

# Donnan equilibria of simple electrolytes in polyelectrolyte solutions

## Part 2.†—Extension to polycations and the effect of charge densities

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Salt exclusion parameters  $\Gamma [(m'_s - m_s)/m_e]$ , where  $m_e$  denotes the polyelectrolyte concentration,  $m_s$  and  $m'_s$  represent the salt concentrations of the solutions with and without polyelectrolyte of polyelectrolyte–simple salt solutions have been determined for poly(2-methacryloxyethyltrimethylammonium) chloride (PMETAC), polyallylamine hydrochloride (PAAm), partially neutralized polyacrylate (PA) and sodium polystyrenesulfonate (NaPSS). For PA,  $\Gamma$  was examined at differing polyelectrolyte charge densities. An empirical equation with a single parameter  $k$ ,  $\Gamma = k/[1 + (1 + kx)^{1/2}]$ , where  $x = m_e/m_s$ , described the results to a good approximation. An empirical but unique relation was obtained between the  $k$  values and the osmotic coefficient in salt-free polyelectrolyte solutions,  $\phi_p$ , irrespective of the polymers and salts, when the present results were supplemented with previous data.

The Donnan distribution of salts has been studied over many years, mainly for polyanions.<sup>1–11</sup> In our previous study,<sup>11</sup> we found that an important parameter,  $k$ , describing the Donnan distribution, is independent of co-ion valences and that there is an approximately linear relationship between  $k$  and  $\phi_p$ , the osmotic coefficient in salt-free polyelectrolyte solution, for sodium polyacrylate (NaPA) and sodium polystyrene sulfonate (NaPSS). We now extend the previous study to include cationic polyelectrolytes and also the effect of the polyelectrolyte charge density.

In the present study the Donnan salt distribution of NaCl in the range of excess polyelectrolyte is investigated for three polyelectrolytes, poly(2-methacryloxyethyltrimethylammonium) chloride (PMETAC), polyallylamine hydrochloride (PAAm) and partially neutralized polyacrylic acid, by the equilibrium dialysis method. The effect of  $\text{NCS}^-$  locating at the opposite positions to  $\text{SO}_4^{2-}$  in the Hofmeister's series will be examined for NaPSS and the result will be compared with the previous results on  $\text{Cl}^-$  and  $\text{SO}_4^{2-}$ .

## Experimental

### Materials

PMETAC was obtained in the usual way by polymerizing 2-methacryloxyethyltrimethylammonium chloride, purchased from Polyscience, Inc. PAAm was purchased from Nitto Boseki Co. Ltd. and purified according to the method described.<sup>12</sup> PA and NaPSS were prepared as described previously.<sup>11</sup> PA was partially neutralized with NaOH.

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

### Procedure

The Donnan salt distribution was determined by the following method: the two solutions under Donnan equilibrium separated by a semipermeable membrane (Viskase Sales Co.) were analysed.<sup>11</sup> The salt concentrations of the inner and the outer solution were determined from the electric conductance. The conductivity was measured with a Toa conductivity meter CM-60V.

## Results and Discussion

### Analysis of the Donnan distribution of uni-univalent salt

The Donnan distribution of a salt is represented in terms of  $\Gamma$ , which is defined as  $(m'_s - m_s)/m_e$ : where  $m_e$  denotes the polyelectrolyte concentration and  $m_s$  and  $m'_s$  represent the salt concentrations of the solutions with and without polyelectrolyte. 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  $m'_e/m'_s$ . According to the limiting law (LL)<sup>13</sup> which is expected to hold when both  $m_e$  and  $m_s$  are small

$$\Gamma_0 = 1/2(1 - 1/2\xi) \quad (\xi \leq 1) \text{ or } 1/(4\xi) \quad (\xi \geq 1)$$

$$\text{or equivalently } \Gamma_0 = \phi_p/2 \quad (1)$$

Parameter  $\xi$  is defined, in terms of the Bjerrum length,  $l_B$ , and the separation of charges,  $b$ , along the polymer chain, as  $\xi = l_B/b$ . For partially neutralized PA,  $\xi$  is estimated from  $\alpha$ , but it is taken as 2.85 for PMETAC, PAAm, NaPA (the degree of ionization  $\alpha = 1$ ) and NaPSS. We analysed the data with the following equation proposed by Vink<sup>9,10</sup>

