Bull. Chem. Soc. Jpn., ***69***, 3075—3079 (1996)

Mean Activity Coefficients of Simple Electrolytes in Polyelectrolyte Solutions

Rie Kakehashi

Department of Chemistry, Faculty of Science, Kyushu University, Hakozaki, Higashi-ku, Fukuoka 812

(Received May 20, 1996)

Mean activity coefficients of NaCl, NaNCS, or Na_2SO_4 were evaluated on the basis of the Donnan salt distribution in sodium polyacrylate ($\alpha = 0.3$, 0.5, 0.8, and 1.0), sodium polystyrenesulfonate, poly(2-methacryloxyethyltrimethylammonium) chloride or polyallylamine hydrochloride solutions. Observed mean activity coefficients were close to those given by Manning's limiting law (LL) at polyelectrolyte concentration $m_e = 0.001$ mol kg^{-1} in all systems examined. The observed activity coefficients showed large deviations from LL at high m_e and for Na_2SO_4 but they were in fair agreement with the theoretical values when corrected for the contribution from the small ion–small ion interaction.

Interactions of polyions with small ions have been reasonably understood on the basis of Manning's limiting law (LL)[1] or the Poisson–Boltzmann (P–B) approach.[2—12] Mean activity coefficients of salts in polyelectrolyte solutions are an important measure of the interactions of polyions with small ions. We have determined the Donnan salt distribution on several salt/polyelectrolyte pairs,[13,14] and in this study, we evaluate the mean activity coefficients on the basis of these Donnan salt distribution data. Observed mean activity coefficients were compared with predicted values from LL. While small ion–small ion interactions are not taken into account in the limiting law, 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,[15] 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.

Experimental

Materials. Poly(acrylic acid) (PA) and sodium poly(styrene sulfonate) (NaPSS) were purchased from Toa Gosei Chemicals Co. and Polyscience Inc. (Lot No. 413336), respectively. Poly(2-methacryloxyethyltrimethylammonium) chloride (PMETAC) was obtained in the usual way by polymerizing 2-methacryloxyethyltrimethylammonium chloride, purchased from Polyscience, Inc. Polyallylamine hydrochloride (PAAm) was purchased from Nitto Boseki Co., Ltd. and purified by the method described.[16]

Results and Discussion

1. The Estimation of Activity Coefficients of Salts.

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

$$(\gamma_\pm)^2(m_s + m_e)m_s = (\gamma'_\pm m'_s)^2, \tag{1}$$

where m_e denotes the polyelectrolyte concentration in mol kg^{-1}, and m_s and m'_s represent the salt concentrations in mol kg^{-1} of the solutions with and without polyelectrolyte, respectively. Primed quantities refer to the external solution without polyelectrolyte.

In the case of Na_2SO_4, Eq. 2 was used in place of Eq. 1.

$$(\gamma_\pm)^3(2m_s + m_e)^2 m_s = 4(\gamma'_\pm m'_s)^3. \tag{2}$$

For NaCl, mean rational activity coefficients $f'_\pm$ were calculated as follows.[17]

$$\log f'_\pm = -A(m'_s)^{1/2}/[1 + (m'_s)^{1/2}] + bm'_s. \tag{3}$$
$$(A = 0.5115 \text{ and } b = 0.16)$$

Here, $\gamma'_\pm$ were calculated as $f'_\pm/(1{+}0.001\nu W_A m)$, where ν, 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.[17]

For NaNCS[18]

$$\log \gamma'_{Na} = -A(m'_s)^{1/2}/[1 + Ba(m'_s)^{1/2}], \tag{4}$$

$$\log \gamma'_{NCS} = -A(m'_s)^{1/2}/[1 + Ba(m'_s)^{1/2}], \tag{5}$$

where A=0.5114, B=0.3291×10^8, a=4.5 and 3.5 for Na$^+$ and NCS$^-$, respectively.

$$\gamma'_\pm = (\gamma'_{Na}\gamma'_{NCS})^{1/2}. \tag{6}$$

For Na_2SO_4[19]

$$\log\gamma'_\pm = -0.708(6m'_s)^{1/2}/\{1+A(6m'_s)^{1/2}\}+B(6m'_s)-\log(1+0.054m'_s), \tag{7}$$

where A=0.719 and B=−0.0053.

