$NiSO_4 \cdot 6H_2O$ and 45.0 g of $CoSO_4 \cdot 7H_2O$ per liter of water reduced the exciting light in the visible and near-infrared.[38] The dc monitoring source was either a 100-W tungsten filament lamp or a 150-W xenon arc lamp (Hanovia). Samples were contained in cylindrical quartz cells having plane windows on the ends and positioned vertically in the center of the dewar and were cooled with either liquid nitrogen or liquid argon. The dimensions of the cells were 8 cm optical length and 13 mm id. The cells were connected to bulbs where the solutions were contained during the degassing procedure. The collimated monitoring light passed through a shutter, the sample cell, and the bottom of the Dewar, reflected 90° from a plane mirror and then focused on the entrance slit of a Bausch and Lomb 250-mm grating monochromator. An RCA 1P28 photomultiplier tube, mounted on the exit slit of the monochromator, served as detector. The optics of the monitoring light beam had narrow aperture so as to reduce the quantity of stray light reaching the detector. Because of the low fractional output of the xenon arc lamp in the ultraviolet, it was necessary to include in the optical path a cell 50 mm in length containing the above $NiSO_4$–$CoSO_4$ filter solution in order to reduce stray light to a tolerable level when monitoring signals at wavelengths shorter than 3200 Å. The signal from the detector was dc coupled through a cathode-follower amplifier to a Tektronix wide-band oscilloscope where it was displayed and recorded photographically.

The oscilloscope transparencies were enlarged by projection and traced onto graph paper in order to facilitate more precise measurement of the transient phenomena. In recording a transient absorption spectrum, the amplitude of the absorbance was measured at a series of closely spaced wavelengths at a constant time interval following initiation of the flash. The lifetime of a transient species was measured by the recovery rate of the monitoring beam after the flash. Kinetic analysis was by the method of Linschitz and Sarkanen.[39]

The relative intensities of the excitation flash were monitored with a photoelectric detector as a function of discharge energy. Duplicate determinations were within 15% of each other. With the photochemical reaction of anthracene in carbon tetrachloride as actinometer,[40–42] the absolute flash intensities were also measured. Table IV lists the quanta per flash incident upon the sample cell within the absorption spectra of both anthracene and *trans*-stilbene.

Table IV. Flash Intensities

Pulse energy, J	Quanta/ml $\times 10^{-16}$ in reaction cell Within anthracene spectrum	 Within *trans*-stilbene spectrum
360	9.0	6
490	11	7
640	14	9

The crystalline solution of *trans-stilbene* in bibenzyl was prepared by doping a zone-refined sample of bibenzyl with a small quantity of stilbene. The two substances were pulverized, mixed together in a tube, and then melted and degassed under a partial atmosphere of helium. A single crystal, 65 mm in length and 6 mm in diameter, was grown by slowly lowering the melt in the tube into a cooled bath. The crystal was contained in a Pyrex tube with open ends during the flash experiments. The concentration of *trans*-stilbene in the crystal was later determined spectrophotometrically to be 0.5%.

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(38) M. Kasha, *J. Opt. Soc. Am.*, **38,** 929 (1948).
(39) H. Linschitz and K. Sarkanen, *J. Am. Chem. Soc.*, 80, 4826 (1958).
(40) E. J. Bowen and K. K. Rohatgi, *Discussions Faraday Soc.*, **14,** 146 (1953).
(41) R. Livingston and D. W. Tanner, *Trans. Faraday Soc.*, **54,** 765 (1958).
(42) R. J. Charlson, H. Harrison, and R. Hardwick, *Rev. Sci. Instr.*, **31,** 46 (1960).

