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Osmotic coefficients of vinylic polyelectrolyte solutions without added salt

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Abstract The osmotic pressures of polyelectrolyte solutions without added salt was measured in the concentration ranges 0.001–0.02 and 0.2–1.9 mol kg^{-1}. Our results show that the osmotic coefficients ϕ_p were strongly dependent on the chemical structures of polyelectrolyte through the polyion radius and the interaction between the ionic moiety and counterions. The osmotic pressures in polyelectrolyte solutions without added salt, calculated on the basis of the counterion contribution, are in agreement with the experimental results. We conclude that the counterion contribution is dominant in the osmotic pressures and thus, the polymer contribution is negligible in the examined concentration range 0.2–1.9 mol kg^{-1}. The P–B approach gave a fair prediction of the absolute values of the osmotic pressures with $\lambda = 4.5$, where λ is the charge density parameter, except for NaPA. In other words, the concentration dependence of the ϕ_p values can be explained in terms of the counterion contribution.

Key words Polyelectrolyte – osmotic coefficient – osmotic pressure – Poisson–Boltzmann approach – semidilute solution

Polyion–counterion interactions have been understood on the basis of Manning's limiting law (LL) [1] or the Poisson–Boltzmann (P–B) approach [2–12]. The osmotic pressure in salt-free polyelectrolyte solutions is a significant measure of the polyion–counterion interaction. According to the LL, thermodynamic properties, such as the osmotic coefficients in salt-free polyelectrolyte solutions and the salt exclusion parameter, could be estimated from a line charge density parameter alone 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 [13–15]. It is important to study the relation between those thermodynamic properties and chemical structures of polyelectrolytes.

The osmotic pressures in the dilute polyelectrolyte solutions without added salt have been explained in terms of the counterion contribution on the basis of the LL [1] or the P–B approach [16]. For the dilute solutions, the osmotic pressures were approximately described by the LL as follows [1]:

$$\pi/kT \approx c/(2\lambda) \tag{1}$$

where the charge density parameter λ is defined in terms of Bjerrum length l_B [$= e_0^2/(4\pi\varepsilon_0\varepsilon_r kT)$; where e_0 the elementary charge, ε_0 the permittivity of a vacuum, ε_r the dielectric constant, and kT the Boltzmann energy factor] and the separation of charges along the polymer chain b by $\lambda = l_B/b$. Note that the prediction by the LL for the osmotic pressures estimates only the counterion contribution.

On the other hand, the scaling theory in semidilute polymer solutions has been extended to polyelectrolyte [17–21], and the osmotic pressures were sometimes explained to be due to the polymer contribution [22, 23].

According to Odijk's theory [22] which evaluates only the polymer contribution, osmotic pressures without added salt were described by

$$\pi/kT \approx 1/\xi^3 \approx 10\,b^{3/8}c^{9/8} \quad (2)$$

where ξ and c represent the correlation length, and the monomer concentration, respectively. Equation (2) predicts that osmotic pressures increase with $c^{9/8}$. Bloomfield et al. [23] showed that this prediction was accurately obeyed with the experimental data for sodium polystyrenesulfonate (NaPSS) and polystyrenesulfonic acid.

We consider that the osmotic pressures in the semidilute polyelectrolyte solutions consist of the counterion contribution and the polymer contribution. Dubrynin et al. [21] examined the published data for NaPSS and concluded that the counterion contribution dominated over the polymer contribution. However, it is ambiguous whether the concentration dependence of the osmotic pressures in the polyelectrolyte solutions without added salt can be explained in terms of the counterion contribution. It is desirable to examine the concentration dependence of the osmotic pressures for the polyelectrolyte solutions other than NaPSS in the semidilute regime.

In the present study, the osmotic pressures are reported 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 ($\alpha = 0.9$) , 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 [22] and the Poisson–Boltzmann approach [16].