The activity coefficient is related to the salt exclusion parameter Γ as follows in terms of x defined as m_e/m_s.

$$(\gamma_\pm/\gamma'_\pm)^2=(\Gamma x+1)^2/(x+1) \qquad \text{for NaCl and NaNCS,} \quad (8)$$

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

Here Γ is defined as $(m'_s-m_s)/m_e$.

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

For 1-1 electrolyte,[1] such as NaCl and NaNCS,

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

and

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

For 1-2 electrolyte, such as Na_2SO_4,

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

and

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

Here ξ is defined in terms of the Bjerrum length l_B and the separation of charged b along the polymer chain as $\xi=l_B/b$. The charge density parameter ξ is estimated to be 2.85 for NaPA, NaPSS, PAAm, and PMETAC. For partially neutralized PA, ξ is taken as $\alpha\times2.85$ in terms of α, the degree of ionization. The mean activity coefficients predicted from LL $(\gamma_\pm)_{LL}$ are shown with dotted lines in all figures.

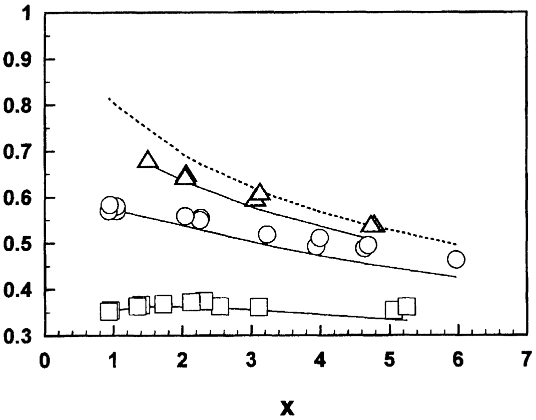

Fig. 2. Mean activity coefficients of Na_2SO_4 as a function of x in NaPA solutions. △: m_e=0.001 mol kg^{-1}; ○: m_e= 0.01 mol kg^{-1}; □: m_e=0.10 mol kg^{-1}. The dotted curve, $(\gamma_\pm)_{LL}$, is predicted from Eq. 11. Solid curves represent $(\gamma_\pm)_{LL}\gamma'_\pm(m_s)$ for m_e=0.001, 0.01, and 0.10 mol kg^{-1}, from top to bottom, respectively.