$$(km_e + m_s)m_s = (m'_s)^2 \quad (2)$$

which can be rewritten as

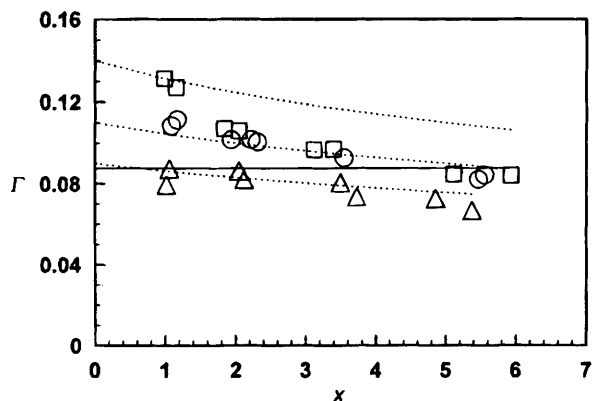
$$\Gamma = k/[1 + (1 + kx)^{1/2}] \quad (3)$$

We analysed the data in terms of eqn. (3). Evaluation of  $k$  was carried out from the slope of a  $(y^2 - 1)$  vs.  $x$  plot. Note that, in the present study,  $x$  was varied by changing  $m_s$  at constant  $m_e$ .

### Distribution of NaCl in PMETAC and PAAm solutions

We determined the Donnan distribution of PMETAC–NaCl at three polymer concentrations,  $m_e$ , 0.001, 0.01 and 0.10 mol  $\text{kg}^{-1}$ . In Fig. 1 values of  $\Gamma$  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  $m_e = 0.01$ , however, the  $x$  dependence was similar to that at  $m_e = 0.001$ ,  $\Gamma$  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) with single  $k$  values, as shown in Fig. 1. 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 with eqn. (3). Parameter  $k$

† Part 1: ref. 11.

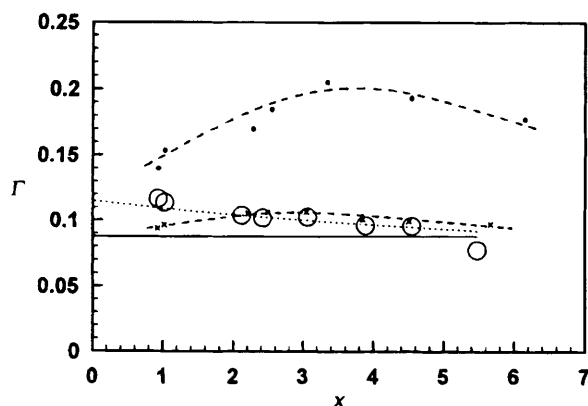


**Fig. 1** Donnan distribution of NaCl for PMETAC at 25°C. The solid straight line represents the result predicted from the LL.  $m_e = (\Delta)$  0.001,  $(\circ)$  0.01 and  $(\square)$  0.10 mol kg<sup>-1</sup>. Dotted curves are calculated from eqn. (3) with  $k = 0.28, 0.22$  and  $0.18$ , from top to bottom, respectively.

increased with  $m_e$  for PMETAC, as for the anionic polyelectrolytes NaPA and NaPSS.<sup>11</sup>

The Donnan distribution of PAAm–NaCl was 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 at ca. 0.14–0.20 and 0.10, respectively. These values decreased as  $m_e$  increased. This strange behaviour of  $\Gamma$  for PAAm at low polymer concentrations might be caused by a change in the degree of ionization of PAAm. On dilution, some bound protons dissociate 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 with eqn. (3) with  $k = 0.23$  as shown in Fig. 2.

Both  $k$  and  $\phi_p$  values for PMETAC were greater than those for PAAm at  $m_e = 0.10$  mol kg<sup>-1</sup>. We found previously that both  $k$  and  $\phi_p$  values were greater for PSS than PA. This can be explained by the difference in the volume occupied by the polyions between PMETAC and PAAm or between PSS and PA. The volume occupied by polyion is related to the radius,  $a$ , of the polyion. For a given linear charge density, the surface charge density, and hence the surface potential, of a rod-like polyion of a larger radius is smaller than that with a smaller radius. The excluded volume effect also makes  $k$  and  $\phi_p$  larger. However, the interpretation in terms of the polyion radius does not give a consistent picture for these four polymers.



**Fig. 2** Donnan distribution of NaCl for PAAm at  $m_e = 0.10$  mol kg<sup>-1</sup> at 25°C. The solid straight line represents the result predicted from the LL. The dotted curves are calculated from eqn. (3) with  $k = 0.23$ . (—) drawn through experimental results represented with crosses and dots at  $m_e = 0.001$  and  $0.01$ , from bottom to top, respectively.

