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Polymer 43 (2002) 2975–2980

polymer

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Osmotic coefficients of polyelectrolyte solutions, measurements and correlation

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Received 26 July 2001; received in revised form 29 January 2002; accepted 4 February 2002

Abstract

Osmotic coefficient data for aqueous sodium polyanetholesulfonic acid, sodium polyacrylate and polydiallyl dimethylammonium chloride solutions were determined at 298 K by employing the isopiestic method. The measured osmotic coefficients increase with increasing concentration in the experimental concentration range (0.1–1.5 m). A molecular thermodynamic model developed previously for polyelectrolyte solutions has been used to fit the experimental data. The concentration dependence of the osmotic coefficients can be described satisfactorily. © 2002 Elsevier Science Ltd. All rights reserved.

Keywords: Polyelectrolyte solution; Osmotic coefficient; Experiment

1. Introduction

Various experimental techniques [1] have been used for the study of osmotic properties of polyelectrolyte solutions. These techniques include freezing point depression [2], boiling point elevation [3], dynamic and static vapor pressure measurement [4], osmotic pressure measurement [5,6] and the isopiestic method [7,8].

The isopiestic method has been long established as a simple but reliable method of measuring the vapor pressure or the solvent activity of a solution of non-volatile solutes. A detailed example of a well-designed isopiestic apparatus and experimental procedure was described by Scatchard et al. [9]. The precision of their experiments was rather high, and also the time for equilibration was rather short. Unfortunately, high expense of the equipment severely prohibited further development of this method. Thiessen and Wilson [10] solved this problem partly by using a 3-legged glass apparatus and a constant-temperature bath. Based on their work, Ochs et al. [11] developed a 9-legged manifold apparatus and measured the solvent activities of divalent electrolyte solutions and aqueous PEG solutions. The error was not greater than 0.02% of mean activities of water. However, it is difficult to achieve equilibrium using Ochs' method. Typically, seven or more days are needed for dilute or high viscous solutions. Lin et al. [12] went one step further to make the sample cell to rotate around an axis inclined at 45° to enhance stirring during the whole equilibration process. In addition, they applied a constant-temperature bath assembly by placing two tanks in series to reduce the temperature fluctuation not more than ±0.01 °C. The time of equilibration was 3–4 days on average and the relative error of water activities of PEG was 0.01%.

In this work, the isopiestic method developed by Ochs [11] and improved by Lin et al. [12] was adopted to determine the osmotic coefficients of aqueous sodium polyanetholesulfonic acid (NaPASA), sodium polyacrylate (NaPAA) and polydiallyldimethylammonium chloride (PDADMA-Cl) solutions. The results are fitted with a molecular thermodynamic model developed previously [13–15].

2. Experimental

2.1. Background theory

Activity and activity coefficient were often introduced to describe the non-ideal behavior of component in polyelectrolyte solutions. The solvent (water) activity, a_w, can be expressed by

$$\ln a_w = \frac{\left(\mu_w - \mu_w^0\right)}{RT} \tag{1}$$

where μ_w is the chemical potential of the solvent, μ_w^0 is the

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PII: S0032-3861(02)00119-2

standard state chemical potential of the solvent. The standard state refers to pure solvent at the same temperature and pressure as the solution [16].

Activity, however, is not sensitive at low molalities and requires several significant digits to express the behavior accurately. The practical osmotic coefficient, ϕ, was introduced to avoid this problem, which was defined as follows [17]:

$$\ln a_\mathrm{w} = -0.001\nu_i m_i \phi M_\mathrm{w} \tag{2}$$

Here, ν_i is the stoichiometric coefficient of solute i, m_i is the molality of solute i, and M_w is the molar weight of the solvent (water).

An isopiestic apparatus contains two or more solutions in contact with each other through the vapor space and in thermal contact through some conducting medium. The vapor space is evacuated to contain only solvent vapor and the solutions approach equilibrium by transferring solvent mass through the vapor phase. The chamber containing the solutions is kept at isothermal conditions at specific temperature until thermodynamic equilibrium is reached.

