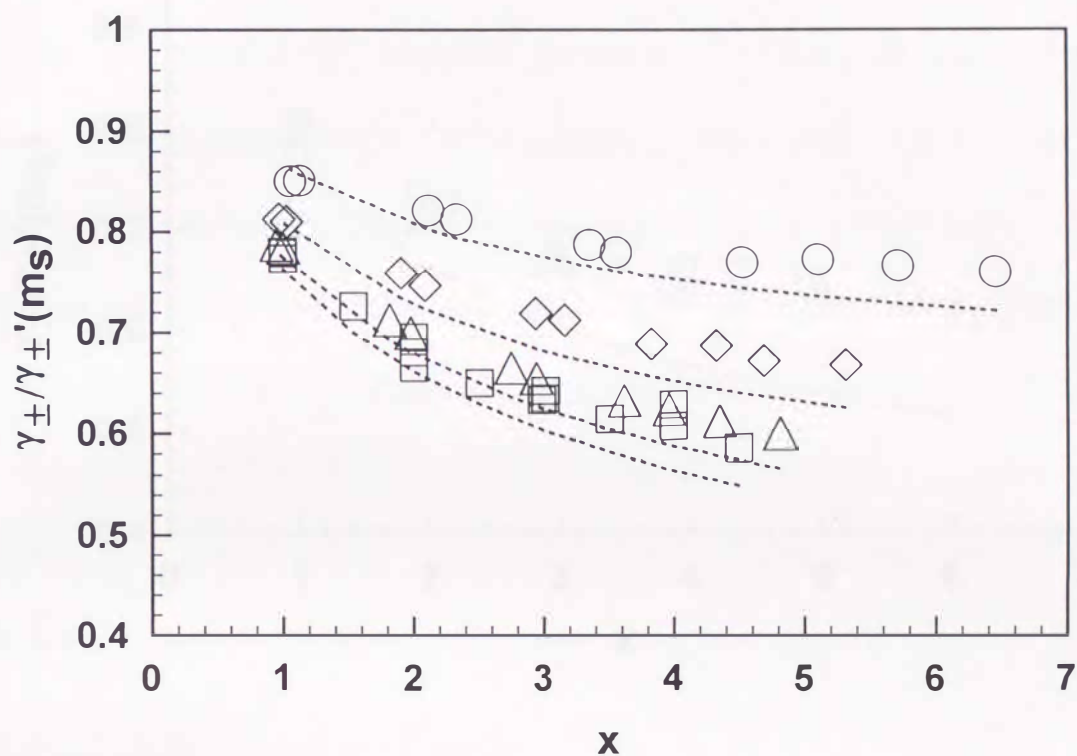


Figure 4-3-3. Plots of  $\gamma_{\pm} / \gamma'_{\pm}(m_s)$  of NaCl against  $x$  for partially neutralized PA at  $m_e = 0.01 \text{ mol kg}^{-1}$ . ( $\circ$ )  $\alpha = 0.3$ ; ( $\diamond$ )  $\alpha = 0.5$ ; ( $\triangle$ )  $\alpha = 0.8$ ; ( $\square$ )  $\alpha = 1.0$ . Dotted curves represent  $(\gamma_{\pm})_{LL}$  predicted from eqn (3-6-10) for  $\alpha = 0.3, 0.5, 0.8$ , and  $1.0$ , from top to bottom, respectively.