### Distribution of NaCl in partially neutralized PA solutions

The Donnan distribution of NaCl was determined in partially neutralized PA ( $\alpha = 0.3, 0.5$  and  $0.8$ ) solutions at  $m_e = 0.01$  as shown in Fig. 3. Note that the chain concentrations increased as  $\alpha$  decreased, in order to keep  $m_e$  constant. At  $\alpha = 0.3$ , the  $\Gamma$  values depended on  $x$  and they were much smaller than the result from the LL. In the present study  $x \rightarrow 0$  corresponds to a large excess of salt. LL behaviour is expected for large  $x$ , that is, small  $m_e$ . However, the deviation becomes more significant as  $x$  increases. At  $\alpha = 0.8$ ,  $\Gamma$  values can be approximated with the LL, as in the case for  $\alpha = 1.0$ .<sup>11</sup> Both the concentration dependence and the deviation from the LL became smaller as  $\alpha$  increased.

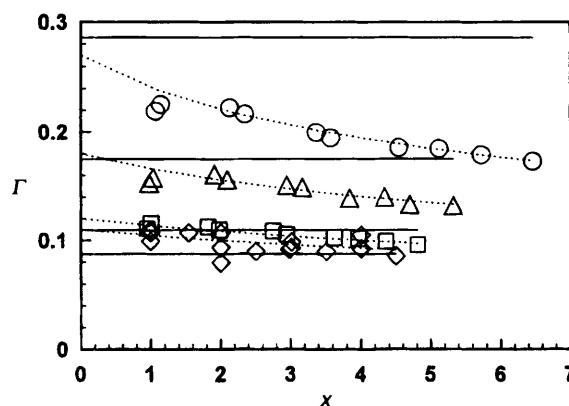
The  $x$  dependence of the  $\Gamma$  values decreased as  $\alpha$  increased. All the results on partially neutralized PA examined can be described with eqn. (3) with single parameters,  $k$ . The  $k$  values also decreased as  $\alpha$  increased, since the interaction between polyions and counterions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

The influence of the charge density on the Donnan equilibrium was previously studied by Vink<sup>10</sup> for hydroxyethyl cellulose substituted with carboxymethyl groups (HEC) and partially neutralized PA for a limited range. For HEC, the deviation from the LL in the range  $1 < x < 5$  is less as the charge density becomes higher. This tendency is similar to our results for 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. An open circle represents the data of Vink for  $\xi = 0.1$  ( $m_e = 0.0027$ ). Indicated in Fig. 4 are  $(\phi_p)_{LL}$  and  $(\phi_p)_{P-B}$  calculated by the Poisson–Boltzmann approach at  $m_e = 0.01$ , as described in a later section. At this  $m_e$ , the  $k$  values are in fair agreement with  $(\phi_p)_{LL}$  except for  $\xi = 2.85$ , corresponding to  $\alpha = 1.0$ . Although the values of  $k$  are close to the calculated values of  $\phi_p$ ,  $(\phi_p)_{LL}$  or  $(\phi_p)_{P-B}$ , they are considerably greater than the observed  $\phi_p$  values, as shown in Fig. 6 (later). Since  $(\phi_p)_{LL}$  is dependent on  $m_e$ , the agreement between  $(\phi_p)_{LL}$  and  $k$  becomes worse at high  $m_e$ .

### Distribution of NaNCS in NaPSS solutions

The Donnan distribution of NaNCS was examined for NaPSS solutions at  $m_e = 0.01$  as shown in Fig. 5.  $\Gamma$  values decrease with  $x$  and they are significantly greater than the result from the LL. The results can be described with eqn. (3) as shown in Fig. 5 with  $k = 0.30 \pm 0.03$ . The  $k$  values with NaNCS is in good agreement with those obtained for NaPSS<sup>11</sup> at the same



**Fig. 3** 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.  $\alpha = (\circ)$  0.3;  $(\Delta)$  0.5;  $(\square)$  0.8;  $(\diamond)$  1. The dotted curves are calculated from eqn. (3) with  $k = 0.54, 0.36, 0.24$  and  $0.22$ , from top to bottom, respectively.

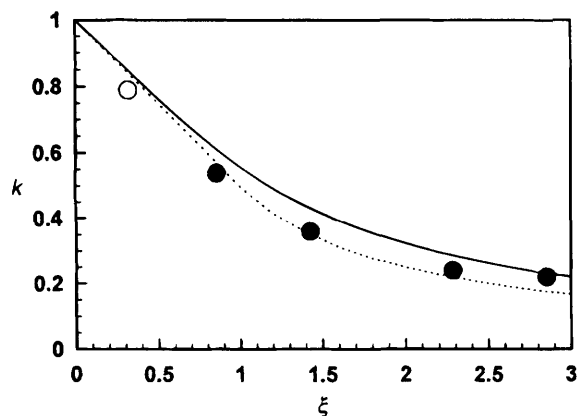


Fig. 4 Relation between  $k$  and  $\xi$  for NaPA. The solid curve represents  $(\phi_p)_{P-B}$  and is calculated from eqn. (6)–(8) with  $a = 2.3$  Å. The dotted curve represents  $(\phi_p)_{LL}$ . (○) work by Vink;<sup>10</sup> (●) this study.