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 analogs to the polymers examined, such as tetramethylammonium chloride (TMACl), methylamine hydrochloride (MAHCl), ethylamine hydrochloride (EAHCl), and sodium ethansulfonate (NaES).

Experimental

Materials

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. 70 mmol of METAC, 40 mmol of ammonium persulfate and 50 mmol NaCl were dissolved in 100 ml of water. The solution was degassed and polymerization was carried out in a container at 60 °C for 3 h and this was followed by the precipitation of the polymer with acetone.

Precipitates were redissolved in water. Low molecular weight materials were removed by ultrafiltration using a membrane (ADVANTEC Q0100). The number-average molecular weight, M_n, was determined to be 1.7×10^5 with the membrane osmometry. Polyallylamine hydrochloride (PAAm) with an average molecular weight of 5×10^4 purchased from Nitto Boseki Co. Ltd. was purified by the same method as described by Ochiai et al. [24]. Sodium polystyrenesulfonate (NaPSS) with an average molecular weight of 5×10^5 was purchased from Polyscience, Inc. Low molecular weight materials were removed by ultrafiltration using a membrane (ADVANTEC Q2000). Polyacrylic acid (PA; $M_n = 2.6 \times 10^5$) was purchased from Toa Gosei Kagaku Co. and dialyzed against pure water. Sodium polyvinylbenzoate (NaPVB) was kindly supplied by Dr. S. 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. PA and PVB were neutralized with NaOH. The polymer concentrations were determined as described previously [15].

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.

Procedure

For the dilute solutions, the osmotic pressures against water were measured at 35.0 ± 0.4 °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 °C.

Results

Osmotic pressures in polyelectrolyte solutions without added salt

The reduced osmotic pressures π/RT in mol dm^{-3} against water are plotted as a function of concentration m_e in

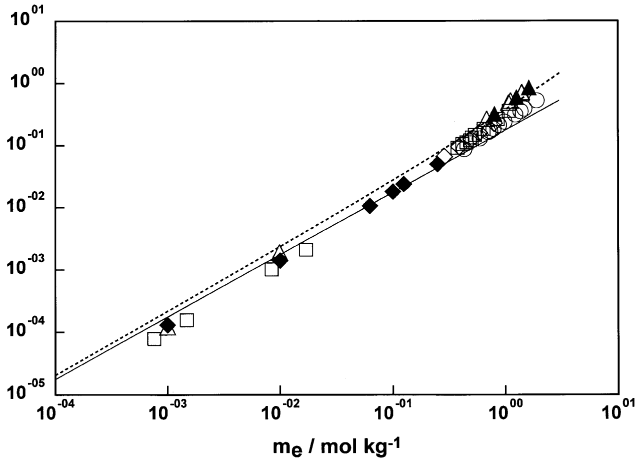

Fig. 1 Reduced osmotic pressures π/RT in mol dm^{-3} of aqueous solutions for PAAm, PMETAC, NaPA, and NaPSS as a function of counterion concentrations m_e. ○: PAAm; □: PMETAC; ◇: NaPA; △: NaPSS; ◆: NaPA taken from the literature [25]; ▲: NaPSS taken from the literature [26]. The dotted curve represents the results calculated according to Eqs. (3)–(5) for $\lambda = 2.85$ with $a = 3$. The solid straight line represents the results from Manning's limiting law

mol kg^{-1} in Fig. 1 for four polyelectrolytes. A part of the data for NaPA was taken from the literature [25]. Comparison between our results on NaPSS and those of Reddy and Marinsky [26] showed a reasonable agreement although both the molecular weights of samples and the measuring method were different.

