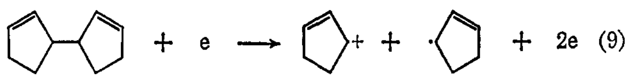
$C_5H_7^+$ and neutral C_5H_7 are formed. From $A(C_5H_7^+)$ for the process



(9)

and the relationships

$$A(R^+)_{RR} = \Delta H_f(R^+) + \Delta H_f(R) - \Delta H_f(RR)$$

and

$$I(R) = \Delta H_f(R^+) - \Delta H_f(R)$$

one can derive

$$I(R) = 2\Delta H_f(R^+) - \Delta H_f(RR) - A(R^+)_{RR}$$
$$= 7.50 \text{ v}$$

This is in good agreement with the directly measured value of 7.54 v. It would appear that both the ionic and neutral fragments in (9) have retained the cyclic structure.

Appendix

ΔH_f(3-methyl-1,4-pentadiene) was calculated to be 18.3 kcal/mole from standard data[25] for isobutane and 3-methyl-1-butene, using the method of Benson and Buss.[27] ΔH_f(3-methylcyclopentene) = 1.0 kcal/mole was calculated from ΔH_f(cyclopentene) = 7.87 kcal/mole[25] by comparison with the increment resulting from substituting CH_3 for H in comparable positions (ΔH_f(methylcyclopentane) − ΔH_f(cyclopentane) = −7.0 kcal/mole, ΔH_f(3-methyl 1-butene) − ΔH_f(1-butene) = −6.9 kcal/mole). ΔH_f(3,3′-bicyclopentenyl) was estimated in two ways: a group equivalent method[28] from cyclopentene and 3-methylcyclopentene gave 24.8 kcal/mole, and a comparison with the analogous change from propylene to 1,5 hexadiene gave 23.2 kcal/mole. The average, 24 kcal/mole, is probably correct to within ±2 kcal/mole. As recommended recently,[24] $\Delta H_f(CH_3)$ was taken to be 34 kcal/mole[29] rather than the earlier value of 32.5 kcal/mole.

[27] S. W. Benson and J. H. Buss, *J. Chem. Phys.*, **29**, 546 (1958).
[28] J. L. Franklin, *Ind. Eng. Chem.*, **41**, 1070 (1949).
[29] D. M. Golden, R. Walsh, and S. W. Benson, *J. Am. Chem. Soc.*, **87**, 4053 (1965).

Mean Activity Coefficient of Polyelectrolytes in the Ternary System Water–Sodium Polyacrylate–Sodium Chloride

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Abstract: Isopiestic vapor pressure measurements were carried out for the ternary system water–sodium polyacrylate–sodium chloride. The variation of the isopiestic ratio with the concentration fraction of an electrolyte component is generally much more pronounced in the water-polyelectrolyte–simple electrolyte system than it is in the water–simple electrolyte–simple electrolyte system. The mean activity coefficients of sodium polyacrylate and sodium chloride are obtained as functions of the concentrations of the two components. From these data, interaction parameters between polyelectrolyte and polyelectrolyte, polyelectrolyte and simple electrolyte, and simple electrolyte and simple electrolyte are obtained as a function of the polyelectrolyte concentration. The magnitude of the polyelectrolyte–polyelectrolyte interaction parameter is much larger than other parameters obtained at zero polymer concentration. The second virial coefficient of the polyelectrolyte is calculated from these interaction parameters and is in good agreement with data from other measurements.

In some previous papers from this laboratory, the mean activity coefficients of polyelectrolytes in the binary systems water-polyelectrolyte were determined by emf measurements of a concentration cell with transference[2-4] and isopiestic vapor pressure measurements.[5] These studies have revealed that the contribution of macroions to the thermodynamic properties of polyelectrolyte solutions is unexpectedly large, and a somewhat regular distribution of electric charges in the solutions can be set up by an intermacroion "linkage" through the intermediary of gegenions. Although these conclusions are important, it has been impossible to compare successfully these experimental data obtained for the mean activity coefficients with those obtained by other methods, since the experiments so far reported from other laboratories, from which the mean activity coefficient data can be derived, were mostly performed not in binary systems but in ternary systems water–polyelectrolyte–simple electrolyte. It was interesting, therefore, to extend our measurements to the ternary systems. The knowledge of these solutions, furthermore, is doubtlessly indispensable to the understanding of naturally occurring biological systems. In the present paper, the mean activity coefficients of sodium polyacrylate (NaPAA) and sodium chloride in water–NaPAA–NaCl are determined by isopiestic vapor pressure measurements. These data are compared with those of binary solutions water–

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[1] To whom inquiries should be addressed.
[2] N. Ise and T. Okubo, *J. Phys. Chem.*, **69**, 4102 (1965).
[3] N. Ise and T. Okubo, *ibid.*, **70**, 1930 (1966).
[4] N. Ise and T. Okubo, *ibid.*, **70**, 2400 (1966).
[5] N. Ise and T. Okubo, presented at the International Symposium on Macromolecular Chemistry, Tokyo–Kyoto, 1966, Preprints No. 6, p 84; *J. Phys. Chem.*, **71**, 1287 (1967).