At equilibrium, the chemical potentials of the solvent in each of the solutions in the closed system are identical

$$\mu_\mathrm{w}^1 = \mu_\mathrm{w}^2 = \cdots = \mu_\mathrm{w}^n \tag{3}$$

where μ_w is the chemical potential of the solvent in each solution of 1 to n. When equilibrium is established in the isopiestic apparatus all phases share the same activity:

$$\ln a_\mathrm{w}^1 = \ln a_\mathrm{w}^2 = \cdots = \ln a_\mathrm{w}^n \tag{4}$$

Therefore, if the activity of the solvent is known for one solution, it is known for all solutions, and by measuring equilibrium concentrations the osmotic coefficient can be calculated for the unknown solutions.

$$\phi_\mathrm{p} = \nu_\mathrm{s} m_\mathrm{s} \phi_\mathrm{s} / \nu_\mathrm{p} m_\mathrm{p} \tag{5}$$

where the subscripts s and p represent salt and polyelectrolyte, respectively. It should be noted here that since m_p is the concentration of polyelectrolyte monomer (monomol/kg water), ν_p is equal to unity in our calculation.

For this study, three sample solutions, one reference solution (NaCl), and one standard solution (KCl) were prepared. The initial concentration and mass of each solution should be known. Following equilibration, the solutions are weighed. The molality of each solution is calculated from the measured weight. The solvent activity and the osmotic coefficient can be obtained from the standard solution using Eqs. (4) and (5). We choose the correlation of Hamer and Wu [17] to represent the KCl standards. The reference solution is used to check the reliability of the experiments and calculate experimental errors.

2.2. Materials

The three polyelectrolyte samples, sodium polyanethole-sulfonic acid (NaPASA, yellow powder), sodium polyacrylate (NaPAA, 45% solution in water) and polydiallyl dimethylammonium chloride (PDADMA-Cl, 20% in water), were all purchased from Aldrich Co. The average relative molar mass of NaPASA was determined to be 80,000–120,000 (Quattro ESI by Shanghai Organic Chemistry Institute). The relative molar mass of NaPAA and PDADMA-Cl are 1200 and 100,000–200,000 as purchased, while the densities of NaPAA and PDADMA-Cl are 1.32 and 1.04, respectively.

The salts, KCl and NaCl, used in this work were dried in a vacuum oven overnight at above 130 °C before dissolution. All salts were analytical reagents and used without further purification. Double distilled deionized water was used for the preparation of all these solutions.

2.3. Procedure

The isopiestic apparatus (the sample cell) consists of a glass multi-legged manifold with nine taper joints. It was attached to a rotating vaporization apparatus (Shanghai Medical Instr. Co., ZFQ-85A) and rotated around an axis inclined at 45° to enhance sample mixing during the equilibration period. The sample cell was then placed in a double-layer constant-temperature tank constructed in this laboratory. In order to minimize the temperature gradient inside the sample tank (the inner one), two temperature controllers were used to control the temperature of both the tanks. The temperature in the inner tank can be controlled at 298 ± 0.01 K.

At the beginning of the experiment, an appropriate amount of each solution constituent was weighed accurately into the solution flasks using an electrical balance (Mettler Toledo Instr. Ltd., AB104-N) accurate to ±0.1 mg. The total mass of the solution in each flask was designed to be about 1 g at equilibrium. The ground-glass surfaces of each flask were slightly coated by silicone vacuum grease. They were then fitted to the manifold. Typically, the nine flasks of the experimental apparatus were used as follows. Three flasks (including the central flask) contained the standard KCl solutions, others, the solutions to be measured, two for one sample.

After assembly, the manifold was slowly evacuated to remove the air and the dissolved gas in the sample solutions using a vacuum pump. It was necessary to evacuate the manifold several times because the dissolved air was slowly released from the solutions. The sample cell was then placed inside the tank and connected to the rotation axis to rotate for 3–4 days.

When equilibrium was reached, heated air (warmer than 298 K) was admitted to the cell to prevent the condensation of water on the inner walls of the apparatus. The flasks were then removed from its arms, wiped free of grease, covered with a ground-glass stopper and weighed. The molality of each solution was calculated from the measured weight. The osmotic coefficient of the sample solution was calculated

Table 1
Estimation of equilibration time

Flask	Sample	Initial concentration (mol/kg solution)	Final concentration (mol/kg H_2O)		
			3 days	4 days[a]	5 days
1	KCl	0.100	0.106	0.142	0.159
5		0.0508	0.107	0.142	0.159
9		0.0514(0.0499)	0.107	0.143	0.158
2	NaCl	0.0913	0.103	0.140	0.158
4		0.0534	0.106	0.139	0.156
7		0.0370(0.0442)	0.100	0.138	0.156
3	NaPAA	0.220	0.388	0.510	0.571
6		0.114(0.113)	0.390	0.514	0.566
8		0.268	0.386	0.520	0.566

[a] The initial concentrations corresponding to those in parenthesis.

from the molalities of the sample solution and of the standard (KCl) solution and from the osmotic coefficient of the standard solution. The activity and osmotic coefficient of the standard KCl solution was calculated from the literature data [17].