We can evaluate the osmotic coefficients in the polyelectrolyte solution without added salt, ϕ_p, on the basis of the P–B equation [16] modified by Marcus [27] as follows:

$$\phi_p = (1 - \beta^2)(1 - e^{-2\gamma})/(2\lambda) \tag{3}$$

where β is a constant defined by

$$\lambda = (1 - \beta^2)/(1 + \beta \coth \beta\gamma) \ . \tag{4}$$

The concentration parameter γ is related to the polymer concentration c in molarity:

$$\gamma = (\tfrac{1}{2}) \ln[10^3/(\pi a^2 b \mathcal{N}_A c)] \tag{5}$$

where a and $\mathcal{N}_A$ are the radius of the polyion and Avogadro's number. The λ value was estimated to be 2.85 for $\alpha = 1$, when the chain is fully extended. The π/RT values were calculated from the relation, $\pi/RT = \phi_p \times m_e$. The result estimated on the basis of the P–B approach is shown with the dotted line in Fig. 1. While, the result evaluated by the LL with $\lambda = 2.85$ is shown with a solid straight line of unit slope. Although the concentration dependence of the ϕ_p is considered in the P–B approach, the ϕ_p is taken as the constant $[= 1/(2\lambda)]$ in the LL. Thus, the osmotic pressures for the P–B approach were in agreement with those in the LL in the dilute region, and were greater than those in the LL in the more concentrated region, as shown in Fig. 1. These values predicted from both the P–B approach and the LL were only due to the counterion contribution but were nevertheless greater than the observed values in the dilute regime (0.001–0.02 mol kg^{-1}). The comparison between the observed values and the results from the P–B approach and the LL shows that the counterion contribution is dominant in the osmotic pressures of polyelectrolyte solutions. The slopes of the plot of log π/RT vs. log m_e are around 1.2 ± 0.1 in the semidilute range (0.2–1.9 mol kg^{-1}) and about 1.0 ± 0.1 in the dilute range ($m_e < 0.03$ 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, ϕ_p, was calculated from the measured osmotic pressures π according to the relation [28]

$$\phi_p = \frac{1000\overline{V_W^0}}{m_e M_W} \frac{\pi}{RT} \tag{6}$$

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

In Fig. 2, the osmotic coefficients ϕ_p of PMETAC, PAAm, NaPA, and NaPSS solutions are shown as functions of concentration m_e. The ϕ_p values increased with increasing m_e significantly in all cases. The ϕ_p values calculated according to Eqs. (3)–(5) for $\lambda = 2.85$ are, however, much greater than the observed values as shown by dotted curves in Fig. 2. Parameter a in Eq. (5) was estimated from the chemical structure of the polymer and the values were 6, 3, 8, and 2.3 A for PMETAC, PAAm, NaPSS, and NaPA, respectively. In the dilute region, we assume $c \approx m_e$. Recently, the actual or effective charge density of PSS was proposed to be greater than the nominal value ($\lambda = 2.85$) by Maarel et al. [29]. According to the small angle neutron scattering study at $m_e = 0.1$ mol dm^{-3} [29], the short mean projected distance between monomeric units (1.6A) resulted in a 1.7 times higher value of λ compared to the value corresponding to a fully stretched chain conformation. From this result, λ was estimated to be 4.5. The ϕ_p values calculated according to Eqs. (3)–(5) for $\lambda = 4.5$ are in fair agreement with the experimental results over the low and semidilute concentration regime, as shown in Fig. 3, except for NaPA.

In this way, the P–B approach with $\lambda = 4.5$ has predicted the absolute values of the measured osmotic pressures as well as their concentration dependence. Judged