NaPAA and ternary systems, *i.e.*, water–simple electrolyte–simple electrolyte. Furthermore, various interaction parameters between polyelectrolyte and polyelectrolyte, polyelectrolyte and simple electrolyte, and finally simple electrolyte and simple electrolyte are directly evaluated from the mean activity coefficients as functions of the polyelectrolyte and simple electrolyte concentrations. Finally the second virial coefficient of the polyelectrolyte at infinite dilution of the polymer component, frequently discussed in relation with the Donnan equilibrium, light scattering, and osmotic pressure measurements,[6,7] is obtained from these interaction parameters.

Experimental Section

Materials. The sodium polyacrylate used was kindly furnished by the Toa Gosei Chemicals Co., Nagoya, Japan; its degree of polymerization was 640 by viscometry. The sample solution was purified by passing through a column containing cation- and anion-exchange resins. The polyacid thus obtained was neutralized with sodium hydroxide by potentiometric titration. The polymer concentration was determined by these titration data. Reagent grade sodium hydroxide and sodium chloride were used without further purification. The densities of the polymer solutions and the sodium chloride solutions were determined in order to obtain their molalities. Conductivity water was used for the preparation of all the solutions.

Isopiestic Measurements. The main part of the apparatus for our isopiestic vapor pressure measurements was similar to the one described by Robinson.[8] The apparatus consisted of a desiccator containing a copper block in good thermal contact with 14 silver cups. Each cup was 1.2 cm in diameter and 2.5 cm deep, weighing about 35 g. Two cups were filled with 2 ml of a reference NaCl solution, with which a series of mixed solutions of NaPAA and NaCl of various concentration ratios was equilibrated. The total ionic concentrations of our solutions in equilibrium were approximately constant. The experiments were carried out at total ionic concentrations higher than 0.1. The 14 cups fitted in cylindrical holes arranged symmetrically in the copper block 2.5 cm thick and 13.0 cm in diameter. This block, weighing 2.4 kg, fitted into the desiccator which was placed on a table in a thermostat bath at 25 ± 0.005°. The table was moved back and forth for rapid equilibration.

The error of our isopiestic measurements was at the highest 2% of the concentration value at high polymer and total ionic concentrations. Usually it was easy to attain an average of 0.5%. These figures were obtained from the discrepancy in the equilibrium concentrations found by duplicate or repeated runs. Undoubtedly they may be quite unsatisfactory to those familiar with the measurements on simple electrolytes. It was considered, however, more than satisfactory in the present work on polyelectrolytes in the light of the comparatively large uncertainty inherent in the determination of polyelectrolyte concentrations. We note here that, in general, the isopiestic ratios, which will be given below, are much larger than those found for solutions containing simple electrolytes only and vary more sharply with polymer fraction than in the simple electrolyte cases. The comparatively low accuracy mentioned above, therefore, may be regarded as gratifying. The time required for the solutions to reach the equilibrium was found by preliminary runs to be about 3 days at high dilutions.

Results and Discussion

The following notations will be used

C_2, m_2	concentrations of NaPAA in NaPAA–NaCl solution in g/ml and in equiv/1000 g of water
m_3	molality of NaCl in NaPAA–NaCl solution
W_2	molecular weight of NaPAA
α	net valency of a macroion ($=\beta z$)
z	stoichiometric valency of a macroion
x	polymer ionic fraction $\{=(\alpha + 1)(m_2/z)/[2m_3 + (\alpha + 1)(m_2/z)]\}$
φ	practical osmotic coefficient
R	isopiestic ratio $\{=2M_3/[2m_3 + (\alpha + 1)(m_2/z)]\}$
R'	isopiestic ratio $\{=(\alpha + 1)(M_2/z)/[2m_3 + (\alpha + 1)(m_2/z)]\}$
γ_2, γ_3	mean activity coefficients of NaPAA and NaCl in a solution of total ionic concentration of $m_3 + (\alpha + 1)m_2/2z$
Γ_2	mean activity coefficient of NaPAA in a solution containing NaPAA only at a concentration M_2 (equiv/1000 g of water) with the same solvent vapor pressure as a ternary solution of total ionic concentration $m_3 + (\alpha + 1)m_2/2z$
Γ_3	mean activity coefficient of NaCl in a solution containing NaCl only at a concentration M_3 (molality) with the same solvent vapor pressure as a mixed solution of total ionic concentration $m_3 + (\alpha + 1)m_2/2z$
Subscript 2	polyelectrolyte
Subscript 3	simple electrolyte

The mean activity coefficients in the ternary system H_2O–NaPAA–NaCl were calculated using the relations derived by McKay and Perring,[9] which are particularly useful for the computation of the mean activity coefficients from isopiestic vapor pressure measurements in solutions containing two electrolytes. For polyelectrolyte and simple electrolyte mixtures, the mean activity coefficient of the polyelectrolyte can be expressed in the following manner

$$\ln \gamma_2 = \ln \Gamma_2 + \ln R' + (1 - x)^2 \times \int_0^{M_3\varphi_3} \frac{b}{M_3}\,\mathrm{d}(M_3\varphi_3) \qquad (1)$$