2.4. Estimation of errors and accuracy

The accuracy of this method depends on temperature stability, sample mixing during the equilibration period, the time allowed for the equilibrium and the solvent vaporization after removed from the arms. Besides, one major uncertainty in the absolute mass of each flask is the presence of trace amounts of vacuum grease. In order to minimize the random error in the experimental method described here, following ways were applied: the series-assembled water-bath to ensure the temperature stability, the rotation of sample cell to achieve sample mixing during the whole equilibration period, a tight cap to prevent the vaporization of the solvent after the flasks were detached.

To illustrate the accuracy attained and the equilibration time required, a preliminary run is performed with KCl, NaCl and NaPAA solutions. The results are shown in Table 1. It is shown that the equilibrium was attained in 3–4 days for 0.1 M KCl. In the light of these preliminary results, the concentration after 4-day equilibration was accepted as reliable in the present work. Table 2 contains the data that were used to estimate the error in the observed solvent activities. The error was calculated by finding the average water activities of NaCl reference solutions, and comparing it with that of the KCl standard solutions using the Hamer and Wu correlation [17]. For the entire set of experiments, the overall average error in the water activities was about ±0.01%.

Table 3 lists the experimental osmotic coefficients of aqueous NaPASA, NaPAA and PDADMA-Cl solutions.

3. Correlation

3.1. Introduction

Due to the long-range electrostatic forces and the complicated polyion conformation, polyelectrolytes are among the most difficult subjects to understand. Extensive efforts have been made to develop theories and models for these complex systems. Prevailing theories, such as the counter-ion-condensation formalism (CC) developed by Manning [18], the Poisson–Boltzman approach (PB) [19] and its modified form (MPB) [20], are mostly based on the cylindrical cell model and rigorous only at infinite dilution. One feature common to all polyelectrolyte solutions is the intimate association between counterions and polyion. Nagvekar et al. [21] suggested an excess Gibbs free energy model, which is a combination of NRTL equation and Manning's approach. Dolar and Bester [22] used a square-well potential to characterize the non-Coulombic force and combined it with PB theory to predict the relative activity coefficient of barium polystyrenesulfonate (BaPSS).

Recently, increasing attention was given to the flexible-chain model of polyelectrolyte in which polyions are more reasonably considered as flexible charged hard-sphere chains. Blum et al. [23] used the WOZ integral-equation theory [24] to describe the polymerization of the monomer ions, however, no numerical results were presented in their work. Jiang et al. [13,14] adopted a statistical association scheme to account for the contribution of chain-formation to the excess Helmholtz energy. Their results are consistent with MD data [25]. Using statistical association fluid theory (SAFT), Cai et al. [15] treated the short-range non-Coulombic

Table 2
Some isopiestic standard solutions used to estimate experimental errors

Set No.	KCl (mol/kg H_2O)	a_w	ϕ_{KCl}	NaCl (mol/kg H_2O)	a_w	ϕ_{NaCl}	ϕ_{NaCl} (cal.)	Relative error (%)
1	0.04794	0.9984	0.9413	0.04753	0.9984	0.9451	0.9494	0.47
2	0.05028	0.9983	0.9403	0.04970	0.9983	0.9441	0.9513	0.76
3	0.05884	0.9980	0.9372	0.05848	0.9980	0.9414	0.9429	0.17
4	0.1421	0.9953	0.9197	0.1390	0.9954	0.9281	0.9402	1.30
5	0.1585	0.9948	0.9176	0.1559	0.9948	0.9265	0.9328	0.68
6	0.2297	0.9925	0.9108	0.2238	0.9926	0.9227	0.9346	1.29
Average relative error (%)								0.78

Table 3
Osmotic coefficients ϕ_p of polyelectrolyte solutions without salt added, at different polyion concentrations m_p