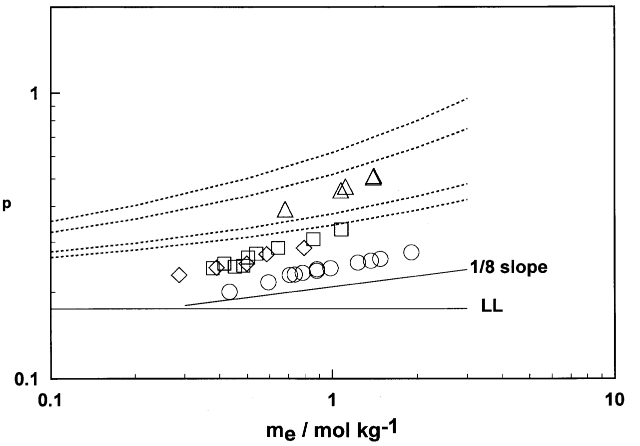

Fig. 2 Osmotic coefficients, ϕ_p, of aqueous solutions for PAAm, PMETAC, NaPA, and NaPSS as a function of counterion concentrations, m_e. Symbols are given in Fig. 1. Dotted curves represent osmotic coefficients estimated from Eqs. (3)–(5) for $\lambda = 2.85$ with $a = 8$, 6, 3 and 2.3, from top to bottom, respectively. The results from the Manning's limiting law is shown with a solid line LL. A solid line with a slope of 1/8 is also shown for comparison

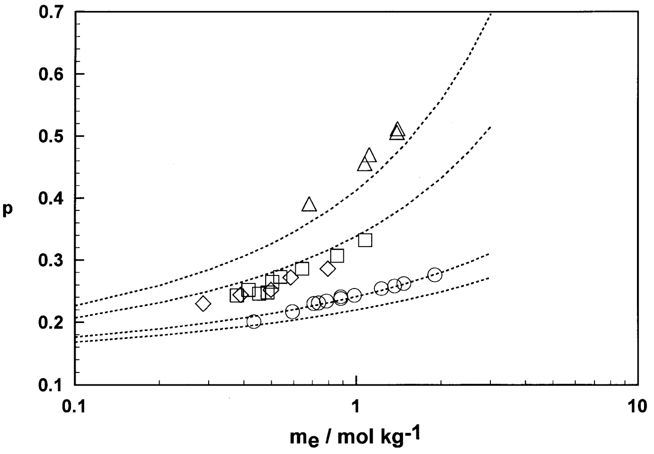

Fig. 3 Osmotic coefficients, ϕ_p, of aqueous solutions for PAAm, PMETAC, NaPA and NaPSS as a function of counterion concentrations, m_e. Symbols are given in Fig. 1. Dotted curves represent osmotic coefficients estimated from Eqs. (3)–(5) for $\lambda = 4.5$ with $a = 8$, 6, 3 and 2.3, from top to bottom, respectively

from this finding, we conclude that the osmotic pressures can be mainly estimated in terms of the counterion contribution. In other words, the scaling theory is not applicable to the osmotic pressures of polyelectrolyte solutions without added salt, since the polymer contribution is expected to be negligible. In fact, the slopes of the plot of log ϕ_p vs. log m_e in Fig. 2 significantly differ from 1/8 and are different for different polymers: 0.36 ± 0.04, 0.27 ± 0.02, 0.19 ± 0.02, and 0.20 ± 0.03 for NaPSS, PMETAC, NaPA, and PAAm, respectively.

Osmotic coefficients of polyelectrolytes and their low-molecular weight analogs

As shown in Fig. 3, the ϕ_p values decrease in the order NaPSS > PMETAC ≈ NaPA > PAAm in the concentration range examined. The ϕ_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 ϕ_p values was also observed between PA and PVB at $\alpha = 0.9$, as listed in Table 1. The ϕ_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 ϕ_p values were approximately equal. The result might be attributed partly to the hydrated radii of counterions ($Cl^- > Na^+$) and partly to the degree of the interaction between ionic moiety and counterions.