For a simple electrolyte the equation has the form

$$\ln \gamma_3 = \ln \Gamma_3 + \ln R + x^2 \int_0^{M_3\varphi_3} \frac{b}{M_3}\,\mathrm{d}(M_3\varphi_3) \qquad (2)$$

where R is assumed to be a function of the following type

$$R = 1 - ax - bx^2 \qquad (3)$$

In order to calculate R, R', and x, one defines that βz of total z ionizable groups of a macroion are ionized and the remaining $(1 - \beta)z$ groups un-ionized. Transference experiments for NaPAA (degree of polymerization, 1640; degree of neutralization, 0.98) showed that β is approximately equal to 0.4, independent of the polymer concentration.[10] According to Wall's experiments,[11] the addition of NaCl to aqueous solutions of NaPAA resulted only in a slight decrease of the β

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(6) (a) H. J. L. Trap and J. J. Hermans, *J. Phys. Chem.*, **58**, 757 (1954); (b) N. S. Schneider and P. Doty, *ibid.*, **58**, 762 (1954); (c) U. P. Strauss and P. L. Wineman, *J. Am. Chem. Soc.*, 80, 2366 (1958); (d) H. Eisenberg and E. Casassa, *J. Polymer Sci.*, 47, 29 (1960).

(7) (a) N. Ise and M. Hosono, *ibid.*, **39**, 389 (1959); (b) N. Ise, *J. Chem. Phys.*, **35**, 1145 (1961); (c) N. Ise, *ibid.*, **36**, 3248 (1962); (d) N. Ise, *J. Phys. Chem.*, **67**, 382 (1963); (e) N. Ise and P. Ander, *J. Chem. Phys.*, **39**, 592 (1963).

(8) R. A. Robinson, *J. Phys. Chem.*, **65**, 662 (1961).

(9) H. A. C. McKay and J. K. Perring, *Trans. Faraday Soc.*, **49**, 163 (1953).

(10) T. Okubo, Y. Nishizaki, and N. Ise, *J. Phys. Chem.*, **69**, 3690 (1965).

(11) F. T. Wall and M. J. Eitel, *J. Am. Chem. Soc.*, **79**, 1556 (1957).

Table I. Isopiestic Data of the Ternary System H_2O–NaPAA–NaCl at 25°

Set	m_2	m_3	x	R	Log γ_2[a]	Log γ_3[b]
1	0.0807	0.186	0.080	0.98_7	-0.79_5	-0.13_9
	0.0948	0.183	0.094	0.99_0	-0.79_3	-0.13_8
	0.114	0.178	0.114	0.99_6	-0.79_0	-0.13_6
	0.210	0.166	0.202	0.96_3	-0.80_5	-0.15_0
	0.359	0.139	0.341	0.94_9	-0.81_3	-0.15_6
	0.513	0.120	0.461	0.89_8	. . .	-0.18_0
	0.825	0.0641	0.720	0.87_3	-0.84_1	-0.19_3
	1.17 (M_2)	0	1.000	0.83_1	-0.85_9	-0.21_4
	0	0.200 (M_3)	0	1.00_0	-0.77_9	-0.13_4
2	0.0404	0.392	0.020	0.99_9	-0.84_4	-0.16_0
	0.0983	0.376	0.050	1.01_1	-0.84_1	-0.15_5
	0.161	0.372	0.080	0.99_0	. . .	-0.16_4
	0.188	0.364	0.094	0.99_7	-0.84_7	-0.16_1
	0.413	0.326	0.202	0.97_9	-0.85_4	-0.16_9
	0.703	0.272	0.341	0.97_0	. . .	-0.17_3
	2.22 (M_2)	0	1.000	0.89_7	-0.89_0	-0.20_7
	0	0.400 (M_3)	0	1.00_0	-0.83_1	-0.15_9
3	0.0832	0.488	0.033	0.98_9	-0.86_0	-0.17_2
	0.141	0.475	0.056	0.99_2	-0.85_9	-0.17_0
	0.211	0.459	0.084	0.99_6	-0.85_7	-0.16_9
	0.421	0.408	0.171	1.01_4	-0.84_9	-0.16_1
	0.782	0.347	0.311	0.99_1	-0.85_9	-0.17_1
	1.01	0.308	0.396	0.97_8	-0.86_5	-0.17_7
	1.28	0.246	0.510	0.99_4	-0.85_8	-0.17_0
	1.47	0.217	0.575	0.97_7	-0.86_6	-0.17_7
	1.83	0.140	0.723	0.98_6	-0.86_1	-0.17_3
	2.28	0.0731	0.862	0.94_3	-0.88_1	-0.19_2
	2.63(M_2)	0	1.000	0.94_9	-0.87_8	-0.190
	0	0.499(M_3)	0	1.00_0	-0.85_5	-0.16_7
4	0.278	1.63	0.033	1.03_2	-0.80_8	-0.16_6
	0.468	1.58	0.056	1.04_0	-0.80_1	-0.16_3
	0.700	1.52	0.084	1.04_8	-0.79_1	-0.16_0
	1.38	1.38	0.171	1.07_7	-0.76_3	-0.15_1
	2.35	1.04	0.311	1.15_2	-0.70_9	-0.12_9
	2.88	0.881	0.395	1.19_4	-0.68_1	-0.12_0
	3.45	0.662	0.510	1.28_7	-0.63_5	-0.09_9
	3.72	0.550	0.575	1.34_5	-0.60_9	-0.08_8
	4.30	0.329	0.723	1.46_3	-0.56_1	-0.07_3
	4.72	0.152	0.861	1.58_8	-0.51_9	-0.06_2
	5.14 (M_2)	0	1.000	1.69_3	-0.48_9	-0.06_3
	0	1.74 (M_3)	0	1.00_0	-0.82_9	-0.18_0
5	0.512	3.00	0.033	1.01_2	-0.57_2	-0.13_6
	0.827	2.79	0.056	1.06_2	-0.54_0	-0.11_6
	1.23	2.68	0.084	1.07_3	-0.52_5	-0.11_2
	2.36	2.28	0.172	1.14_1	-0.46_5	-0.09_0
	3.73	1.65	0.311	1.31_1	-0.36_0	-0.04_4
	4.39	1.34	0.396	1.41_6	-0.30_2	-0.02_4
	5.05	0.970	0.510	1.58_6	-0.22_6	0.00_3
	5.23	0.772	0.575	1.72_7	-0.17_6	0.02_5
	6.29	0.202	0.862	2.15_1	-0.04_6	0.03_1
	6.63 (M_2)	0	1.000	2.36_8	0	0.01_8
	0	3.14 (M_3)	0	1.00_0	-0.59_1	-0.14_1