The Partial Molal Volume of Polyelectrolytes

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Abstract: The densities of aqueous solutions of polyelectrolytes were measured by a pycnometric method. The materials used were polyacrylates (PAA), polystyrenesulfonates (PSt), polyethylenesulfonates (PES), and salts of polyethylenimine (PEI) and its low molecular weight analogs having various gegenions. The apparent molal volumes of the polyelectrolytes were practically concentration independent. From the partial molal volume obtained, the individual molal volume of macroions was calculated and discussed in terms of three contributions, namely intrinsic volume of macroions, hydrophobic structural effect (P_{2p}), and electrostrictional hydration (E_{2p}). P_{2p} was negative for all polyelectrolytes studied, ranging from about −20 to 0 ml monomole^{-1}. The magnitude of P_{2p} was in the order PEI < PES < PAA < polymethacrylate < PSt < polyphosphate. E_{2p}, which was also negative, varied from −50 to 0 ml monomole^{-1}, depending on the macroion. The magnitude of E_{2p} increased in the order PSt < PEI < PAA < polyphosphate < polymethacrylate < PES. It was found that the P_{2p} term was influential in determining thermodynamic properties of polyelectrolyte solutions, as was the electrostrictional hydration term, which was already known to be exclusively important in the ordinary simple electrolytes.

In previous papers the mean activity coefficients of polyelectrolytes were determined by the isopiestic equilibration method[1–6] and electrochemical measurements.[7–9] The results show that the mean activity coefficients were largely influenced by solute–solvent interaction. It is feasible that there are two types of solute–solvent interaction, namely electrostrictional hydration by electric charges of gegenion or macroion, *i.e.*, charge effect, and hydrophobic structural enhancement or "iceberg" formation by hydrophobic parts of the electrolytes, *i.e.*, hydrophobic effect. Using the

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(1) N. Ise and T. Okubo, *J. Phys. Chem.*, **71,** 1287 (1967).
(2) N. Ise and T. Okubo, *ibid.*, **71,** 1886 (1967).
(3) T. Okubo, N. Ise, and F. Matsui, *J. Amer. Chem. Soc.*, **89,** 3697 (1967).
(4) N. Ise and T. Okubo, *J. Phys. Chem.*, **72,** 1361 (1968).
(5) N. Ise and K. Asai, *ibid.*, **72,** 1366 (1968).
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(8) N. Ise and T. Okubo, *ibid.*, **70,** 1930 (1966).
(9) N. Ise and T. Okubo, *ibid.*, **70,** 2400 (1966).

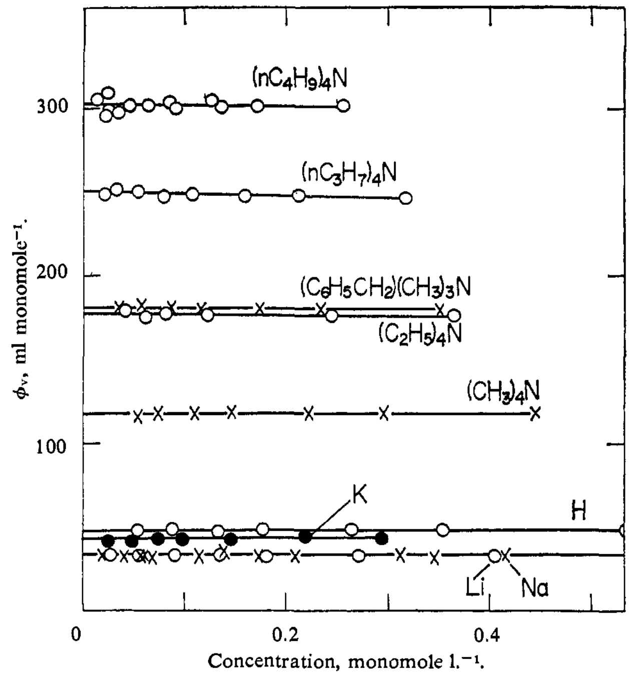

Figure 1. Apparent molal volumes of polyacrylates at 25°.

mean activity coefficient data, however, it is difficult to discuss these two kinds of interaction separately. It is most plausible that the measurement of the partial molal volume of polyelectrolyte gives useful information on the structural factors mentioned above, since both the electrostrictional effect and the hydrophobic effect have a large influence on the solution density. Furthermore, the partial molal volume attracted our attention because it is the pressure derivative of the mean activity coefficient. In spite of its importance, however, only a few measurements of the partial molal volume of synthetic polyelectrolytes have so far been reported.[10] Thus we initiated the experimental study on this quantity. In the present paper the solution densities are systematically measured for several polyelectrolytes having various gegenions. The partial molal volume of the polyelectrolyte is computed from these experiments for various temperatures, degrees of polymerization, and charge densities of macroion, and is discussed quantitatively in terms of the above-mentioned two solute–solvent interactions. The results, furthermore, are compared with those previously obtained by isopiestic vapor-pressure measurements.[1-6]