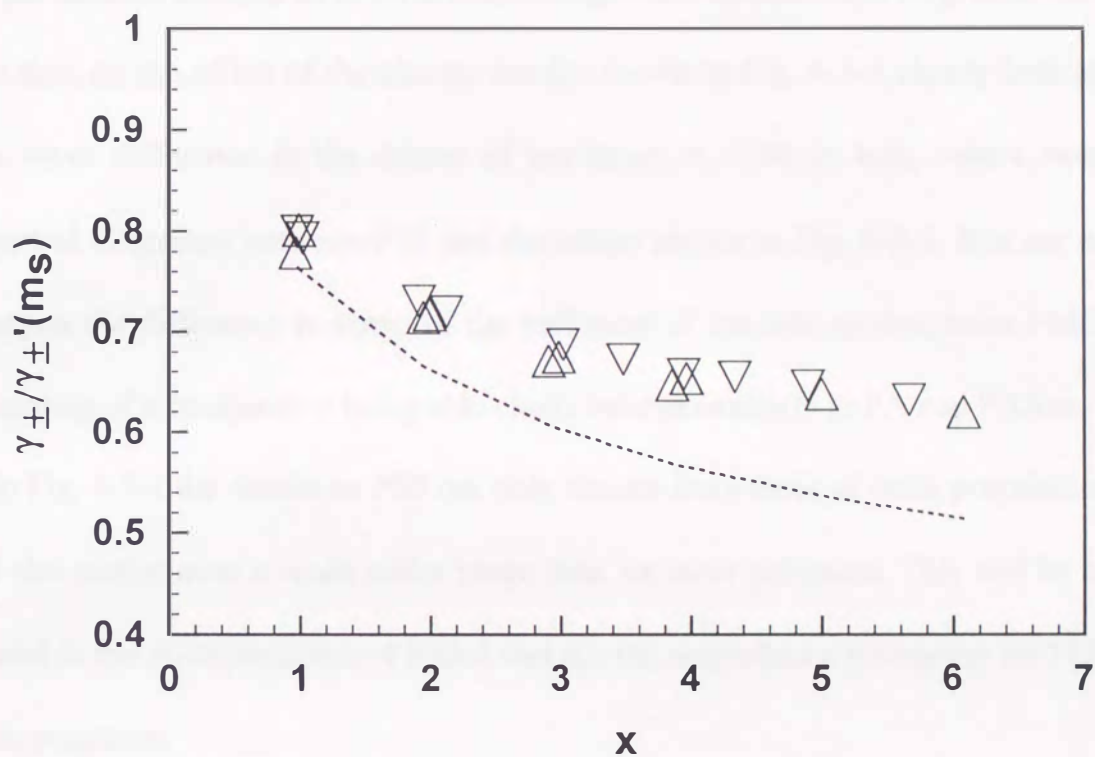


Figure 4-3-4. Plots of  $\gamma_{\pm} / \gamma'_{\pm}(m_s)$  of NaCl and NaNCS against  $x$  for NaPSS at  $m_e = 0.01 \text{ mol kg}^{-1}$ . ( $\Delta$ ) NaCl; ( $\nabla$ ) NaNCS. The dotted curve,  $(\gamma_{\pm})_{LL}$ , is predicted from eqn (3-6-10).



possibility that our PSS sample has lower charge densities was found to be not the case. The amounts of ionized groups in the samples of known dry weights determined with  $H^+$  ion titration allowed us to conclude the degree of sulfonation to be greater than 0.94. The data on the effect of the charge density shown in Fig. 4-3-3 clearly indicate that this small difference in the degree of ionization  $\alpha$ , 0.06 or less, cannot cause the observed difference between PSS and the others shown in Fig. 4-3-1. It is not easy to interpret the difference in terms of the bulkiness of the side chains, since PMETAC, consisting of a comparably bulky side chain, behave similarly to PA and PAAm.

In Fig. 4-3-1 the results on PSS not only deviate from those of other polyelectrolytes, but also scatter over a much wider range than for other polymers. This will be closely related to the  $m_e$ -dependence of both  $k$  and  $\phi_p$ : the dependence is stronger for PSS than other polymers.

#### 4-4. Osmotic coefficients in polyelectrolyte solutions without added salt

We put the charge density parameter  $\xi=4.5$  for the estimation of the osmotic coefficients. Although this value of  $\xi$  is much greater than the value corresponding to a fully stretched chain conformation,  $(\phi_p)_{PB}$  values for  $\xi=4.5$  are in good agreement with the observed values. The dielectric constant in the polymer domain is assumed to be equal to that of water for  $\xi=2.85$ . However, there is good reason to believe that the dielectric constant in the vicinity of the polyion is lower, owing to the hydration of ions, which would mean that  $\epsilon_{\text{effective}} < \epsilon_{\text{water}}$ .<sup>23</sup> Hence, the observed osmotic coefficients are lower than calculated values for  $\xi=2.85$ . On the other hand,  $(\phi_p)_{PB}$  values calculate

for  $\xi=2.85$  are in good agreement with the parameter  $k$  describing the Donnan salt distribution.