[a] The Γ_2 value at $M_2 = 6.63$ was chosen as unity. [b] The Γ_3 values were taken from A. S. Brown and D. A. MacInnes, *J. Am. Chem. Soc.*, **57**, 1356 (1935), and R. H. Stokes and B. J. Levien, *ibid.*, **68**, 333 (1946).

values of the polyelectrolyte (degree of polymerization, 250; degree of neutralization, 0.99). The assumed $\beta = 0.4$ for the ternary system H_2O–NaPAA–NaCl seems, therefore, reasonable.

The results of our isopiestic measurements for H_2O–NaPAA–NaCl systems are given in Table I. The concentrations of NaPAA (m_2) and NaCl (m_3) in mixed solutions in isopiestic equilibrium with binary solutions of H_2O–NaPAA (M_2) and H_2O–NaCl (M_3) are given in the second and third columns. The fourth column gives the polymer ionic fraction x, and the fifth the isopiestic ratio R. The R values can be adequately represented by eq 3, which is quadratic in x. The observed values for the constants a and b of eq 3 are listed in Table II. It appears that R is a linear function of x at low total ionic concentrations. The constants a and b are compared with those of ternary systems containing simple electrolytes only, *i.e.*, H_2O–KCl–NaCl,[12]

Table II. The Parameters of Eq 3

M_3	a	b
0.200	0.18_6	~ 0
0.400	0.10_8	~ 0
0.499	0.04_4	~ 0
1.74	-0.42_7	-0.26_6
3.14	-0.92_1	-0.44_7

(12) R. A. Robinson, *J. Phys. Chem.*, **65**, 662 (1961).

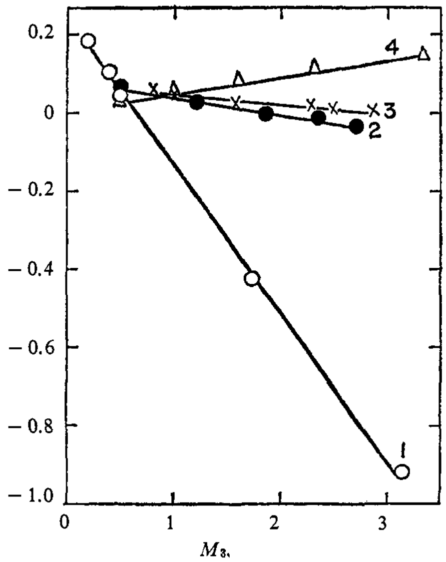

Figure 1. The *a* parameter of eq 3: ○, curve 1, H_2O–NaPAA–NaCl; ●, curve 2, H_2O–$BaCl_2$–NaCl; ×, curve 3, H_2O–$BaCl_2$–KCl; △, curve 4, H_2O–KCl–NaCl.

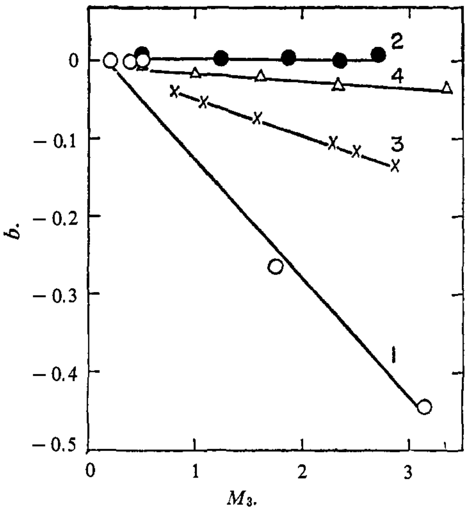

Figure 2. The *b* parameter of eq 3: ○, curve 1, H_2O–NaPAA–NaCl; ●, curve 2, H_2O–$BaCl_2$–NaCl; ×, curve 3, H_2O–$BaCl_2$–KCl; △, curve 4, H_2O–KCl–NaCl.

