

In conclusion it ought to be mentioned that Box, *et al.*,<sup>19</sup> have obtained evidence for the presence of radical-ions in single crystals of cysteine hydrochloride irradiated with ultraviolet light at 77°K. Although the possibility of radical-ion production in irradiated cysteine itself cannot be ruled out, it would appear unlikely that CySBz and CySSBz are produced *via* radical-ion reactions in 0.1 M HCl, where rapid neutralization with hydrogen or chloride ions would occur.

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## The Osmotic Pressure of Polyelectrolyte in Neutral Salt Solutions

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Most theories<sup>1,2</sup> on the second virial coefficient ( $A_2$ ) of spherical colloidal electrolytes so far published predict that the second virial coefficient is proportional to  $1/C_s^0$ , where  $C_s^0$  is the concentration of added salt in mol/l. in the solvent with which the sample solution is in equilibrium. Moreover, the second virial coefficient is believed to be independent of molecular weight. These predictions arise from the fact that electroneutrality must be fulfilled in both the sample solution and the solvent, and, hence, the second virial coefficient is determined primarily by the Donnan distribution of diffusible ions between them. In practice, there were several experimental studies<sup>3-5</sup> which supported the speculation. Our recent light scattering experiment using a linear polyelectrolyte,<sup>6</sup> however, showed that the invariance of  $A_2$  with molecular weight and the linearity between  $A_2$  and  $1/C_s^0$  holds only at low ionic strengths, whereas at high ionic strengths  $A_2$  depends on molecular weight and is linear with respect to  $1/\sqrt{C_s^0}$ .

The second virial coefficient of linear polyelectrolytes in the salt-added system is determined not only by the electrostatic interaction between ions, but also by the intermolecular interaction of polyion coils.<sup>6-8</sup> We concluded<sup>6</sup> that the deviation from the linear plot of  $A_2$  vs.  $1/C_s^0$  as well as the molecular weight dependence of  $A_2$  observed at high ionic strengths arises from the

intermolecular interaction between coils. If the concentration of added salt is low, the expansion of the polyion coil is so high that the effect of intermolecular interaction on  $A_2$  becomes practically independent of both molecular weight and added-salt concentration. Consequently,  $A_2$  appears to be linear with respect to the reciprocal salt concentration and independent of molecular weight.

An ambiguity concerning the above conclusion still exists since in osmotic pressure measurements reported in the literature,<sup>9</sup>  $A_2$  was always proportional to  $1/C_s^0$  though not many measurements at high salt concentrations were made. We speculated<sup>6</sup> that the polymer concentration used in the osmometry may be too high to obtain  $A_2$ .

The purpose of this work is to carry out careful measurements of osmotic pressure both in salt-free and salt-added systems of the same sample as used for light scattering and to compare the second virial coefficients determined by both methods.

## Experimental Section

**Polymer Sample.** The F-8 fraction of sodium poly(styrenesulfonate) [Na-PS] (mol wt =  $4.3 \times 10^5$ ) used in a previous investigation<sup>6</sup> was selected in this study. A measured amount of the sample was dissolved into NaCl aqueous solutions of specified concentrations in volumetric flasks.

**Osmometer.** The most important criterion in the osmometry of polyelectrolyte solutions in salt-added systems is to confirm the complete Donnan equilibrium between the sample solution and solvent separated by a membrane. To this end, a Zimm-Myerson osmometer<sup>10</sup> was modified by incorporating two magnetic stirrers inside the cell. They were swung as pendulums with a magnet operated from outside of the cell. To avoid the contamination of the solution with ions, the whole cell was made of poly(methyl methacrylate) resin, 6-10 Nylon, and glass. A stainless steel rod in the original design was replaced by a long-stem glass syringe, and the glass capillaries were fastened to the cell with synthetic rubber stoppers.