We have shown that the  $k$  value is not equal to the observed  $\phi_p$  value although these two quantities are closely related. The difference between the parameter  $k$  and the observed  $\phi_p$  value might correspond to possible different local dielectric constants in the vicinity of the polymer skeleton between the case with added salt and that without added salt. Or, the local dielectric constant has less influence in the Donnan equilibria with added salts than the osmotic coefficients without added salts.

## 5. Conclusion

- (1) The Alexandrowicz-Vink (A-V) equation is valid for describing the Donnan distribution of salts in the range of polyion excess ( $1 < x < 5$ ).
- (2) The parameter in the A-V equation,  $k$ , does not depend on coion species.
- (3) An empirical unique relation between  $k$  and  $\phi_p$  (osmotic coefficients in salt-free polyelectrolyte solutions) was found:  $k = (1.09 \pm 0.18) \phi_p + (0.08 \pm 0.03)$  for  $0.1 < \phi_p < 0.3$ ;  $k = 1.88 \phi_p^2 + 0.37 \phi_p + 0.14$  for  $0.1 < \phi_p < 0.5$ .
- (4) PSS<sup>-</sup> ions behave differently from other polyions examined. Both  $k$  and  $\phi_p$  are greater in the case of PSS than for others.
- (5) Osmotic pressures in polyelectrolyte solutions without added salt increased with polymer concentrations  $m_e$  as  $m_e^{1.2 \pm 0.1}$ . The P-B approach gave fair predictions of the absolute values of the osmotic pressures. We conclude that the osmotic

pressures can be estimated in terms of the counterion contribution, as Dobrynin et al. pointed out.<sup>37</sup>

- (6) The  $\phi_p$  values were strongly dependent of the chemical structures of polyelectrolyte.

Both the polyion radius and the degree of the ionic moiety-counterion interaction are significant on the estimation of  $\phi_p$  values.



## Appendix

### Overview about theoretical and experimental investigation of the electrostatic persistence length of flexible polyelectrolytes

In the present study, the regime where we measured the osmotic pressures with the vapor pressure osmometer corresponded to the semidilute solutions on the basis of the phase diagram of vinyl polyelectrolyte solutions given by Kaji et al.<sup>50</sup> with the degree of polymerization and the concentration. This diagram was constructed, based on the theories of de Gennes *et al.*<sup>33</sup> and Odijk<sup>38</sup>, and the electrostatic persistence length calculated by Le Bret<sup>51</sup>.

The semidilute region was separated into three regimes, called isotropic, transition, and lattice in the order of decreasing concentration, while the dilute region is divided into two regimes, termed order and disorder. The isotropic and lattice regimes are depicted by de Gennes *et al.*, and the transition regime is described by Odijk<sup>38</sup>.

The order and disorder regime are distinguished from each other by whether an intermolecular single correlation due to the electrostatic repulsive force exists or not.

#### A-1. Theoretical investigation of the electrostatic persistence length of flexible polyelectrolytes

The persistence length  $L_p$  was assumed to be the sum of two contributions  $L_0$  and  $L_e$

$$L_p = L_0 + L_e \quad (\text{A-1-1})$$

where  $L_0$  is the intrinsic persistence length of the corresponding neutral polymer and  $L_e$

is the electrostatic persistence length due to the charges on the polymer. Skolnick and Fixman<sup>35</sup>, and Odijk et al.,<sup>34,52,53</sup> (SOF) calculated the increase in free energy due to electrostatic interaction and elastic bending energy for a slightly bent configuration with reference to a rodlike configuration. This was used to analyze the effect of the charges on the chain stiffness, leading naturally to the crucial concept of  $L_e$ . The electrostatic contribution to the chain stiffness due to the departure from the rod limit allows for the calculation of  $L_e$  which in the limit of  $\kappa L_r \gg 1$  is given by