Experimental Section

Materials. Sodium polyacrylate (NaPAA) was furnished by the Toa Gosei Chemicals Co., Nagoya, Japan. The weight-average degree of polymerization was 640. Samples of sodium polystyrenesulfonate (NaPSt) (degree of polymerization = 2500), and sodium polyethylenesulfonate (NaPES) (degree of polymerization = 770) were gifts from the Dow Chemical Co., Midland, Mich., and the Hercules Powder Co., Wilmington, Del., respectively. Dilute solutions of these polyelectrolytes were passed through columns of cation- and anion-exchange resins to the acid form. Completeness of the conversion was assured by a flame test.

Various salts of the anionic polyelectrolytes such as Li, Na, K, $(CH_3)_4N$, $(C_2H_5)_4N$, $(n\text{-}C_3H_7)_4N$, and $(n\text{-}C_4H_9)_4N$ salts were prepared by neutralization with aqueous solutions of the corresponding hydroxides. Then the resulting solutions were concentrated at reduced pressure below 50°. The final solutions had concentrations of 0.2∼1.0 monomole/1000 g and were used as stock solutions. Polyethylenimine (PEI) was obtained from the Sumitomo Chemical Co., Osaka; its degree of polymerization was 100. Ethylenediamine (ED), diethylenetriamine (DT), triethylenetetramine (TT), and tetraethylenepentamine (TP) were commercially available. The purification of these bases has been described previously.[9] Hydrochlorides, hydrobromides, and hydriodides of PEI, ED, DT, TT, and TP were prepared by neutralization of these bases with solutions of HCl, HBr, and HI (reagent grade), respectively. Solutions for density measurements were prepared volumetrically at 25° using calibrated volumetric flasks of 5-, 10-, 15-, 20-, 30-, 50-, and 100-ml content from the stock solutions. The water used to prepare solutions was ion-exchanged with cation- and anion-exchange resins, and distilled under a nitrogen atmosphere.

Density Measurement. The densities of the solutions were determined by Pyrex pycnometers of an ordinary bicapillary type having a volume of about 7 ml, a capillary radius of about 0.1 cm, and a capillary length of 4 cm. In the middle of each capillary, a horizontal razor mark was etched and the volume of the pycnometer was standardized with distilled water. The sample solution was transfused into the pycnometer by using a medical syringe until two menisci reached near the horizontal marks of the capillaries. The pycnometer was then tightly fixed in a thermostat at 15 ± 0.005, 25 ± 0.005, or 35 ± 0.005°. After thermal equilibrium was attained, the height difference between the meniscus and the mark was measured by means of a traveling microscope reading to ±0.01 mm in order to determine the accurate volume of the solution. Thereafter the weight of the pycnometer containing the solution was determined, from which the accurate weight of the solution was obtained after the buoyancy correction. Density measurements are believed to be precise within ±0.00005, which is satisfactory for our purpose.

The apparent molal volume of each polyelectrolyte divided by the degree of polymerization, ϕ_v, was calculated from the density data using the following equation

$$\phi_v = \frac{M_2}{d} + \frac{1000d - M_2N}{N}\left(\frac{1}{d} - \frac{1}{d_0}\right) \qquad (1)$$

where d and d_0 are densities of the solution and the water, respectively, M_2 is the molecular weight of polyelectrolyte divided by the degree of polymerization, and N the polyelectrolyte concentration in monomoles liter^{-1}. The experimental uncertainty of the apparent mclal volume was at the highest 2%, and usually within 1%.

Results

First we note that the apparent and partial molal volumes of polyelectrolytes discussed in this paper refer to those of a repeating unit and are denoted by ϕ_v and $\bar{V}_2$, respectively.