H_2O–$BaCl_2$–NaCl,[13] H_2O–$BaCl_2$–KCl[13] (Figures 1 and 2). For the ternary system containing a polyelectrolyte, *a* and *b* decrease more rapidly with increasing M_3 than in the case for ternary systems containing simple electrolytes alone.

The Γ_2 values in eq 1 were obtained by using the Gibbs–Duhem equation

$$\ln(\Gamma_{2_0}/\Gamma_2) = \varphi_{2_0} - \varphi_2 + 2\int_{M_{2_0}}^{M_2} \frac{1-\varphi_2}{\sqrt{M_2}}\,d\sqrt{M_2} \qquad (4)$$

where M_{2_0} is the concentration of a reference solution of NaPAA. Γ_{2_0} and φ_{2_0} represent the mean activity coefficient of the polyelectrolyte and the osmotic coefficient of the solution at M_{2_0}. The practical osmotic coefficient of the NaPAA solution (φ_2) was obtained by the condition of equal vapor pressure between the NaPAA and NaCl solutions

$$\varphi_2 = \frac{2M_3}{(\alpha + 1)(M_2/z)}\varphi_3 \qquad (5)$$

where φ_3 is the osmotic coefficient of a NaCl solution in equilibrium with a NaPAA solution.

Using the values of Γ_2, Γ_3, *R*, *R′*, *x*, and *b*, one obtains ln γ_2 and ln γ_3 given in the sixth and seventh columns of Table I, respectively. At a total ionic concentration of 0.22 (set 1), the addition of NaCl to a solution of NaPAA increases the mean activity coefficient of NaPAA; on the other hand, the addition of NaPAA to a solution of NaCl decreases its mean activity coefficient. At a total concentration of 0.51 (set 3), however, the mean activity coefficient does not significantly vary when one component is replaced by another. When the total ionic concentration is 1.45 (set 4), the addition of NaCl to a solution of NaPAA decreases the mean activity coefficient of NaPAA, whereas the addition of NaPAA to a solution of NaCl increases log γ_3. The observed dependence of the mean activity coefficient–*x* relation is qualitatively the same as the one in the case of the H_2O–$BaCl_2$–NaCl system, where, for a total ionic concentration of 1, both log γ_{BaCl_2} and log γ_{NaCl} decrease with *x*, whereas they increase for a total ionic concentration of 2.5.[13,14]

The polymer concentration dependence of the mean activity coefficient of the polyelectrolyte at constant concentration of the simple electrolyte was examined. This can be accomplished by interpolation of the data given in Table I. In previous papers,[3-5] the mean activity coefficients of polyelectrolytes (in binary systems) have been found to decrease linearly with the cube root of the polymer concentration, suggesting the existence of a "linkage" between macroions through the intermediary of gegenions.[3-5,15] The top graph of Figure 3 shows the cube-root plot for the NaPAA system studied (degree of polymerization, 640; degree of neutralization, 1.00) in water. It is seen that the cube-root rule holds for this sample with a slope of −0.97. According to a previous investigation,[3] the slope was −0.74 for NaPAA having a degree of polymerization of 1640 and a degree of neutralization of 1.00. This difference agrees well with the previous observation that the magnitude of the slope decreases with increasing degree of polymerization.[3] The cube-root plots for γ_2, the mean activity coefficient of the polyelectrolyte in the presence of added simple electrolyte, are also given in Figure 3. As seen from the figure, the cube-root rule also holds for the mean activity coefficient of the polyelectrolyte at constant concentration of simple electrolyte when m_3 is below 0.5. The rule does not apply when m_3 is 1.74 in the range of polymer concentration studied. The slopes of the cube-root plots for m_3 = 0.1, 0.3, and 0.5 were −0.16, −0.068, and −0.013, respectively, and the magnitude decreased strongly with increasing concentra-

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(13) R. A. Robinson and V. E. Bower, *J. Res. Natl. Bur. Std.*, **69A**, 19, 439 (1965).

(14) Harned's rule is known to hold for some ternary systems containing simple electrolytes only (see, for example, H. S. Harned and B. B. Owen, "The Physical Chemistry of Electrolytic Solutions," 3rd ed, Reinhold Publishing Corp., New York, N. Y., 1963, Chapter 14). The present work shows, however, that it does not hold for the H_2O–NaPAA–NaCl system. A detailed discussion on this matter will be given later.

(15) A previous observation that the single-ion activity of macroions decreases with increasing concentration [N. Ise and T. Okubo, *J. Phys. Chem.*, 70, 2407 (1966)] can also be explained in terms of the linkage.