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**Table I:** Number-Average Molecular Weight, Second and Third Virial Coefficients of Na-PS-Aqueous NaCl Solution Determined from Osmotic Pressure Measurements

$C_s^\circ$ mol/l.	$(\frac{\pi}{C})_0$	$M_n \times 10^{-5}$	$\Delta_2$	$\Delta_3$	$\Delta_3/\Delta_2^2$	$A_2 \times 10^4$ , cc, mol $\frac{g^2}{(OS)}$	$A_3 \times 10^2$	$A_2 \times 10^4$ , cc mol $\frac{g^2}{(LS)}$
0.500	0.792	3.194	0.513	0.118	0.448	1.60 <sup>a</sup>	1.45 <sup>b</sup>	0.369
0.100	0.776	3.259	1.428	1.258	0.616	4.38 <sup>a</sup>	4.36 <sup>a</sup>	3.86
0.050	0.792	3.194	2.20	2.50	0.516	6.88 <sup>a</sup>	6.47 <sup>b</sup>	7.82
0.020	0.792	3.194	3.95	9.40	0.602	12.36 <sup>a</sup>	12.38 <sup>b</sup>	29.43
0.010	0.792	3.194	6.65	26.60	0.601	20.82 <sup>a</sup>	20.59 <sup>b</sup>	83.28
0.005	0.792	3.194	11.35	78.88	0.612	35.53 <sup>a</sup>	35.45 <sup>b</sup>	246.96
(Average) 3.204								

<sup>a</sup> Evaluated by the procedure of Stockmayer and Casassa. <sup>b</sup> Evaluated assuming  $g = 5/8$ .

**Measurements of Osmotic Pressure.** When the polymer concentration was low, the static equilibrium method was employed. When the pressure was higher than 20 cm H<sub>2</sub>O in salt-free systems, a dynamic method with a mercury manometer system was employed. Both the osmometer and the manometer were immersed in a thermostat regulated at  $25 \pm 0.001^\circ$ . Membranes used were gel Cellophane No. 600 and conditioned by the standard method.<sup>11</sup> The membrane dissymmetry pressures observed were smaller than  $0.01 \pm 0.005$  cm H<sub>2</sub>O and this correction was applied to all measured osmotic pressures. After the cell was filled with solution and temperature equilibrium was reached, the pressure change was recorded. Usually, the initial steep rising of pressure was observed, then it fell with time elapsed, and a steady state was reached. At this stage an inhomogeneity in the concentrations of both polymer and NaCl inside the cell was diminished by swinging the magnetic stirrers. Then, the second run followed, and the equilibrium pressure was determined. The inside solution was stirred again and the outside solvent was refreshed. Then run III was repeated. The osmotic pressures thus determined in both runs II and III agreed with each other within the experimental error. This procedure was employed in all measurements to obtain really reliable osmotic pressures.

## Results

The relationship between  $\pi/C$  and  $C$  obtained for the sample in NaCl solutions of various concentrations is shown in Figure 1. The plots are not straight lines but curve upward. In order to determine the second virial coefficient ( $A_2$ ), we assumed that the quadratic function, eq 1, is adequate to express  $\pi/C$  of polyelectrolytes in salt solution

$$(\pi/C) = (\pi/C)_0 [1 + \Delta_2 C + \Delta_3 C^2] \quad (1)$$

where  $(\pi/C)_0 = RT/M_n$ ,  $\Delta_2 = A_2 M_n$  and  $\Delta_3 = g \Delta_2^2$ .

First, the limiting value of  $\pi/C$  was determined by extrapolation to infinite dilution from measurements in 0.500 M solution, in which  $\Delta_2$  is low. Then, adopting the procedure of Stockmayer and Casassa,<sup>12</sup> the