As seen from Figure 1, the ϕ_v values can be said to be practically independent of concentration for the salt of PAA, though it is true that they vary slightly with concentration for a few cases as will be mentioned below. The insensitivity of ϕ_v toward concentration was also found for the salts of PSt and PEI, though the graphical presentation of ϕ_v was not given. The ϕ_v values of these electrolytes are approximately equal to $\bar{V}_2^0$ values in Tables Ia and Ib. It is probable that the concentration change of ϕ_v can be accounted for in terms of two factors, namely hydrophobic effect and charge effect. It can be accepted that the hydrophobic effect tends to lower ϕ_v with concentration, as was earlier discussed in detail by Wen and Saito.[11] On the other hand, the charge effect (or electrostrictional effect) operates to cause a positive concentration dependence of ϕ_v because the overlapping of already electrostricted regions of water around ions will diminish the constrictive effect per ion.[11] Thus the observed insensi-

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[10] (a) B. E. Conway, J. E. Desnoyers, and A. C. Smith, *Phil. Trans. Roy. Soc.* (London), **256**, 389 (1964); (b) H. Inagaki and A. Teramoto, *Makromol. Chem.*, **47**, 185 (1961).

[11] W.-Y. Wen and S. Saito, *J. Phys. Chem.*, **68**, 2639 (1964).

Table Ia. $\bar{V}_2^0$ of Various Salts of PAA, PSt, and PES

	$\bar{V}_2^0$, ml monomole^{-1}													
	H			Na			Li	K	$(CH_3)_4N$	$(C_2H_5)_4N$	$(n\text{-}C_3H_7)_4N$	$(n\text{-}C_4H_9)_4N$		
Macroion^a	15°	25°	35°	15°	25°	35°	25°	25°	25°	25°	25°	15°	25°	35°
PAA	47.5	47.8	48.4	30.7	33.0	33.3	33.0	43.0	118.0	178.0	250.0	298.6	301.4	302.8
PSt	...	110.0	...	106.5	108.2	109.5	110.0	121.0	213.0	252.0	324.0	373.8	376.6	380.0
PES	...	−13.2	...	−11.7	−10.6	−10.1	...	...	...	...	...	267.0	270.2	272.5

^{a} At α = 1.00.

Table Ib. $\bar{V}_2^0$ of Various Salts of PEI at 25°

	$\bar{V}_2^0$, ml monomole^{-1}		
Macroion^a	Cl	Br	I
PEI	46.9	53.1	62.4

^{a} At α = 0.80.

Table Ic. $\bar{V}_2^0$ of Hydrochlorides of ED, DT, TT, and TP at 25°

	ED	DT	TT	TP
$\bar{V}_2^0$,^{a} ml monomole^{-1}	40.3	44.1	44.5	44.8

^{a} At α = 0.80.

Table Id. $\bar{V}_2^0$ of Partially Neutralized NaPAA and PEI(HCl) at 25°

	$\bar{V}_2^0$, ml monomole^{-1}					
	α					
Macro-ion	1.0	0.8	0.6	0.4	0.2	0
NaPAA	33.0	36.0	38.6	41.7	44.9	47.8
PEI(HCl)	...	46.9	43.1	39.5	36.1	33.2

tivity of ϕ_v toward concentration indicates a delicate balancing of these two counteracting effects and is in an interesting contrast to the simple electrolyte cases.[12] A convenient comparison can be made for the ϕ_v values of polyethylenimine hydrochloride [PEI(HCl)] and its low molecular weight analogs at a degree of neutralization of 0.8, which are given in Figure 2. It is seen that the ϕ_v values of PEI(HCl) remain constant whereas those of ED(HCl), DT(HCl), TT(HCl), and TP(HCl) vary with concentration. The insensitivity of ϕ_v toward concentration for polyelectrolytes was earlier found for bovine serum albumin, bovine plasma albumin, etc.[13,14] Because the electrostriction does not take place for the unneutralized polyacrylic acid (HPAA), its ϕ_v values are larger than those of its monovalent metal salts such as Li, Na, and K salts, for which the electrostrictional hydration is expected to occur as is shown in Figure 1.