KCl	NaPASA		PDADMA-Cl		NaPAA	
m_s (mol/kg H_2O)	m_p (monomol/kg H_2O)	ϕ_p	m_p (monomol/kg H_2O)	ϕ_p	m_p (monomol/kg H_2O)	ϕ_p
0.04794	0.1852	0.4873	0.1716	0.5259	–	–
0.05028	0.2012	0.4900	0.1750	0.5403	–	–
0.05884	0.2212	0.4980	0.2054	0.5370		
0.07142	0.2675	0.4984			0.2710	0.4920
0.08143	0.2994	0.5062	0.2809	0.5395		
0.09319	0.3241	0.5337	0.3164	0.5467	0.3459	0.5000
0.1312			0.4353	0.5553	0.4796	0.5040
0.1421	–	–	–	–	0.5146	0.5079
0.1585	–	–	–	–	0.5659	0.5140
0.2297	0.6824	0.6132	0.7066	0.5927	–	–
0.3136	0.9449	0.6012	0.9514	0.5971	1.0751	0.5284
0.4534	1.2835	0.6366	1.2877	0.6346	1.5142	0.5396

interactions as stickiness between counterions and monomers of polyions and obtained explicit expressions for thermodynamic properties of the polyelectrolyte solutions.

In this work, we adopted the molecular thermodynamic model developed previously [13–15] by using statistical association scheme to treat the stickiness between polyions and counterions. The osmotic coefficients of three polyelectrolyte solutions were analyzed using the proposed model. Model parameters from regression data are used to fit the properties of the polyelectrolyte solutions.

3.2. Fitting procedure

Similar to our previous work, the polyions are modeled as freely tangent-jointed charged hard-sphere chains with chain length l, segment density ρ_m, hard-core diameter σ_m and segment charge $z_m e$ (e is the elementary charge). Also, there are counterions with density ρ_c, diameter σ_c and charge $z_c e$. All of them are embedded in a continuum medium with a certain permittivity ε. The whole system is electrically neutral

$$\sum_{i=0}^{K} \rho_i z_i = 0 \tag{6}$$

To treat the short-range non-Coulombic force, the sticky-sheild model with a δ-form sticky interaction at contact between monomers of polyion and counterions is adopted. The total residual Helmholtz energy is expressed by two contributions, a charged hard-sphere chain term as a reference and a sticky term

$$A^{\mathrm{r}} = A^{\mathrm{r}}(\mathrm{ref}) + \Delta A(\mathrm{sticky}) \tag{7}$$

The reference term can be further separated into three contributions

$$\frac{\beta A^{\mathrm{r}}(\mathrm{ref})}{V} = \frac{\beta A^{\mathrm{r(hs)}}}{V} + \frac{\beta \Delta A^{(\mathrm{e})}}{V} + \frac{\beta \Delta A^{(\mathrm{chain})}}{V} \tag{8}$$

where the first one (hs) is a hard-sphere term derived by Mansoori–Carnahan–Starling–Leland equation of state [26], it is a function of densities and diameters ρ_m, σ_m, ρ_c and σ_c. The term (e) is an electrostatic term obtained by MSA theory of Blum [27]. To estimate the electrostatic contribution, besides ρ_m, σ_m, ρ_c and σ_c, we need charge z_m, z_c, and permittivity ε. The third (chain) is a chain connectivity term expressed by

$$\frac{\beta \Delta A^{(\mathrm{chain})}}{V} = -\rho_m (1 - 1/l) \ln y_{\mathrm{mm}}(\sigma_m) \tag{9}$$

Here we need a two-particle cavity correlation function between contact ionic segments $y_{\mathrm{mm}}(\sigma_m)$, which is estimated again by the Blum theory [27].

The sticky term is expressed by

$$\frac{\beta \Delta A(\mathrm{sticky})}{V} = \rho_m \ln(1 - \alpha_m) + \rho_c[\alpha_c + \ln(1 - \alpha_c)] \tag{10}$$

where α_m and α_c are determined by the sticky parameter τ_{mc}, which measures the strength of the stick interactions.

The osmotic pressure Π is then calculated by thermodynamic equation

$$\Pi = -\left(\frac{\partial A}{\partial V}\right)_T = -\left(\frac{\partial A(\mathrm{i.g.})}{\partial V}\right)_T - \left(\frac{\partial A^{\mathrm{r}}(\mathrm{ref})}{\partial V}\right)_T - \left(\frac{\partial \Delta A(\mathrm{sticky})}{\partial V}\right)_T \tag{11}$$

where A(i.g.) is the contribution of the ideal gas.

The osmotic coefficient is calculated by

$$\phi = \beta \Pi / \rho \tag{12}$$

For details of the expressions refer to Refs. [13–15].