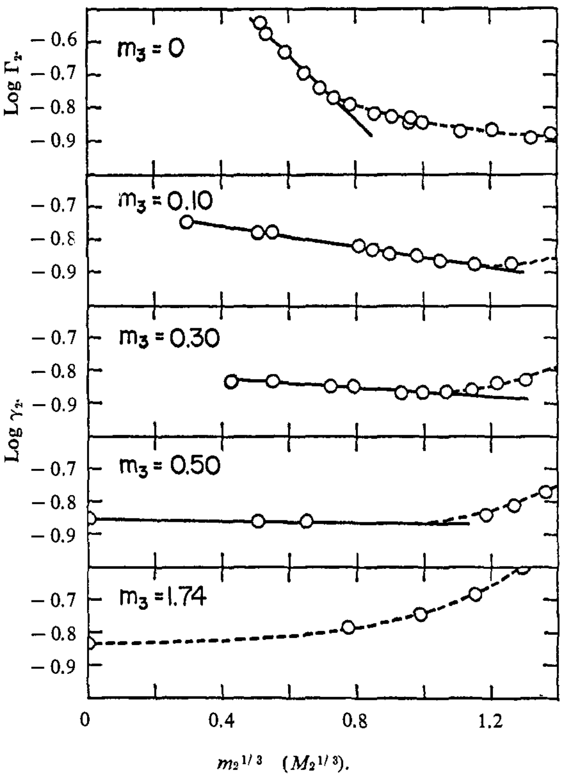

Figure 3. Cube-root plots of log Γ_2 and log γ_2 at 25°.

tion of the simple electrolyte. The upper limits of concentration, at which the cube-root rule begins to fail, are $m_2 = 0.42$, 1.64, 1.26, and 0.61 for $m_3 = 0$, 0.1, 0.3, and 0.5, respectively. With increasing m_3, the upper limit shifts first toward higher and then toward lower concentration. This tendency may be explained in the following manner; when a simple electrolyte is added to a polyelectrolyte solution, a local regularity of ionic distribution, to which the cube-root rule is attributable, may be more easily formed than in the absence of the simple salt, since the newly added sodium ions are drawn in the vicinity of macroions causing a stronger over-all attraction between macroions. The upper limit will, therefore, move toward a higher concentration range. The further addition of simple electrolyte, however, might weaken the inter-macroion "attractive" forces because the shielding effect of the simple electrolyte ions comes into effect. By the addition of the simple electrolyte the local regular distribution may be destroyed to such an extent that the cube-root rule begins to fail; *i.e.*, for sufficiently high NaCl concentrations, the rule is no longer valid.

Figures 4 and 5 show the general concentration dependences of log γ_2 and log γ_3 at constant concentration of NaCl (m_3). It appears that log γ_2 first decreases and then increases later with increasing polymer concentration (m_2) when m_3 is smaller than 0.5. On the other hand, log γ_2 increases monotonously with increasing m_2 when m_3 is larger than 0.5. For comparison, the mean activity coefficients of NaPAA at $m_3 = 0$ are presented in Figure 4 as a dotted line. The activity coefficient of the polyelectrolyte is strikingly influenced by its concentration.

From the data presented in Figures 4 and 5, it is possible to estimate interaction parameters such as

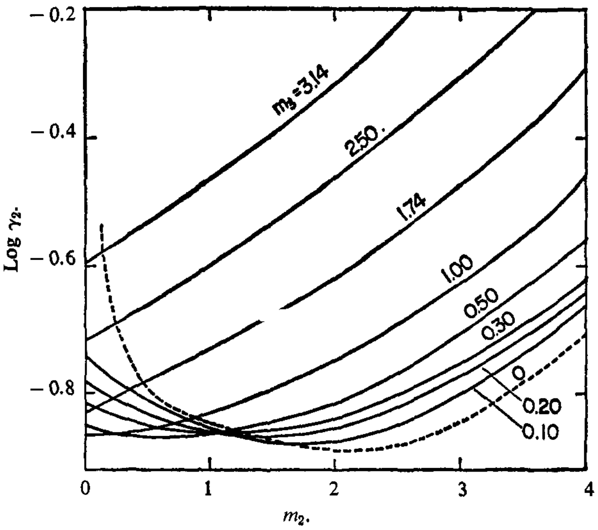

Figure 4. Polymer concentration dependence of log γ_2 at constant concentration of simple electrolyte.

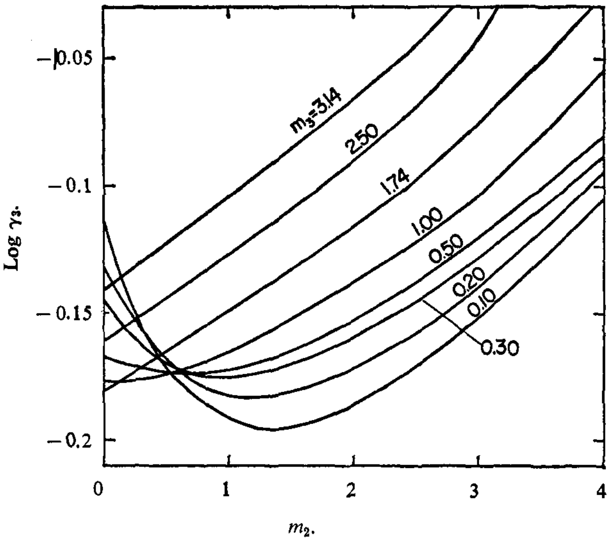

Figure 5. Polymer concentration dependence of log γ_3 at constant concentration of simple electrolyte.