The influence of the charge number of a macroion on ϕ_v was studied using NaPAA and PEI(HCl) and is shown in Figure 3 and Table Id. The ϕ_v value of polyacrylate decreases with increasing degree of neutralization, whereas that of PEI(HCl) increases. This is due to the differences in the intrinsic volume of gegenion and in the strength of the electrostriction. We note that the tendency of the insensitivity of ϕ_v toward concentration is observed even in the low charge densities of macroions.[15]

Figures 4 and 5 give the temperature dependence of the apparent molal volume. It is possible to conclude, beyond experimental errors, that the ϕ_v values increase with temperature. The temperature coefficients of ϕ_v for the three tetrabutylammonium salts of the polyacids are in the range of 0.2~0.3 ml monomole^{-1} deg^{-1}.

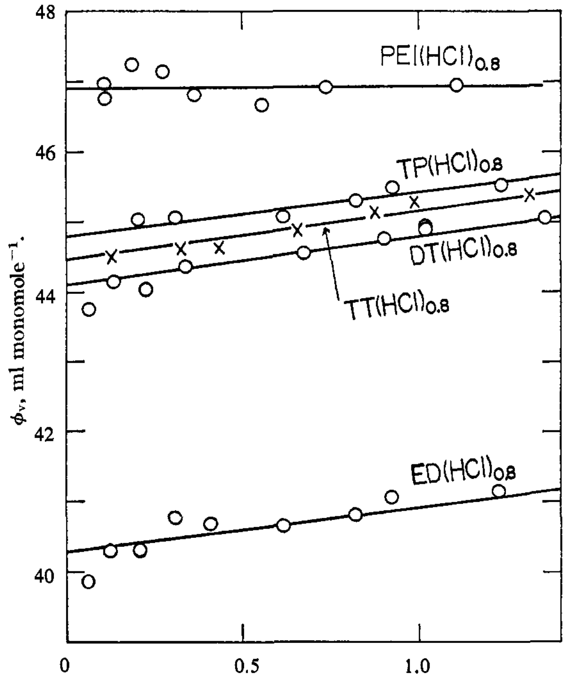

Figure 2. Apparent molal volumes of hydrochlorides of polyethylenimine and its low molecular weight analogs at 25°.

This value is approximately equal to that found for $(n\text{-}C_4H_9)_4NBr$,[11] *i.e.*, 0.2~0.5 ml mole^{-1} deg^{-1}. As shown in Figures 4 and 5, the ϕ_v values of $(n\text{-}C_4H_9)_4$NPES decrease with polymer concentration, whereas those of $(n\text{-}C_4H_9)_4$NPSt and $(n\text{-}C_4H_9)_4$NPAA remain constant as mentioned above. The ϕ_v values of NaPES and NaPAA increase with concentration. We recall here, however, that the concentration dependences are extremely small compared to those for most simple electrolytes.

The apparent molal volume at infinite dilution (ϕ_v^0) is equal to the partial molal volume ($\bar{V}_2^0$) at zero concentration, which is listed in Tables Ia–d for all samples studied. The degree of neutralization is denoted by α.

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(12) O. Redlich and D. M. Meyer, *Chem. Rev.*, **64**, 221 (1964).

(13) M. O. Dayhoff, G. E. Perlmann, and D. A. MacInness, *J. Amer. Chem. Soc.*, **74**, 2515 (1952).

(14) M. J. Hunter, *J. Phys. Chem.*, **71**, 3717 (1967).

(15) Conway, *et al.*,[10] observed that ϕ_v of KPMA increased with its concentration, and more markedly at low degrees of neutralization. This tendency might be associated with the specific influence of methyl groups of the α position.