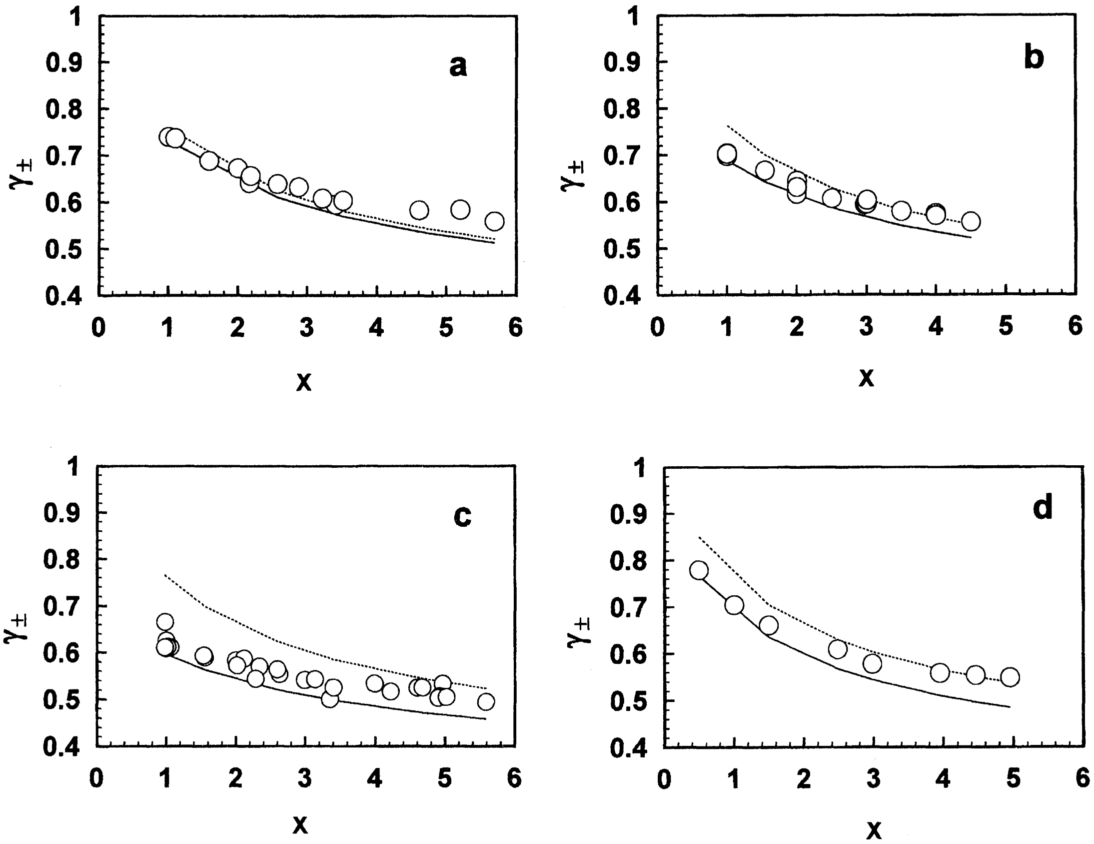

Fig. 1. Mean activity coefficients of NaCl as a function of x in NaPA solutions. (a) m_e = 0.001 mol kg^{-1}. (b) m_e = 0.01 mol kg^{-1}. (c) m_e = 0.10 mol kg^{-1}. (d) m_s = 0.01 mol kg^{-1}. Dotted curves, $(\gamma_\pm)_{LL}$, are predicted from Eq. 10. Solid curves represent $(\gamma_\pm)_{LL}\gamma'_\pm(m_s)$.

2. Comparison of Experimental Activity Coefficients with Theoretical Values. The activity coefficients of NaCl and Na_2SO_4 for NaPA are shown in Figs. 1 and 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 $(\gamma_\pm)_{LL}$ in the case of Na_2SO_4 over the entire range of x examined. While small ion–small ion interactions are not taken into account in the limiting law, 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, LL would be-

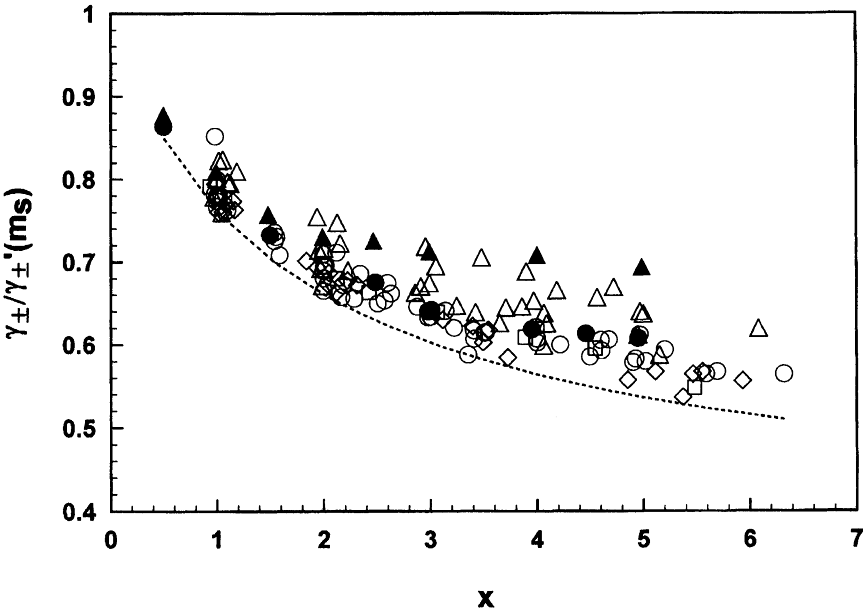

Fig. 3. Plots of $\gamma_\pm/\gamma'_\pm(m_s)$ of NaCl against x for NaPA, NaPSS, PMETAC, and PAAm. ○: NaPA at constant m_e; ●: NaPA at constant m_s; △: NaPSS at constant m_e; ▲; NaPSS at constant m_s; □: PMETAC at constant m_c; ◇: PAAm at constant m_e. The dotted curve, $(\gamma_\pm)_{LL}$, is predicted from Eq. 10.