To make comparison with experimental data, several considerations should be taken into account. Firstly, a transformation should be made from molality (monomer mole per kilogram solvent) used as concentration unit in the experimental work into amount-of-substance concentration (monomer mole per cubic meter). Secondly, since most experimental solutions are at medium or low concentration and the apparent volume of the polyelectrolyte does not vary

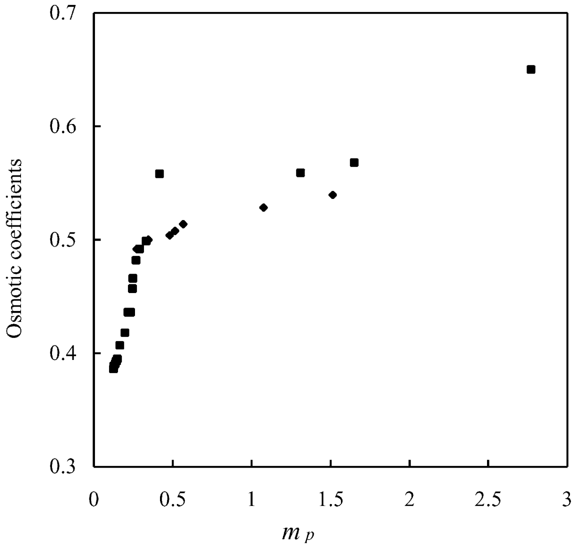

Fig. 1. Comparison between the experimental osmotic coefficients of NaPAA solutions (diamonds) with reference data (squares).

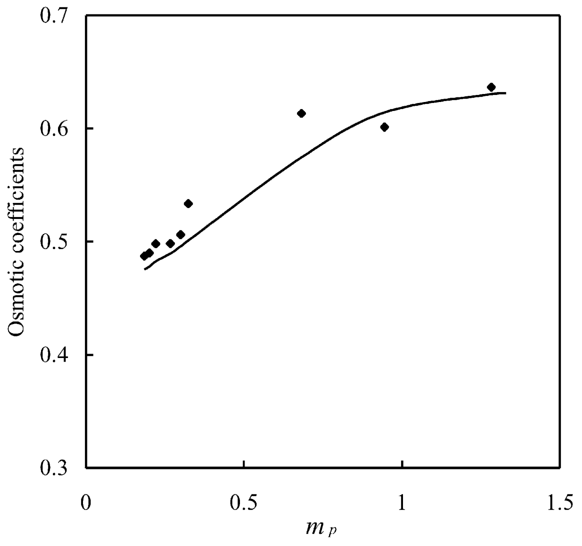

Fig. 2. Osmotic coefficients of NaPASA solutions. Line: calculated results by molecular thermodynamic model with parameters $\sigma_m = 1.29$ nm, $z_m = -3.5$ and $\tau_{mc}^{-1} = 60.8$. Diamonds: experimental data.

sharply with concentration, we can then use the infinite dilute apparent volume to calculate the amount-of-substance concentration. The volumetric data for this transformation are taken from Refs. [28,29]. Thirdly, for the diameter of ions, we adopt the solvated-ion value as those used by Ball et al. [30], for Na^+ and Cl^-, $\sigma_{Na^+} = 0.352$ nm, $\sigma_{Cl^-} = 0.36$ nm. The three model parameters: the segment diameter of polymer chain σ_m, the charge of a segment z_m, and the sticky parameter τ_{mc}^{-1} are obtained by fitting the experimental data. The chain length l is calculated by $l = z_{mono}\bar{M}/(z_m M_{mono})$, where z_{mono} and M_{mono} are the charge and molar mass of the monomer, respectively, $\bar{M}$ is the average molar mass of the polyion.

4. Results and discussions of experiments and fits

Table 2 contains the experimental osmotic coefficient data for the NaPASA, PDADMA-Cl, NaPAA soltuions. Generally, the measured osmotic coefficients increase with increasing concentration. This tendency is the same as previously found [4,5]. In the polyelectrolyte solutions, the osmotic coefficients were strongly dependent on the chemical structures of polyion and the interactions between ions. According to Manning's theory [18], counterions condensation takes place at infinite dilution. In this concentration range, the ϕ_p values decrease with increasing polyion concentration. However, this decreasing tendency has not been shown in our experiment because of the limitation of experimental techniques. In the semi-dilute and high concentration solutions, the effect of counterion-condensation diminishes with increasing concentration while the volume effect is dominant.