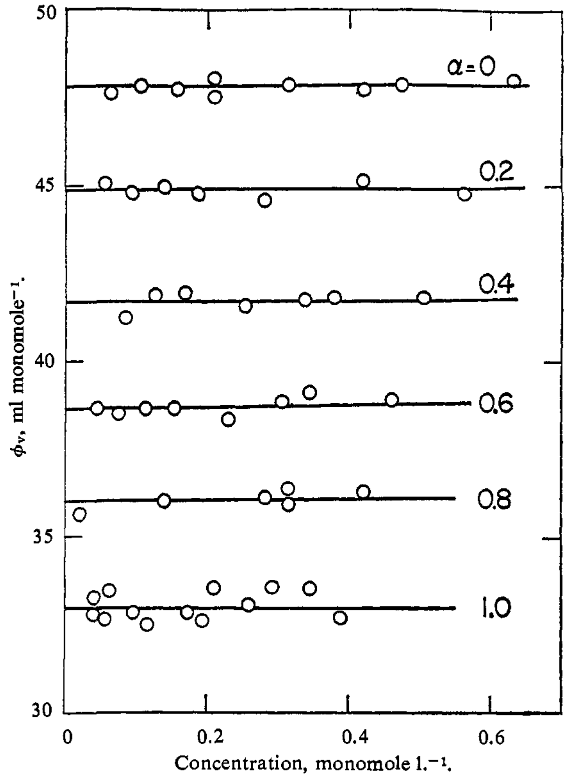

Figure 3. Apparent molal volumes of sodium polyacrylates of various degrees of neutralization at 25°.

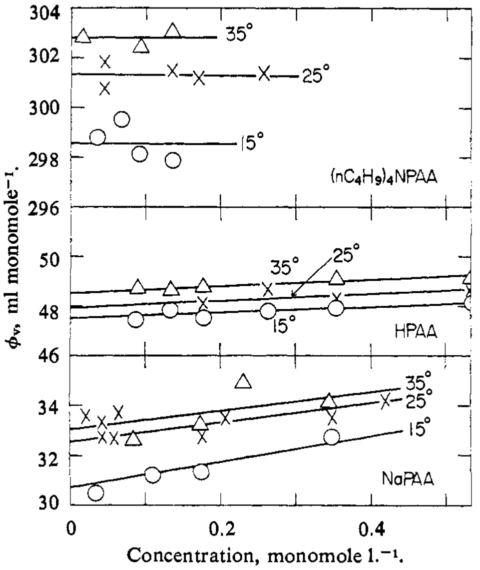

Figure 4. Apparent molal volumes of (n-C$_4$H$_9$)$_4$N-, H-, and Na-PAA at 15, 25, and 35°.

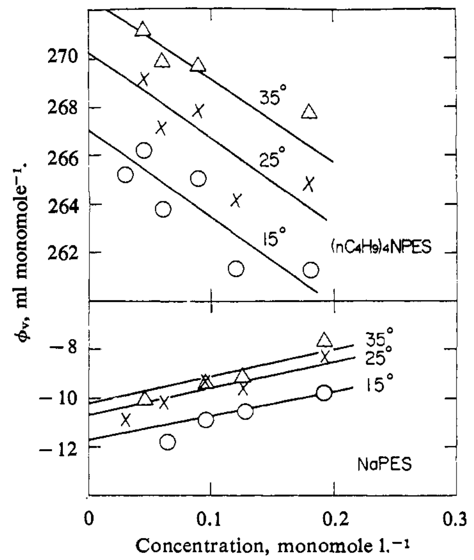

Figure 5. Apparent molal volumes of (n-C$_4$H$_9$)$_4$N- and NaPES at 15, 25, and 35°.

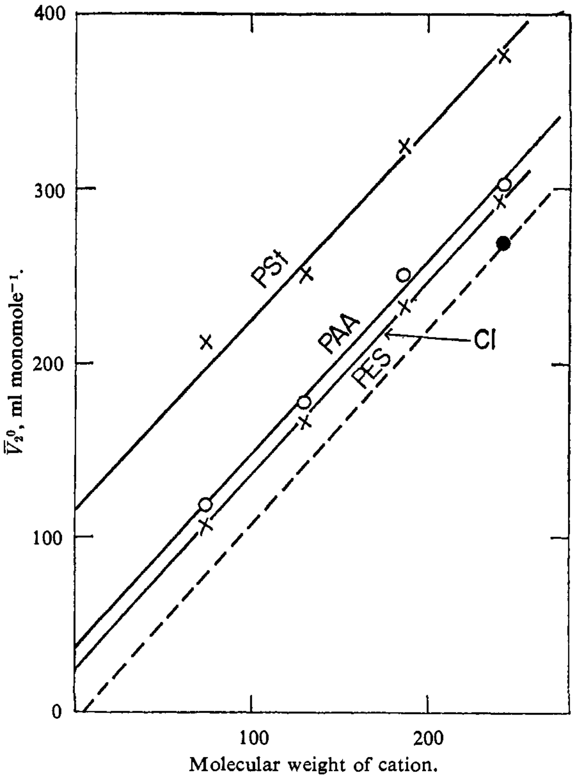

Figure 6. Partial molal volumes at infinite dilution of tetraalkylammonium salts as a function of the molecular weight of the cation at 25°.