In order to investigate the relation between the ϕ_p values and the ionic moiety of the polyelectrolytes, the osmotic coefficients ϕ 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 analogs to polyelectrolytes examined. For sodium acetate (NaAC), the value in the literature [30] was used. Figure 4 shows the results. The molal osmotic coefficient for 1–1 electrolytes is related to the osmotic pressure by [26]

$$\phi = \frac{1000\overline{V_W^0}}{2mM_W}\frac{\pi}{RT} . \tag{7}$$

For MAHCl, EAHCl and TMACl, the ϕ values were identical within the experimental error and decreased with concentrations m over the concentration range examined. On the contrary, the ϕ values for

Table 1 Osmotic coefficients in polyelectrolyte solutions without added salt, ϕ_p, at different counterion concentrations, m_e, for partially neutralized polyvinylbenzoic acid (PVB) and polyacrylic acid (PA)

PVB ($\alpha = 0.88$)		PA ($\alpha = 0.84$)	
m_e [mol kg^{-1}]	ϕ_p	m_e [mol kg^{-1}]	ϕ_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		

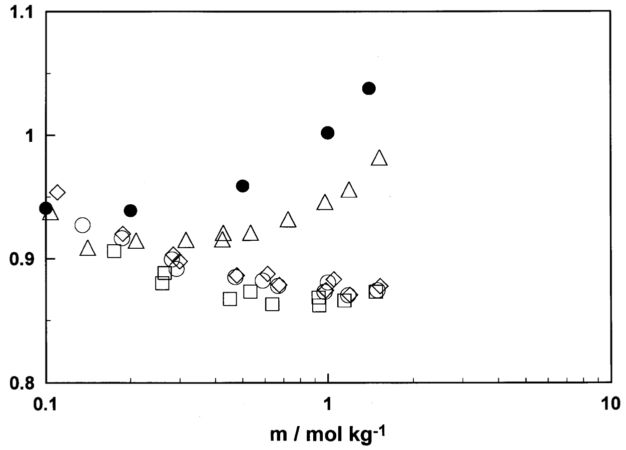

Fig. 4 Osmotic coefficients, ϕ, of low molecular electrolytes for TMACl, MAHCl, EAHCl, NaES, and NaAC as a function of concentrations m. ○: TMACl; □: MAHCl; ◇: EAHCl; △: NaES; ●: NaAC taken from the literature [30]

NaES and NaAC increased with m. In the concentration range $m > 0.2$, the ϕ values were in the following order: NaAC > NaES > MAHCl ≈ EAHCl ≈ TMACl. Large ϕ values correspond to the weak attractive interaction between ionic moiety and counterions. Judged from the results of monomer analogs, the interaction of sulfonate group with counterions is weak. This has caused the ϕ_p value for NaPSS the greatest among others when combined with the large polyion radius. The ϕ_p value 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 ϕ_p value for NaPA is much greater than the prediction from the polymer radius alone due to weak interactions between carboxylate groups and sodium ions.

Discussion

We put the charge density parameter $\lambda = 4.5$ for the estimation of the osmotic coefficients. Although this value of λ is much greater than the value corresponding to a fully stretched chain conformation, $(\phi_p)_{PB}$ values for $\lambda = 4.5$ are in good agreement with the observed values. The dielectric constant in the polymer domain ε_r is assumed to be equal to that of water ε_{water} in the estimate of $\lambda = 2.85$. However, there is good reason to believe that the dielectric constant in the vicinity of the polyion is lower than that of bulk water, owing to the hydration of ions, which would mean that $\varepsilon_r < \varepsilon_{water}$ [25]. Consequently, l_B $[= e_0^2/(4\pi\varepsilon_0\varepsilon_r kT)]$ and hence λ can be larger than 2.85. For example, instead of $\varepsilon_r = 78.5$ for $\lambda = 2.85$, we have $\varepsilon_r = 49.7$ for $\lambda = 4.5$.

We have shown that the parameter k corresponding to the fraction of the free counterion in describing the Donnan salt distribution is not equal to the observed ϕ_p value although these two quantities are closely related [15]. The difference between the k value and the observed ϕ_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 on the Donnan equilibria with added salts than the osmotic coefficients without added salts. It should be stated that $(\phi_p)_{PB}$ values calculated for $\lambda = 2.85$ are in good agreement with the parameter k [15].