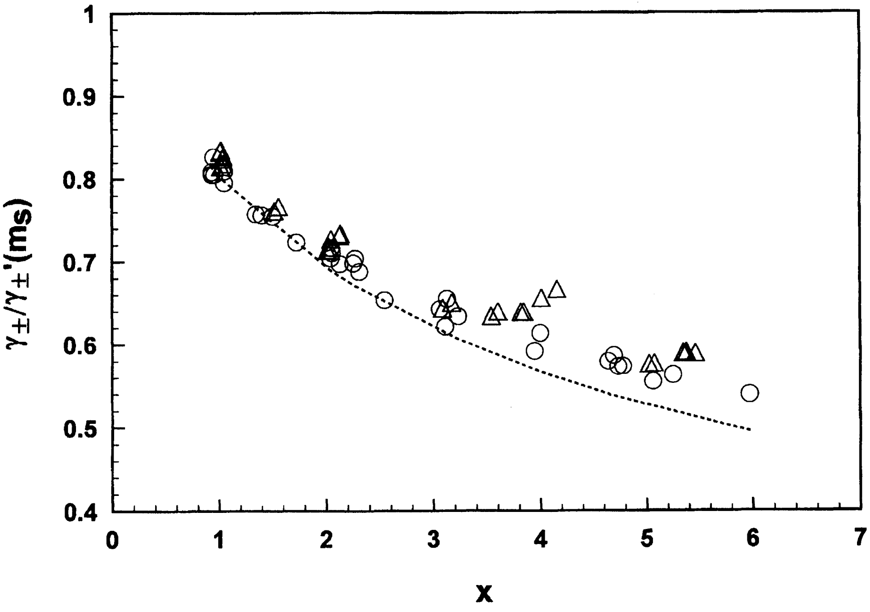

Fig. 4. Plots of $\gamma_\pm/\gamma'_\pm(m_s)$ of Na_2SO_4 against x for NaPA and NaPSS. ○: NaPA at constant m_e; △: NaPSS at constant m_e. The dotted curve, $(\gamma_\pm)_{LL}$, is predicted from Eq. 11.

come applicable to finite concentrations of simple salt under low polyelectrolyte concentrations. Observed activity coefficients should be compared with $(\gamma_{\pm}^{\mathrm{ss}})(\gamma_{\pm})_{\mathrm{LL}}$ rather than $(\gamma_{\pm})_{\mathrm{LL}}$.

Wells approximated $\gamma_{\pm}^{\mathrm{ss}}$ with $\gamma'_{\pm}(m_{\mathrm{s}})$, 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 Donnan equilibrium is m'_{s}. The values $(\gamma_{\pm})_{\mathrm{LL}}$ $\gamma'_{\pm}(m_{\mathrm{s}})$ are shown in Figs. 1 and 2 with solid lines. The two curves $(\gamma_{\pm})_{\mathrm{LL}}$ and $(\gamma_{\pm})_{\mathrm{LL}}\gamma'_{\pm}(m_{\mathrm{s}})$ tend to merge as x increases (as m_{s} decreases). However, when x varies at a constant m_{s}, Fig. 1(d), the two curves are parallel. Observed $\gamma_{\pm}$ values show weaker x-dependence than those two curves. It is to be noted that the agreement between the observed $\gamma_{\pm}$ and $(\gamma_{\pm}^{\mathrm{ss}})(\gamma_{\pm})_{\mathrm{LL}}$ is greatly improved in the case of $\mathrm{Na_2SO_4}$.