The $\bar{V}_2^0$ values for the members of each series of tetraalkylammonium salts are plotted as a function of the molecular weight of the organic cation in Figure 6, which gives linear relationships for polystyrenesulfonate and polyacrylate. In this figure, the previously determined $\bar{V}_2^0$ values of the chlorides[16,17] were plotted for comparison. We note here that the slopes of the straight lines are the same as those of corresponding chlorides. The partial molal volume of the individual macroions ($\bar{V}_{2p}^0$) can be obtained by extrapolation of the $\bar{V}_2^0$ value to zero cation molecular weight.

Discussion

The partial molal volume of polyelectrolytes at infinite dilution ($\bar{V}_2^0$) may be written as

$$\bar{V}_2^0 = \bar{V}_{2g}^0 + \bar{V}_{2p}^0 \qquad (2)$$

with

$$\bar{V}_{2g}^0 = V_{\mathrm{int},2g} + P_{2g} + E_{2g} \qquad (3)$$

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[16] B. E. Conway, R. E. Verrall, and J. E. Desnoyers, *Trans. Faraday Soc.*, **62**, 2738 (1966).

[17] J. E. Desnoyers, R. E. Verrall, and B. E. Conway, *J. Chem. Phys.*, **43**, 243 (1965).

and

$$\bar{V}_{2p}{}^0 = V_{int,2p} + P_{2p} + E_{2p} \tag{4}$$

where E is the contribution from the electrostrictional hydration of water (or charge effect) by ions indicated by subscripts, P is the nonelectrostrictional contribution of water (or hydrophobic term) by ions indicated by subscripts, V_{int} is the intrinsic ionic volume including dead space between ion and solvent molecules, and the subscripts 2g and 2p are gegenion and macroion. Our main interest is to discuss the contribution from macroions ($\bar{V}_{2p}{}^0$).

The $\bar{V}_{2g}{}^0$ term can be estimated by using the following equations[18]

$$V_{int,2g} = 2.51r^3(1 + K)^3 \tag{5}$$

$$E_{2g} = -B/r(1 + K) \tag{6}$$

where r is Pauling's crystal radius of the ion (in Å), K a volume factor (=0.213), and B a constant (=9.7). The r values were taken as 0.60, 0.95, 1.33, 1.81, 1.95, and 2.16 Å for Li^+, Na^+, K^+, Cl^-, Br^-, and I^-, respectively, in these equations. The intrinsic volume of hydrogen atom was taken as zero.

For weak polyelectrolytes, the $[V_{int,2p} + P_{2p}]$ value can be estimated by the measurements of $\bar{V}_2{}^0$ at a degree of neutralization = 0, at which E_{2p} vanishes. The $V_{int,2p}$ term can be calculated for cylindrical macroions by using Conway's equation[10a]

$$V_{int,2p} = \pi\lambda N_A\{1 + (4/\pi - 1)(r_w/a)\}a^2 \tag{7}$$

where λ denotes the length of monomer, a its radius, N_A the Avogadro number, and r_w the radius of solvent water molecules. The values of λ and a were determined by taking into consideration the van der Waals radius and the covalent bond radius of the constituent atoms. The λ values thus obtained were 3.0, 4.0, 3.0, 3.95, 3.9, 3.8, and 3.7 Å for PAA, PEI, PMA, TP, TT, DT, and ED, respectively, and a values of PAA and PMA were 3.1 and 3.5 Å, respectively. For PEI and its low molecular weight analogs, the a value was 2.4 Å. Using these values of λ and a, $V_{int,2p}$ was calculated. Then P_{2p} and finally E_{2p} were obtained and are listed in Table II.

It is noteworthy that gegenion specificity could not be observed in the calculated values of $\bar{V}_{2p}{}^0$, E_{2p}, and P_{2p}, as it should be. For example, $\bar{V}_{2p}{}^0$ for Li, Na, K, and tetraalkylammonium salts of polyacrylic acid were 38.2, 38.7, 38.5, and 38.7[19] ml monomole^{-1}, respectively. The remarkable agreement strongly supports the validity of the treatment.