As shown in Table 2, the ϕ_p values decrease in the order PDADMA-Cl > NaPASA > NaPAA in the concentration range examined. The ϕ_p order between polyanions (NaPASA and NaPAA) can be explained by the difference in the volume occupied by polyions. While the osmotic coefficients of polyanions (NaPASA and NaPAA) are much smaller than that of polycation (PDADMA), the result might be attributed partly to the hydrated radii of counterions ($Cl^- > Na^+$) and partly to the degree of the electrostatic interaction between polyions and counterions. Unfortunately, there are no experimental data of NaPASA and PDADMA-Cl solutions in literature, so it is impossible for us to compare our results with literature data. In Fig. 1, the data of NaPAA solution is compared with the literature data of Ise and Okubo [31]. There is a reasonable agreement

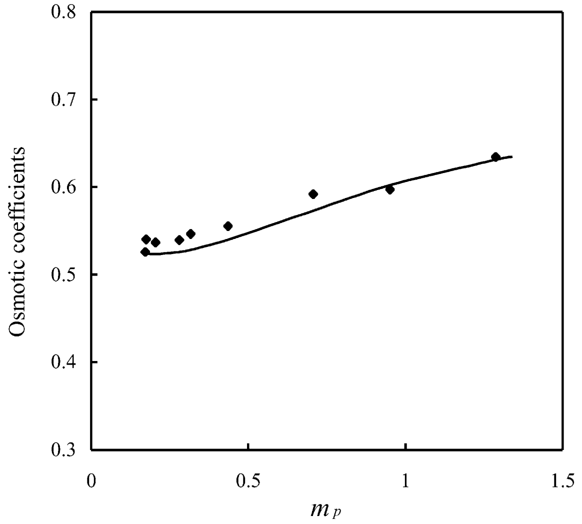

Fig. 3. Osmotic coefficients of PDADMA-Cl solutions. Solid line: calculated results by molecular thermodynamic model with parameters $\sigma_m = 0.98$ nm, $z_m = 2.5$ and $\tau_{mc}^{-1} = 30.3$. Diamonds: experimental data.

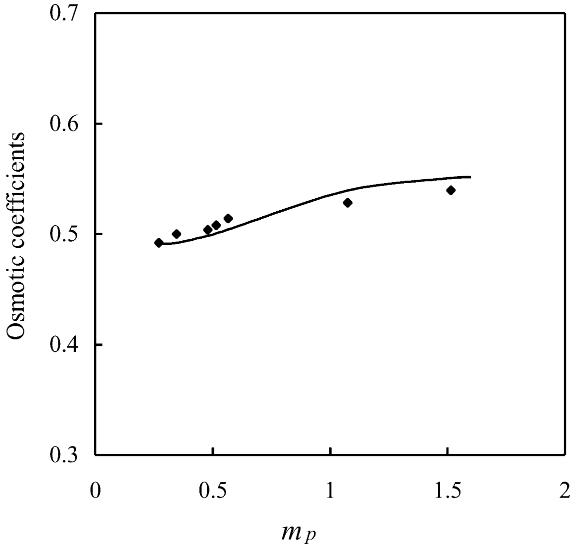

Fig. 4. Osmotic coefficients of NaPAA solutions. Solid line: calculated results by molecular thermodynamic model with parameters $\sigma_m = 0.96$ nm, $z_m = -2.5$ and $\tau_{mc}^{-1} = 40.5$. Diamonds: experimental data.

between this research and that of Ise and Okubo. The discrepancy can be explained reasonably by a difference in charge density between the NaPAA samples employed.

Figs. 2–4 show comparisons between experimental osmotic coefficients of these polyelectrolyte solutions and calculated results by the flexible-chain model. The figures indicate that the osmotic coefficients of the polyelectrolyte solutions can be satisfactorily described by this model in the concentration range of this work. However, it should be mentioned that for low concentrations (monomer concentration less then 0.1 mol/dm^3) the applied model gives results much different from experimental results [15]. The reason is probably that the reference system in this work is partly described by the MSA theory of electrolyte solutions. The electrostatic force between counterion and polyion is simplified and the associative action of many counterions has not been adequately accounted for.

5. Conclusions

The investigation of polyelectrolytes in salt free aqueous solutions has proved to be particularly difficult, giving rise to some diverging results. A part of the lack of agreement and reliability may be due to the presence of ionic residues in the solutions.

In this work, an improved isopiestic method was used to determine the osmotic coefficients of three polyelectrolyte solutions. The experimental data are fitted with a molecular thermodynamic model of polyelectrolyte solutions developed previously, in which the polyion is modeled as a flexible charged hard-sphere chain with additional stickiness between polyion and counterions. The model correctly describes the osmotic data in the concentration range under study.

Acknowledgements

This work was supported by the National Science Foundation of China (Project No. 29736170, No. 29876006).

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