second and third virial coefficients were evaluated from a plot of the quantity

$$[(\pi/C)/(\pi/C)_0 - 1]/C$$

against  $C$ . Very good straight lines were obtained at each ionic strength, and  $\Delta_2$  and  $\Delta_3$  were determined from intercept and from slope of the lines, respectively. The results are summarized in Table I. The values of  $g = \Delta_3/\Delta_2^2$  are also shown in Table I, column 6. It is observed that  $g$  is always smaller than  $g = 5/8$ , and gradually decreases with the increase of  $C_s^\circ$ . However,  $g$  thus determined is not much smaller than  $5/8$  at lower ionic strengths since the polyion is expanded markedly. Even if we assume  $g = 5/8$  and adopt Flory's procedure<sup>13</sup> to determine  $(\pi/C)_0$  and  $\Delta_2$ , that is, even if we determine  $(\pi/C)_0$  and  $\Delta_2$  by comparing the calculated plot of the form  $\log [I + \Delta_2 C + 5/8 \Delta_2^2 C^2]$  against  $\log \Delta_2 C$  with the experimental results, no appreciable difference is caused in the values of  $A_2$  as indicated in Table I, column 8.

The values of  $A_2(LS)$  reported previously were determined from the initial slope of  $Kc/R_0$  vs.  $C$  plots. In order for comparisons with  $A_2(OS)$ , the light scattering data reported were treated in the same way and the results are shown in Table I, column 10.  $A_2(LS)$  at  $C_s^\circ = 0.005$  previously reported was found to be a little overestimated, but no change need be given to the discussion in the previous paper. The values of  $A_2(LS)$  at some ionic strengths are not available but can be estimated from the data for other samples of different molecular weight, since  $A_2$  for polyelectrolytes does not depend on molecular weight except at very high ionic strengths. Remarkable agreement between  $A_2(LS)$  (column 10) and  $A_2(OS)$  (column 7) is manifest.

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In Figure 2a are shown the plots of  $A_2(\text{OS})$  vs.  $1/C_s^0$  together with  $A_2(\text{LS})$ . The linearity of  $A_2$  with respect to  $1/C_s^0$  holds over a wide range of ionic strengths, but at high ionic strengths the experimental data deviate from the linear relationship. In Figure 2b, the same data are plotted against  $1/\sqrt{C_s^0}$ . The linear relationship between  $A_2$  vs.  $1/\sqrt{C_s^0}$  appears to hold at high ionic strengths, although a careful examination of the data of both  $A_2(\text{LS})$  and  $A_2(\text{OS})$  reveals that the straight line in Figure 6 of ref 6 should have been drawn with a slightly lower slope, as shown in Figure 2b. These

From the osmotic pressure measurement of Na-PS in deionized water, the osmotic coefficient  $\phi$  was calculated according to

$$\pi(\text{obsd}) = \frac{Z+1}{M_n} \phi CRT = \phi c_p RT \quad (2)$$

where  $Z$  is the number of charges on a polyion and  $c_p$  is expressed in (equiv/l.).  $\phi$  (or  $\pi/C$ ) is also plotted against  $c_p$  (equiv/l.) or  $C$  (g/100 ml) in Figure 1. If  $c_p$  is lower than 0.005 equiv/l.,  $\phi$  gradually increases with increasing polymer concentration, while at concentrations higher than 0.005 equiv/l.,  $\phi$  is almost constant and about 0.17. The similar characteristic curves were obtained by Kern<sup>15</sup> and Takahashi and Kagawa<sup>16</sup> and Alexandrowicz<sup>17</sup> for various polyelectrolytes in water.