Conclusion

Our results show that the ϕ_p values were strongly dependent on the chemical structures of polyelectrolyte through the polyion radius and the interaction between the ionic moiety and counterions. The osmotic pressures in polyelectrolyte solutions without added salt, which arise from the counterion contribution, is in agreement with the experimental results. We can conclude that the counterion contribution is dominant in the osmotic pressures and thus, the polymer contribution is negligible [21] in the examined regime 0.2–1.9 mol kg^{-1}. The P–B approach gave a fair prediction of the absolute values of the osmotic pressures with $\lambda = 4.5$ except for NaPA. In other words, the concentration dependence of the ϕ_p values can be explained in terms of the counterion contribution. This implies that the concentration dependence of the ϕ_p values is no evidence for the validity of the scaling theory for the osmotic pressures in the polyelectrolyte solutions without added salt.

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References

1. Manning GS (1969) J Chem Phys 51:924–933
2. Oosawa F (1971) In: Polyelectrolytes. Marcel Dekker, New York
3. Anderson CF, Record Jr MT (1980) Biophys Chem 11:353–360
4. Klein BK, Anderson CF, Record Jr MT (1981) Biopolymers 20:2263–2280
5. Stigter D (1975) J Colloid Interface Sci 53:296–306
6. Stigter D (1977) Biopolymers 16: 1435–1448

7. Shellman JA, Stigter D (1977) Biopolymers 16:1415–1434
8. Gueron M, Weisbuch G (1979) J Phys Chem 83:1991–1998
9. Gueron M, Weisbuch G (1980) Biopolymers 19:353–382
10. Weisbuch G, Gueron M (1981) J Phys Chem 85:517–525
11. Alexandrowicz Z (1960) J Polym Sci 43:337–349
12. Katchalsky A, Alexandrowicz Z (1963) J Polym Sci A1:2093–2099
13. Kakehashi R, Maeda H (1994) Rep Progr Polym Phys Jpn 37:91–94
14. Kakehashi R, Maeda H (1996) J Chem Soc Faraday Trans 92:3117–3121
15. Kakehashi R, Maeda H (1996) J Chem Soc Faraday Trans 92:4441–4444
16. Lifson S, Katchalsky A (1954) J Polym Sci 13:43–55
17. de Gennes PG, Pincus P, Velasco RM, Brochard FJ (1976) J Phys (Paris) 37:1461–1473
18. Odijk T (1977) J Polym Sci Polym Phys Ed 15:477–483
19. Skolnick J, Fixman M (1977) Macromolecules 10:944–948
20. Pfeuty P (1978) J Phys Collog 39:C2-149–160
21. Dobrynin AV, Colby RH, Rubinstein M (1995) Macromolecules 28:1859–1871
22. Odijk T (1979) Macromolecules 12: 688–693
23. Wang L, Bloomfield V (1990) Macromolecules 23:804–809
24. Ochiai H, Handa M, Matsumoto H, Moriga T, Murakami I (1985) Makromol Chem 186:2547–2556
25. Katchalsky A, Alexandrowicz Z, Kedem O (1966) In: Conway BE, Barradas RG (eds) Chemical Physics of Ionic Solutions. pp 295–346, Wiley, New York
26. Reddy M, Marinsky JA (1970) J Phys Chem 74:3884–3891
27. Marcus RA (1955) J Chem Phys 23: 1057–1068
28. Robinson RA, Stokes RH (1959) In: Electrolyte Solutions. p 30, Academic Press, New York
29. van der Maarel JRC, Groot LCA, Hollander JG, Jesse W, Kuil ME, Leyte JC, Leyte-Zuiderweg LH, Mandel M, Cotton JP, Jannink G, Lapp A, Farago B (1993) Macromolecules 26:7295–7299
30. Robinson RA (1935) J Am Chem Soc 57:1165–1168