$$L_e = l_B/4\kappa^2 b^2 \sim I^{-1} \quad (\xi < 1) \quad \text{and} \quad L_e = 1/4\kappa^2 l_B \sim I^{-1} \quad (\xi > 1) \quad (\text{A-1-2})$$

due to  $\kappa^2 = 8\pi l_B n$ , where  $L_r$  is the contour length of the polyelectrolyte, and  $n$  is the total concentration of the counterions assumed to be monovalent.

In the theories of Fixman<sup>54</sup> and of Le Bret<sup>51</sup>,  $L_e$  was calculated by solving numerically the Poisson–Boltzmann equation for toroidal polymer. Particularly in the high salt limit, numerical calculations of Le Bret and Fixman yield a much weaker ionic strength dependence of  $L_e$  but merge into the SFO results at intermediate ionic strength. For the high ionic strength ( $I > 10^{-2}$  M),  $L_e \sim I^{-1/2}$ , and for the low ionic strength ( $I < 10^{-2}$  M),  $L_e \sim I^{-1}$ .

Koyama evaluated  $L_p$  of wormlike polyelectrolyte chains in the salt-free semidilute solution.<sup>55</sup> Koyama's theory contained the flexibility of polymer chain as a parameter  $f$ . When the  $f$  value was given (0.8–0.9) and the monomer concentration  $n_e$  was assumed to be  $2I/0.35$ , we obtained the relation that  $L_e \sim I^{-1/2}$  ( $L_0 \ll L_e$ ).

J. L. Barrat and J. F. Joanny<sup>56</sup> took into account the effect of fluctuations in the chain



configuration, and found that  $L_e$  was proportional to the Debye length  $\kappa^{-1}$ ;  $L_e \sim \kappa^{-1} \sim I^{-1/2}$ .

Forster et al.,<sup>57</sup> calculated numerically  $L_e$  values based on Koyama's probability density function for wormlike chains as a function of the ionic strength.<sup>58</sup> The theoretical values were qualitatively in agreement with the experimental values obtained from the static and the dynamic light scattering measurements, but yield to high  $L_e$ , quantitatively.

## **A-2. Experimental investigation of the electrostatic persistence length of flexible polyelectrolytes**

The experimental results reported for the vinyl polymer showed that  $L_e \sim I^{-1/2}$  for the high ionic strength ( $I > 10^{-3}$  mol dm<sup>-3</sup>), and  $L_e$  values level off and deviate from the these predictions for  $I < 10^{-3}$  mol dm<sup>-3</sup>. Some recent experimental studies of the estimation for the electrostatic persistence length of the polyelectrolyte are summarized below.

### **A-2-1. Static and dynamic light scattering measurement**

Schmidt estimated the  $L_p$  value from the mean square radius of gyration obtained from the static light scattering (SLS) measurement in the following procedure. An analytical expression is obtained for the radius of gyration for polydisperse, wormlike chains when a Schulz–Zimm type distribution is assumed for the chain length. The weight distribution  $W(L)$  is given by



$$W(L_r) = \frac{L_r^m}{m!} y^{m+1} \exp(-yL_r) \quad (\text{A-2-1-1})$$

with  $y = (m + 1)/L_w$  and  $L_w$  the weight-average contour length of the polymer. The experimentally obtained quantity is the z-average mean square radius of gyration,  $\langle S^2 \rangle_z$ , which in terms of the contour length  $L_r$  is defined as

$$\langle S^2 \rangle_z = \int_0^L W(L_r) L_r \langle S^2 \rangle dL_r / \int_0^L W(L_r) L_r dL_r \quad (\text{A-2-1-2})$$