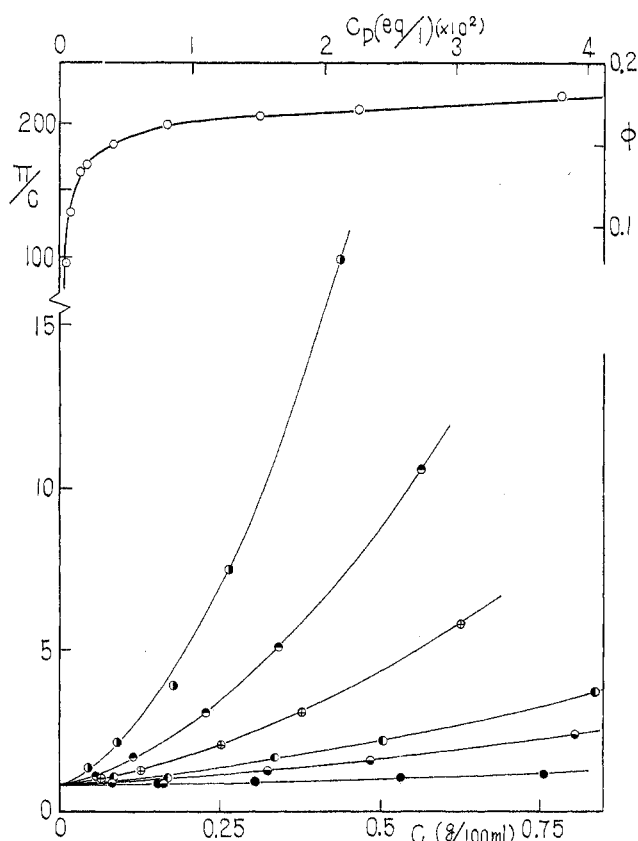


Figure 1. Plots of  $\pi/C$  vs. polymer concentration  $C$  for Na-PS (F-8) in aqueous NaCl Solutions. NaCl concn,  $\circ$ , 0;  $\bullet$ , 0.005;  $\ominus$ , 0.01;  $\oplus$ , 0.02;  $\odot$ , 0.05;  $\ominus$ , 0.1;  $\bullet$ , 0.5 M.  $\phi$  denotes the osmotic coefficient. The solid lines for salt-added systems denote the values calculated from eq 1 using the values of  $A_2$  shown in Table I and assuming  $g = 5/8$ .

experimental data appear to support our previous conclusions better than before. Alexandrowicz<sup>14</sup> presented a theory which accounts for the linear dependence of  $A_2$  on  $1/\sqrt{C_s^0}$ . Thus, we withdraw our statement that the polymer concentrations used for osmotic pressure measurements are too high to obtain reliable second virial coefficients. If we take into account the third virial coefficient in a proper way, we can determine the second virial coefficient of polyelectrolyte solution with high reliability by osmometry.

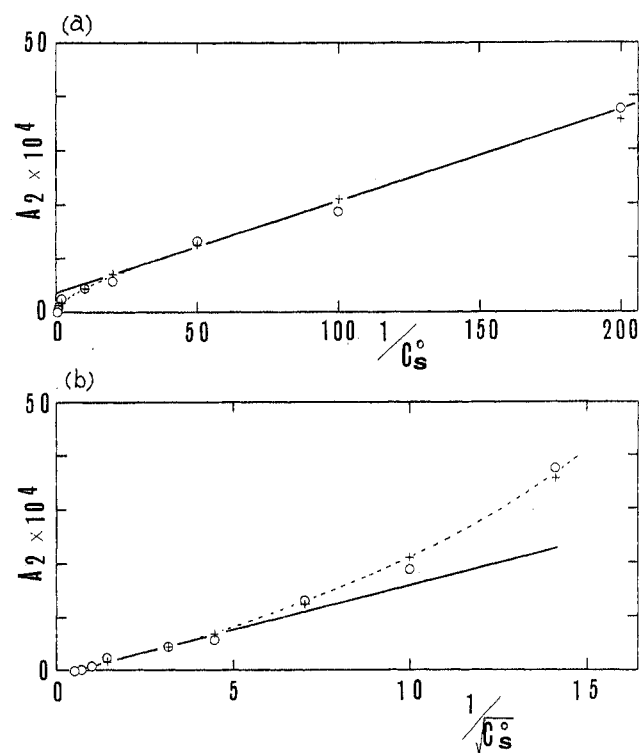


Figure 2. Plots of second virial coefficient vs. reciprocal ionic strength (a) and reciprocal square root of ionic strength (b).  $\circ$ ,  $A_2(\text{LS})$ ;  $+$ ,  $A_2(\text{OS})$ .

Moreover,  $\phi = 0.17$  is favorably compared with the average value of counterion activity coefficient ( $\gamma_\pm = 0.2$ ) evaluated from light scattering experiments previously.

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