β_{22}, β_{23}, and β_{33} as a function of the polymer concentration. These parameters are defined by eq 6–8. β_{22}

$$\beta_{22} = (1 + \alpha)\frac{\partial \ln \gamma_2}{\partial(m_2/z)} \tag{6}$$

$$\beta_{23} = (1 + \alpha)\frac{\partial \ln \gamma_2}{\partial m_3} \tag{7}$$

$$\beta_{33} = 2\frac{\partial \ln \gamma_3}{\partial m_3} \tag{8}$$

values obtained at constant concentration of simple electrolyte ($m_3 = 0.1 \sim 3.14$) are given in Figure 6. β_{22} increases strongly with increasing m_2 when m_3 is small, but is not sensitively affected for a large m_3. This might be due to the shielding effect of the simple electrolyte ions. β_{23} values are presented as a function of the polymer concentration in Figure 7. As in the case of β_{22}, β_{23} increases sharply with increasing m_2 for small m_3, whereas it is almost independent of m_2 when m_3 is high. Figure 8 shows that β_{33} changes significantly on the addition of polyelectrolyte when m_3

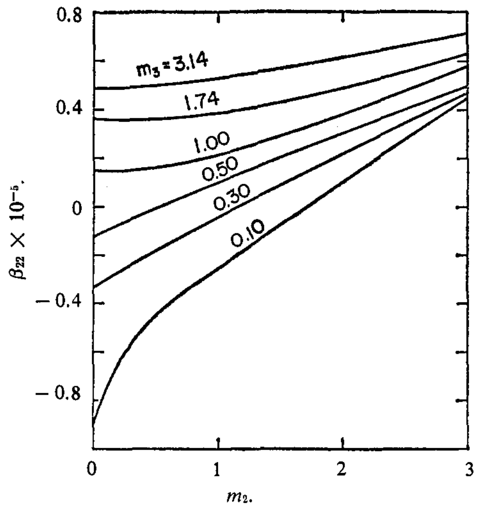

Figure 6. Polyelectrolyte–polyelectrolyte interaction parameter β_{22} against polyelectrolyte concentration.

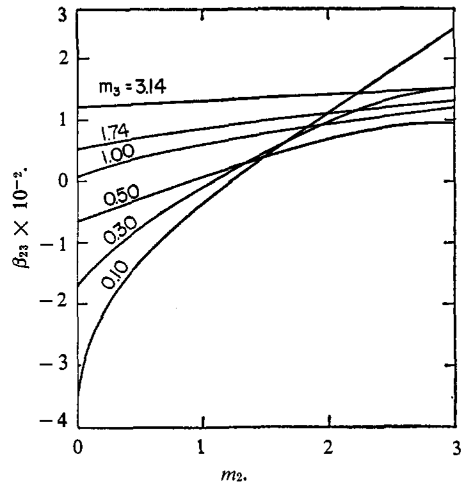

Figure 7. Polyelectrolyte–simple electrolyte interaction parameter β_{23} against polyelectrolyte concentration.

is low. On the other hand, β_{33} is rather insensitive to m_2 when m_3 is high.

In a similar manner, the interaction parameters at constant polymer concentration can be evaluated as a function of the concentration of the simple electrolyte from the data given in Table I. For reasons of space, the graphs are not given. The parameters increase strongly with m_3 when m_2 is low, whereas they are rather insensitive toward m_3 for a large m_2. It should be noted that the m_2 and m_3 dependences of the interaction parameters are qualitatively similar. This suggests that the shielding effect can be due not only to simple electrolyte ions but also to macroions and gegenions. This means that, in the theory of polyelectrolyte solutions, the electrostatic contribution of macroions and gegenions should be taken into account as well as that of simple electrolyte ions.

Using our data, the discussion can be extended to the second virial coefficient of polyelectrolytes (B_2) studied by various authors by osmotic pressure, light scattering, and membrane equilibrium measurements.[6,7] According to Scatchard,[16] B_2 can, for zero polymer concentration, be expressed in terms of β_{22}, β_{23}, and β_{33}

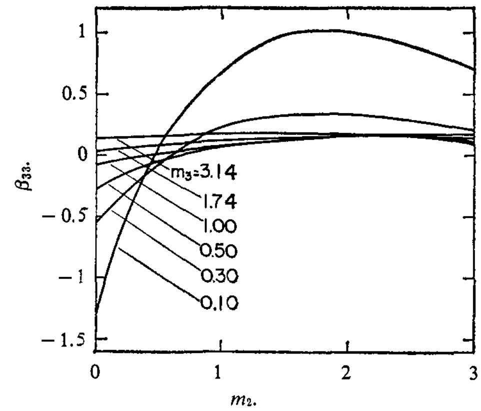

Figure 8. Simple electrolyte–simple electrolyte interaction parameter β_{33} against polyelectrolyte concentration.