$m_e$  with NaCl ( $k = 0.28 \pm 0.03$ ) and  $\text{Na}_2\text{SO}_4$  ( $k = 0.28 \pm 0.03$ ), within the experimental error. Thus, it is shown that  $k$  remains constant when the co-ion species varies from one end to the other of the Hofmeister's series. This suggests that  $k$  is determined by the interaction of the polyelectrolyte with its counterions.

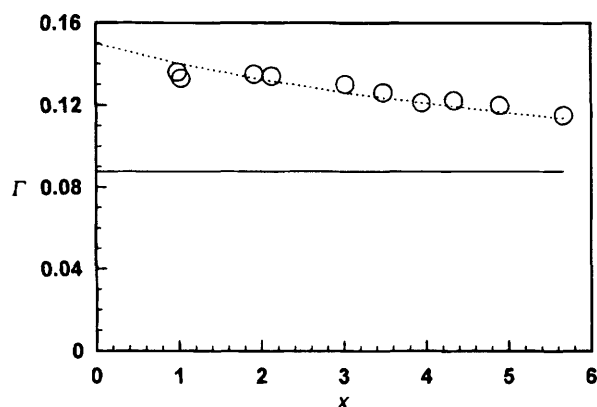


Fig. 5 Donnan distribution of NaNCS for NaPSS at  $m_e = 0.01$  mol  $\text{kg}^{-1}$  at 25 °C. The solid straight line represents the result predicted from the LL. The dotted curve is calculated from eqn. (3) with  $k = 0.30$ .

### Relation between $\phi_p$ and parameter $k$

In Table 1, the values of  $k$  and  $\phi_p$  are shown. When the values of  $k$  and  $\phi_p$  are supplemented with the data from the previous study,<sup>11</sup> we found an empirical relationship between  $\phi_p$  and  $k$  as shown in Fig. 6. For polyions of linear charge density  $\xi = 2.85$ , the following linear relation was obtained.

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

In Fig. 6 data at a low degree of ionization ( $\alpha = 0.11$ ) obtained by Vink<sup>10</sup> are also shown. It is clear that 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  $\phi_p = 0.1$ –0.5:

$$k = 1.876\phi_p^2 + 0.374\phi_p + 0.138 \quad (5)$$

The above empirical equations, eqn. (4) and (5), could be universally applied for different polymer concentrations, polymer species and co-ion 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 mean activity coefficient of salt is set up in Manning's theory.<sup>13</sup> According to the additivity, the  $k$  value is expected

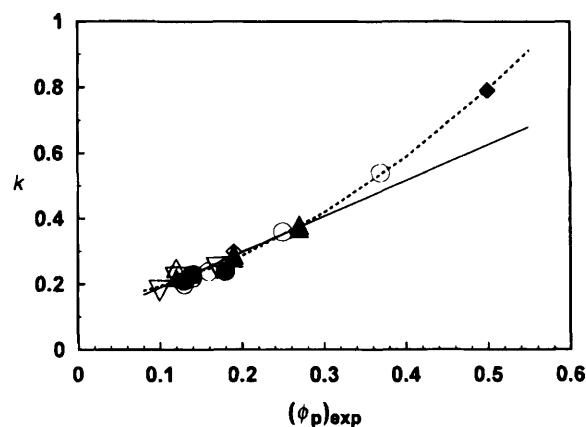


Fig. 6 Relation between  $k$  and  $\phi_p$ . Some values of  $k$  and  $\phi_p$  are taken from the literature.<sup>19–21</sup> (○) NaPA( $\alpha = 0.3, 0.5, 0.8, 1.0$ )–NaCl; (●) NaPA( $\alpha = 1$ )– $\text{Na}_2\text{SO}_4$ ; ( $\Delta$ ) NaPSS–NaCl; ( $\blacktriangle$ ) NaPSS– $\text{Na}_2\text{SO}_4$ ; ( $\nabla$ ) PMETAC–NaCl; ( $\square$ ) PAAm–NaCl; ( $\diamond$ ) NaPSS–NaNCS; ( $\blacklozenge$ ) NaPA( $\alpha = 0.1$ )–NaCl.<sup>10</sup> The solid straight line represents eqn. (4). The dotted curve represents eqn. (5).