In Fig. 3, values of $\gamma_{\pm}/\gamma'_{\pm}(m_{\mathrm{s}})$ of NaCl are shown for several polyelectrolytes. In this section, 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, these data have nearly identical results. Different values of $\gamma_{\pm}$ obtained at different m_{e} converge to values within a narrow width after corrected for $\gamma_{\pm}^{\mathrm{ss}}$. The value $\gamma_{\pm}/\gamma'_{\pm}(m_{\mathrm{s}})$ is regarded as a good approximation to $\gamma_{\pm}^{\mathrm{ps}}$ and hence compared with $(\gamma_{\pm})_{\mathrm{LL}}$ given by a dotted curve. The values $\gamma_{\pm}/\gamma'_{\pm}(m_{\mathrm{s}})$ show systematic upward deviation from $(\gamma_{\pm})_{\mathrm{LL}}$ by about 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

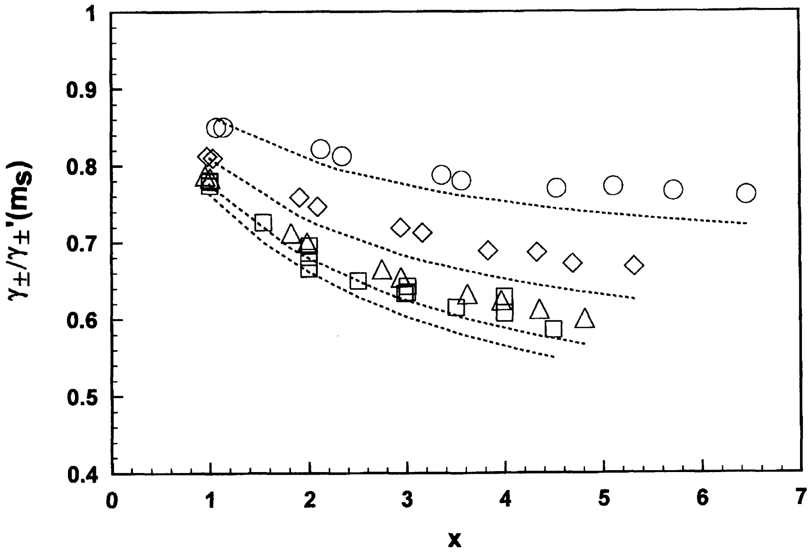

Fig. 5. Plots of $\gamma_{\pm}/\gamma'_{\pm}(m_{\mathrm{s}})$ of NaCl against x for partially neutralized PA at m_{e}=0.01 mol kg^{-1}. ○: α=0.3, ◇: α=0.5; △: α=0.8; □: α=1.0. Dotted curves represent $(\gamma_{\pm})_{\mathrm{LL}}$ predicted from Eq. 10 for α=0.3, 0.5, 0.8 and 1.0, from top to bottom, respectively.

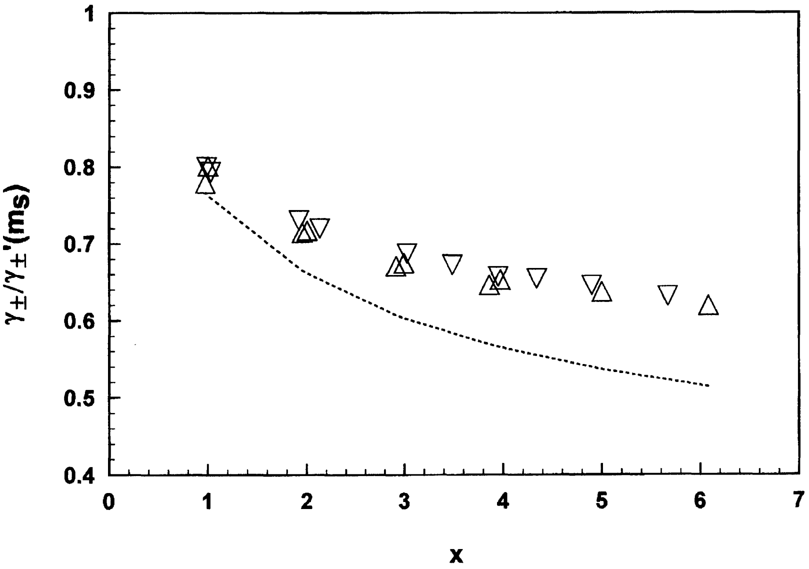

Fig. 6. Plots of $\gamma_{\pm}/\gamma'_{\pm}(m_{\mathrm{s}})$ of NaCl and NaNCS against x for NaPSS at m_{e}=0.01 mol kg^{-1}. △: NaCl; ▽: NaNCS. The dotted curve, $(\gamma_{\pm})_{\mathrm{LL}}$, is predicted from Eq. 10.

upward deviation indicates $\gamma_{\pm}^{\rm ss} > \gamma'_{\pm}$. It is reasonable that at small $m_{\rm s}$, $\gamma_{\pm}^{\rm ss}$ is closer to unity and hence greater than $\gamma'_{\pm}(m_{\rm s})$ because of the strong influence of the polyion electric field. In other words, the superposition approximation is not good at small $m_{\rm s}$. In the case of Na_2SO_4 shown in Fig. 4, the agreement is fair over the entire range of x for both NaPA and NaPSS, suggesting $\gamma_{\pm}^{\rm ss}$ are still smaller than unity for this salt.