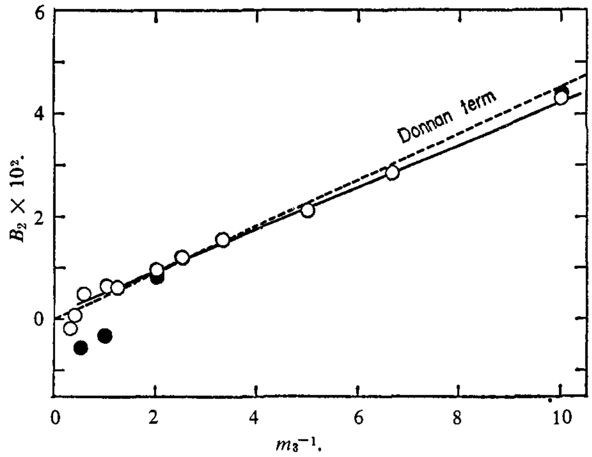

Figure 9. Second virial coefficient of polyelectrolyte as a function of simple electrolyte concentration: O, isopiestically observed (present paper); ●, osmometrically observed;[20] ×, osmometrically observed by Takahashi, *et al.*[19]

$$B_2 = \frac{10^3}{2W_2^2}\left[\frac{\alpha^2}{m_3} + \beta_{22} - m_3\left(\frac{\alpha}{m_3} + \beta_{23}\right)^2\Big/(2 + \beta_{33}m_3)\right] \qquad (9)$$

when π/C_2 can be represented by the linear equation

$$\pi/C_2 = RT\left(\frac{1}{W_2} + B_2C_2\right) \qquad (10)$$

where π denotes the osmotic pressure. The B_2 values computed from these interaction parameters are represented by open circles in Figure 9. A linear relationship exists between B_2 and $1/m_3$, except for a large m_3, as earlier found by Pals and Hermans.[17] It has been tempting to suggest that this linearity might be due solely to the contribution of the Donnan term, $\alpha^2/2m_3$. In Figure 9, this contribution is shown as a broken line. It will be noted that the B_2 value calculated from the interaction parameters by eq 9 (solid line) is very close to the value of the Donnan contri-

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(17) D. T. Pals and J. J. Hermans, *Rec. Trav. Chim.*, 71, 458 (1952).

bution.[18] The agreement shown in this figure does not imply that the interaction parameters are negligible, but indicates that the large β_{22} term and the terms containing β_{23} and β_{33} nearly cancel.

The filled circles in Figure 9 denote the B_2 values obtained osmometrically in this laboratory for the same NaPAA as used in the present work.[20] The agreement between the values is fairly good, but less satisfactory for a large m_3; m_3 giving $B_2 = 0$ is 2.5 by the vapor pressure measurements, whereas it is between 0.5 and 1 by our osmometry.[20] This discrepancy may be due in part to the invalidity of our assumption in the computation of B_2 from the vapor pressure measurements that the number of effective charges, α, is independent of m_3.

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[18] In previous studies, the large discrepancy between the observed B_2 and the value calculated from the Donnan term has often been noted; see, for example, ref 6a, 7a, and 19. In these studies, however, the Donnan term has been evaluated by using the stoichiometric valency z of a macroion, whereas the effective valency α is used in Figure 9.

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Solvation of Ions. XI.[1] Solubility Products and Instability Constants in Water, Methanol, Formamide, Dimethylformamide, Dimethylacetamide, Dimethyl Sulfoxide, Acetonitrile, and Hexamethylphosphorotriamide

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Abstract: Solubility products of silver, cesium, and potassium salts and instability constants of AgX_2^- and I_3^- in the protic solvents water, methanol, and formamide and in the dipolar aprotic solvents DMF, DMAC, DMSO, CH_3CN, and hexamethylphosphorotriamide at 25° are considered. Linear correlations are observed between equilibrium constants, expressed as concentration quotients, within each class of solvent, but there is absolutely no correlation of behavior between protic and dipolar aprotic solvents. The response of equilibria to transfer from protic to dipolar aprotic solvents is very dependent on the nature of any anions involved in the equilibria. The effects of solvation on the chemistry of anions in protic and dipolar aprotic solvents have been put on a quantitative basis by the tabulation of "*P* values." These measure the free energy of transfer of anions, relative to a standard anion, from a reference solvent to another solvent at 25°. *P* values range over 23 kcal mole^{-1} between acetate ion and the triiodide ion. Even bigger solvent effects than this can be anticipated.

Anion solvation strongly influences the relative solubilities of salts in protic and dipolar aprotic solvents.[3] To take a rather extreme example which is recorded in this paper, potassium chloride is very much less soluble ($\log K_S = -5.4$) than potassium perchlorate ($\log K_S = -0.1$) in DMF, whereas the situation is reversed in methanol, in that KCl ($\log K_S = -2.5$) is considerably more soluble than $KClO_4$ ($\log K_S = -4.5$) at 25°.

Instability constants of complexes are also strongly influenced by transfer from protic to dipolar aprotic solvents. The silver halides are slightly soluble in dimethylformamide and in water. Their solubility in the presence of excess chloride ion is very much greater in DMF than in water. This situation arises because AgX_2^- is much more stable in DMF than in water. The tribromide ion is likewise much more stable in DMF ($\log K_{\text{diss}} = -6.3$[4]) than in water ($\log K_{\text{diss}} = -1.2$[5]).

These observations are typical of the sometimes spectacular changes when systems are transferred from a protic solvent to a dipolar aprotic solvent.[3,6–8] We feel that these changes are often due to anion solvation, rather than to solvation of cations or of polar molecules. They arise because protic solvents have some structure and are hydrogen-bond donors and acceptors, whereas dipolar aprotic solvents have much weaker structures and are not hydrogen-bond donors. Small anions are strong H-bond acceptors, whereas large polarizable anions are not.[3]

Solubilities offer the most obvious way of studying solvation, but very few solubility products, for other

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