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

$m_e/\text{mol kg}^{-1}$		$k$ (NaCl)	$\phi_p$	$(\phi_p)_{P-B}^b$	
PMETAC					
0.001		$0.18 \pm 0.02$	$0.10^a$	0.23	
0.01		$0.22 \pm 0.02$	$0.12^a$	0.26	
0.10		$0.25 \pm 0.03$	$0.17^a$	0.32	
PAAm					
0.10		$0.23 \pm 0.03$	$0.14^a$	0.27	
	$\alpha$				
PA					
0.01	0.3	$0.54 \pm 0.01$	$0.37^c$	0.61	
0.01	0.5	$0.36 \pm 0.01$	$0.25^c$	0.43	
0.01	0.8	$0.24 \pm 0.01$	$0.16^c$	0.29	
		$k$			
		NaCl	Na <sub>2</sub> SO <sub>4</sub>	NaNCS	
NaPSS					
0.01	$0.28 \pm 0.03$	$0.28 \pm 0.03$	$0.30 \pm 0.03$	$0.19^a$	0.27

<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 eqn. (6)–(8) (see text). <sup>c</sup> From ref. 19.

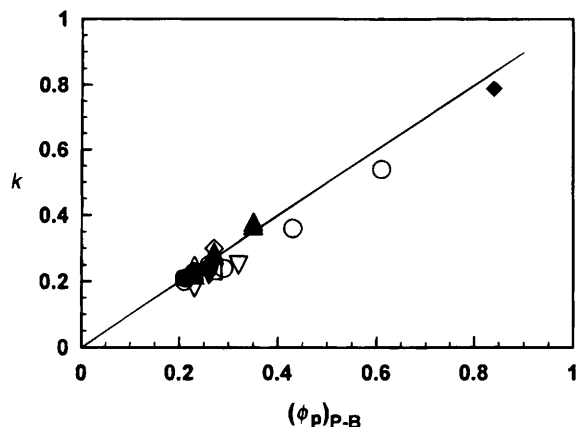


Fig. 7 Relation between  $k$  and  $(\phi_p)_{P-B}$ . Symbols as given in Fig. 6. The solid straight line with a slope equal to unity is shown.

to be equal to  $\phi_p$ . However, the obtained  $k$  values were significantly greater than  $\phi_p$ . Since the  $k$  value is introduced as an empirical parameter, it is not easy to estimate it theoretically. 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 Poisson–Boltzmann (P–B) approach.<sup>14,15</sup> However, it is not easy to evaluate the Donnan distribution of salt under the excess polyelectrolyte condition by the P–B approach.

In contrast to the salt distribution problem, we can evaluate  $\phi_p$  on the basis of the P–B equation<sup>16</sup> modified by Marcus<sup>17</sup> as follows:

$$\phi_p = (1 - \beta^2)[1 - \exp(-2\gamma)]/2\xi \quad (6)$$

where  $\beta$  is a constant defined by

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

The concentration parameter  $\gamma$  is related to  $m_e$

$$\gamma = (1/2)\ln(10^3/\pi a^2 b N_A m_e) \quad (8)$$

where  $a$  and  $N_A$  are the radius of the polyion and Avogadro's number.

Parameter  $a$  was estimated from the chemical structure of the polymers and the values were 2.3, 8.0, 5.7 and 2.7 Å for NaPA, NaPSS, PMETAC and PAAm, respectively. The charge density parameter,  $\xi$ , was estimated to be 2.85.

Values of  $k$  are plotted against  $(\phi_p)_{P-B}$  in Fig. 7, 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 values. In the case of partially neutralized PA, the deviation from the relation  $k = (\phi_p)_{P-B}$  is already evident in Fig. 4. When the charge density is small, the chain might be easy to bend. Therefore, the effective charge density might be higher than that calculated from the chemical structure.<sup>13,18</sup>

The above results provide us with an empirical method of estimating the Donnan osmotic pressure  $\Pi_D$  by the following procedures for the condition  $1 < x < 6$ . (i) Set  $k = (\phi_p)_{P-B}$  or  $(\phi_p)_{LL}$ . (ii)  $\phi_p$  is evaluated from eqn. (4) and the  $k$  value is obtained by procedure (i). (iii) 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.

## Conclusions

(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 co-ion 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  $0.1 < \phi_p < 0.3$ ;  $k = 1.876\phi_p^2 + 0.374\phi_p + 0.138$  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 for PSS than for the others.

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