This general trend prevails for other charge densities when examined on NaPA as shown in Fig. 5. Both observed and theoretical activity coefficients show weaker x-dependence as charge density decreases.

We conclude that the approximation $\gamma_{\pm}^{\rm ss}$ with $\gamma'_{\pm}(m_{\rm s})$ works at small x, smaller than about 4 or 5, and that $\gamma_{\pm}^{\rm ss}$ 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.

3. Results on NaPSS. In this study, NaPSS showed different behavior from the others. Mean activity coefficients of NaCl in NaPSS solution are greater than those of other polyelectrolytes examined as judged from Fig. 3. Similar results were obtained for both NaNCS and NaCl as shown in Fig. 6. Activity coefficients of Na_2SO_4 are also slightly greater than those of NaPA (Fig. 4). 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 results that the salt exclusion in NaPSS solution is significantly greater than those of other polyelectrolytes examined.[13] 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 PSS^- ion with counterions is weaker than those of other polymers examined. A 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. 5 clearly indicate that this small difference in the degree of ionization α, 0.06 or less, cannot cause the observed difference between PSS and the others shown in Fig. 3. 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. 3 the results on PSS not only deviate from those of other polyelectrolytes, but also scatter within a much wider range than for other polymers. This will be closely related to the $m_{\rm e}$-dependence of both k and $\phi_{\rm p}$: the dependence is stronger in the case of PSS than other polymers.

The author thanks Professor H. Maeda for helpful discussions. This research is partially supported by the Sasakawa Scientific Research Grant from The Japan Science Society.

References

1) G. S. Manning, *J. Chem. Phys.*, **51**, 924 (1969).

2) F. Oosawa, in "Polyelectrolytes," Marcel Dekker, New York (1971).

3) C. F. Anderson and M. T. Record, Jr., *Biophys. Chem.*, **11**, 353 (1980).

4) B. K. Klein, C. F. Anderson, and M. T. Record, Jr., *Biopolymers*, **20**, 2263 (1981).

5) D. Stigter, *J. Colloid Interface Sci.*, **53**, 296 (1975).

6) D. Stigter, *Biopolymers*, **16**, 1435 (1977).

7) J. A. Shellman and D. Stigter, *Biopolymers*, **16**, 1415 (1977).

8) M. Gueron and G. Weisbuch, *J. Phys. Chem.*, **83**, 1991 (1979).

9) M. Gueron and G. Weisbuch, *Biopolymers*, **19**, 353 (1980).

10) G. Weisbuch and M. Gueron, *J. Phys. Chem.*, **85**, 517 (1981).

11) Z. Alexandrowicz, *J. Polym. Sci.*, **43**, 337 (1960).

12) A. Katchalsky and Z. Alexandrowicz, *J. Polym. Sci., Part A*, **A1**, 2093 (1963).

13) R. Kakehashi and H. Maeda, *J. Chem. Soc., Faraday Trans.*, **92**, 3117 (1996).

14) R. Kakehashi and H. Maeda, *J. Chem. Soc., Faraday Trans.*, in press.

15) J. D. Wells, *Biopolymers*, **12**, 223 (1973).

16) H. Ochiai, M. Handa, H. Matsumoto, T. Moriga, and I. Murakami, *Makromol. Chem.*, **186**, 2547 (1985).

17) R. A. Robinson and R. H. Stokes, in "Electrolyte Solutions," Academic Press, New York (1959).

18) J. Kielland, *J. Am. Chem. Soc.*, **59**, 1675 (1937).

19) G. Åkerlöf, *J. Am. Chem. Soc.*, **48**, 1160 (1926).