The unperturbed mean-square radius of gyration of a monodisperse, wormlike chain was first calculated by Benoit and Doty<sup>59</sup>

$$\langle S^2 \rangle_0 = L_r L_p / 3 - L_p^2 + 2L_p^3 / L_r - 2(L_p^4 / L_r^2) [1 - \exp(-L_r / L_p)] \quad (\text{A-2-1-3})$$

When the perturbed mean-square radius of gyration,  $\langle S^2 \rangle$ , is substituted for  $\langle S^2 \rangle_0$  in eqn (A-3-1-3), the substitution of eqn (A-2-1-3) into eqn (A-2-1-2) yields

$$\langle S^2 \rangle_z = (m + 2)L_p / (3y) - L_p^2 + 2yL_p^3 / (m + 1) - 2L_p^4 / [m(m + 1)] [y^2 - y^{m+2} / (y + 1/L_p)^m] \quad (\text{A-2-1-4})$$

Schmidt also evaluated  $L_p$  from the hydrodynamic radius. According to Stokes and Einstein, a hydrodynamic radius can be obtained from the z-average translational diffusion coefficient,  $D_z$ , which is evaluated from the intensity time correlation function in the dynamic light scattering (DLS) measurement.

$$\langle 1/R_H \rangle_z^{-1} = kT / (6\pi \eta_0 D_z) \quad (\text{A-2-1-5})$$

with the solvent viscosity  $\eta_0$ . The hydrodynamic radius for polydisperse chains is given by

$$\langle 1/R_H \rangle_z^{-1} = \left[ \int_0^L W(L_r) L_r R_H^{-1} dL_r / \int_0^L W(L_r) L_r dL_r \right]^{-1} \quad (\text{A-2-1-6})$$

Schmidt et al. followed the procedure where Koyama's<sup>58</sup> expression for the segment distribution function was used, which yields

$$R_H = [(1/L_p L_r^2) \int_0^{L_r} (L_r - s) B^{-1} \text{erf}(B/2A) ds]^{-1} \quad (\text{A-2-1-7})$$

with  $A^2 = \langle R^2 \rangle (1-\eta)/6$  and  $B = \eta \langle R^2 \rangle$ , where  $2\eta^2 = 5-3 \langle R^4 \rangle / \langle R^2 \rangle^2$ .  $\langle R^n \rangle$  denotes the  $n$ th moment of the Kratky–Porod distribution function. Inserting eqn (A-2-1-7) into eqn (A-2-1-6), they obtained a double integral, which had been solved numerically with the IMSL library program DCADRE.

Schmidt<sup>60</sup> [for poly( $\gamma$ -benzylglutamate) in dimethylformamide] and Forster et al.<sup>57</sup> [for poly(2-vinylpyridiniumbenzyl bromide)] evaluated the total persistence length  $L_p$  on the basis of the Kratky–Porod wormlike chain model as described above. Forster et al.<sup>57</sup> calculated  $L_e$  as  $L_p - L_0$ , where  $L_0$  was approximated to be 15A, which is the value derived by Tricot<sup>61</sup> for vinylic polyelectrolytes.

Reed et al. estimated apparent persistence length  $L_p'$  from the angular intensity of light scattered by solutions successively titrated with salt. The term “apparent” is used because no account is taken of excluded volume. Operationally,  $L_p'$  is the value of  $L_p$  found from eqn (A-2-1-3) for a given contour length when  $\langle S^2 \rangle_0$  is replaced by the measured perturbed  $\langle S^2 \rangle$ .

The assumptions made in estimating the apparent persistence lengths are the following:

(1) The polymers scatter like ideal Gaussian chains

$$P(u) = \frac{2}{u^2} (e^{-u} + u - 1) \quad (\text{A-2-1-8})$$



where  $u = q^2 \langle S^2 \rangle$ ,  $q = (4\pi n / \lambda) \sin (\theta / 2)$ ,  $n$  is the index of refraction of the solvent,  $\lambda$  is the laser vacuum wavelength, and  $\theta$  is the scattering angle.

(2) For the light scattering by a polydisperse population,

$$Kc / I(q) = \frac{\int m N(m) dm}{\int m^2 N(m) P(q, m) dm} + 2A_2 Q(q) c \quad (\text{A-2-1-9})$$

where  $N(m)$  is the number distribution of the molecules, and  $Q(q)$  is a complicated function of intermolecular interactions.

(3) The slope of  $Kc/I$  vs  $q^2$  in isoionic dilution is independent of  $c$  for  $c < c^*$  ( $c^*$  is the overlap concentration); that is,  $Q(q) = \text{constant}$ . They took  $Q(q) = 1$ .

(4) The radius of gyration in the absence of excluded-volume effects is related to the apparent persistence length of the polymer through the wormlike chain model by eqn (A-2-1-3), and since experimental evidence indicates that, for this high molecular weight sample,  $L_p/L_r \ll 1$  under all condition studied, the molecules are assumed to be near the coil limit and

$$\langle S^2 \rangle_0 \cong L_r L_p / 3 \quad (\text{A-2-1-10})$$

However, since light scattering measures  $\langle S^2 \rangle$ , the apparent persistence length  $L_p'$  is computed when  $\langle S^2 \rangle$  is substituted  $\langle S^2 \rangle_0$  in eqn (A-2-1-11)

$$L_p' = 3 \langle S^2 \rangle / L_r \quad (\text{A-2-1-11})$$

(5) If  $u$  is large enough that  $e^{-u} \ll 1$  for the whole population (in practice  $u$  should be larger than about 3), then to second order in  $u^{-1}$

$$Kc/I(q) \cong 1/(2M_n) + \gamma q^2/2 + 2A_2 c \quad (\text{A-2-1-12})$$

where the relation

$$\langle S^2 \rangle = \gamma M \quad (\text{A-2-1-13})$$

for ideal coils is used. Using assumption (3),

$$\frac{d[Kc / I(q)]}{dq^2} = \gamma / 2 \quad (\text{A-2-1-14})$$

and eqns (A-2-1-11) and (A-2-1-13) yields

$$L_p' = \frac{6m}{b} \frac{d[Kc / I(q)]}{dq^2} \quad (\text{A-2-1-15})$$

where  $m$  is taken as the mass of a monomer,  $b$  is the contour distance between monomers, and  $M = L_p m / b$ .

Reed et al. estimated  $L_e$  as  $L_p - L_0$ , where  $L_0$  was infinite ionic strength limit of  $L_p$ .<sup>62-</sup>

<sup>64</sup> The excluded volume correction for the SFO theory fits the experimental data much better than the  $L_e$  calculated in terms of SFO theory without any excluded volume correction. They also evaluated  $L_e$  from the values of  $\langle S^2 \rangle$  obtained in terms of the Monte Carlo simulation for a polyelectrolyte with Debye-Huckel screening and no hard core repulsion.<sup>65,66</sup> They concluded that the corrections due to polyelectrolyte excluded volume theories do not consistently yield good fits to the data, but do give weakly changing power laws similar to those obtained from the Monte Carlo and experimental data.

## A-2-2. Small-angle neutron scattering measurement

M. Nierlich et al.<sup>67</sup> estimated the persistence length from the small-angle neutron scattering measurements for salt-free semidilute polyelectrolyte solutions. Specific labeling associated with an extrapolation methods has allowed the separation of the



form factor of a single polyelectrolyte chain  $S_1(q)$  and the structure factor  $S_2(q)$ , where  $q$  is the scattering vector. Two lengths are deduced from these two factors: the persistence length  $L_p$  which characterizes the electrostatic interactions along the chain by a fitting of  $S_1(q)$  with calculation of the scattering function for a wormlike chain, and from  $S_2(q)$ ,  $q_m^{-1}$  which characterizes the interactions between chains. They used the calculations of Yoshizaki<sup>68</sup> valid at low  $q$  and des Cloizeaux<sup>69</sup> valid at high  $q$  to fit the experimental scattering functions  $S_1(q)$ .

For an infinite Kratky–Porod chain of persistence length  $L_p$ , the form factor  $s_x(\mathbf{q})$  can be defined by

$$s_x(\mathbf{q}) = L_p S(L_p q) \equiv \int_{-\infty}^{+\infty} \langle \exp[i\mathbf{q} \cdot \mathbf{r}(L)] \rangle dL \quad (\text{A-2-2-1})$$

where  $q$  is the momentum transfer,  $r(L)$  represents the position of a point of the chain, and  $S(p)$  is a universal function.

For  $p (=L_p q) \gg 1$ , des Cloizeaux<sup>69</sup> found

$$S(p) = \pi/p + 2/(3p^2) \quad (\text{A-2-2-2})$$

Yoshizaki and Yamakawa<sup>68</sup> evaluated the scattering function covering the range of light, small-angle X-ray, and neutron scattering on the basis of the wormlike and helical wormlike chain models. The evaluation is carried out numerically by the weighting function method and the  $\varepsilon$  method.

### A-2-3. Transient electric birefringence measurement

Degiorgio et al.<sup>70</sup> measured the birefringence relaxation time  $\tau$  by transient electric

birefringence (TEB) for NaPSS solutions at low ionic strength ( $I$ ) and estimated the  $L_p$  from the  $\tau$ . For the short chains at very low  $I$ , the birefringence relaxation time can be simply considered as the rotational relaxation time of the macromolecule. They used the expression for the  $\tau$  of a semi-flexible chain of given  $L_p$ <sup>71</sup>:

$$\tau(x) = \tau_{\text{rod}} [x + \{\exp(-2x) - 1\}/2]^{3/2} [1 + 0.539526 \ln(1 + x)]/x^3 \quad (\text{A-2-3-1})$$

where  $\tau_{\text{rod}}$  is the rotational relaxation time of a rigid rod length  $L_r$ ,  $x = L_r/2L_p$ , and  $L_r$  corresponds to the contour length. The  $L_0$  value was assumed to be 14Å for NaPSS<sup>61</sup> to obtain  $L_e$  in terms of eqn (A-1-1).

#### A-2-4. The viscosity measurement

Tricot<sup>61</sup> derived the persistence length with a computer fitting procedure<sup>72</sup> on the basis of Yamakawa's theory<sup>73,74</sup> for the literature values of the intrinsic viscosity-molecular weight dependence of some polyelectrolytes (NaPA,<sup>75,76</sup> NaPSS,<sup>77</sup> poly[(acrylamido)-(methyl)propanesulfonate],<sup>78</sup> carboxymethylcellulose,<sup>79</sup> and the sodium salt of an isobutyl vinyl ether-maleic anhydride copolymer<sup>80</sup> in the 0.005–1.0M ionic strength range. The Fujii-Yamakawa relationship for wormlike chains can be expressed as

$$[\eta] = \frac{\Phi_{\infty} M^{1/2}}{(M_L/2L_p)^{3/2}} \left[ 1 - \sum_{i=1}^4 \left( \frac{L_r}{2L_p} \right)^{-i/2} \right]^{-1} \quad \text{for } L_r/2L_p > 2.28 \quad (\text{A-2-4-1})$$

if intrinsic viscosity  $[\eta]$  is expressed in  $\text{cm}^3 \text{g}^{-1}$ .  $\Phi_{\infty}$  is the theoretical Flory constant for infinitely large molecular weights ( $\Phi_{\infty} = 2.87 \times 10^{23}$ ),  $M$  is the molecular weight,  $M_L$  is the mass per unit length, and  $C_i$  are coefficients that depend on the ratio  $d/2L_p$ , where  $d$



is the cylinder diameter according to expressions given in ref. 74 for different  $d/2L_p$  ranges. The form of the Fujii–Yamakawa relationship is changed when the ratio  $L_r/2L_p$ , which defined the number of Kuhn statistical segments, is smaller than 2.28. Tricot associated the Fujii–Yamakawa relationship with a multiparametric nonlinear least-squares fitting program and obtained the  $L_p$  values. He regarded  $L_p$  at the infinite ionic strength as  $L_0$ , and obtained the  $L_e$  values in terms of eqn (A-1-1).

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