Next we note that P_{2p} is negative in all cases. This can be accepted when we recall that solute molecules fill up part of the space that would be unoccupied in an ordinary water cluster.[20,21] The hydrophobic parts of macroions give rise to an increase in the volume of the solvent. The volume increase, however, will be outweighed by a larger decrease of the volume caused by the compact orientation of water and solute in the boundary region, so that the P_{2p} term becomes negative.

Table II. Individual Molal Volumes of Macroions from Weak Polyelectrolytes at 25° [a]

Weak polyelectrolytes (α)	$\bar{V}_{2p}{}^0$	$V_{int,2p}$	P_{2p}	E_{2p}
NaPAA (1.0)	38.7	65.3	−17.5	−9.1
(0.8)	40.6			−7.2
(0.6)	42.0			−5.8
(0.4)	44.0			−3.8
(0.2)	46.0			−1.8
KPMA (0.95)	43.5[b]	81.6	−9.1	−29.0
(0.75)	46.6[b]			−25.9
(0.6)	51.3[b]			−21.2
(0.4)	60.0[b]			−12.5
PEI(HCl) (0.8)	29.1	54.7	−21.5	−4.1
TP(HCl) (0.8)	24.9	54.0	−20.3	−8.8
TT(HCl) (0.8)	24.9	53.3	−19.6	−8.8
DT(HCl) (0.8)	24.5	52.0	−18.4	−9.1
ED(HCl) (0.8)	20.3	50.6	−19.2	−11.1

[a] Values in ml monomole^{-1}. [b] From the work at 30° cited in ref 10a.

According to Masterton,[22] the partial molal volumes of methane, ethane, and propanes in water are smaller than in nonpolar or pure liquids by about 20 ml mole^{-1}. The P_{2p} values given in Table II except for PMA are fairly close to those for the nonpolar gases. The small magnitude of P_{2p} of PMA can be attributed to the methyl group of PMA, which facilitates the iceberg formation.[23]

For strong polyelectrolytes, $[V_{int,2p} + P_{2p}]$ cannot be determined experimentally, since they dissociate even in the unneutralized state. Thus we assume that the P_{2p} value of PES at 25° is −20 ml monomole^{-1}, which has been found for nonpolar hydrocarbons.[22] Similarly, the P_{2p} value of PSt ions is assumed to be −6 ml monomole^{-1}, which has been previously found for benzene.[22] The P_{2p} value of PP was taken to be zero because of a strong charge-transfer-type interaction of the monomer units with water molecules and the nonhydrophobic nature of the polymer chain.

The $V_{int,2p}$ values of strong polyelectrolytes are listed in Table III, together with $\bar{V}_{2p}{}^0$. The r value used

Table III. Individual Molal Volumes of Macroions from Strong Polyelectrolytes at 25° [a]

Strong polyelectrolytes[b] (DP)	$\bar{V}_{2p}{}^0$	$V_{int,2p}$	P_{2p}	E_{2p}
NaPSt	116.0	125.0	−6.0	−3.0
NaPES	−4.9	61.5	−20.0	−46.4
NaPP (6800)	28.5[c]	55.0[c]	0	−26.5
NaPP (2800)	27.5[c]	55.0[c]	0	−27.5
NaPP (800)	25.9[c]	55.0[c]	0	−29.1

[a] Values in ml monomole^{-1}. [b] α = 1.0 in each case. [c] From the work at 30° cited in ref 10a.

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(18) P. Mukerjee, *J. Phys. Chem.*, **65**, 740 (1961).

(19) The $\bar{V}_{2p}{}^0$ values of tetraalkylammonium salts were determined by the extrapolation of $\bar{V}_2{}^0$ to zero cation molecular weight; see Figure 6.

(20) G. Némethy and H. A. Scheraga, *J. Chem. Phys.*, **36**, 3382 (1962).

(21) G. Némethy and H. A. Scheraga, *ibid.*, **36**, 3401 (1962).

(22) W. L. Masterton, *ibid.*, 22, 1830 (1954).

(23) It is interesting to evaluate the number of hydrogen bonds newly produced by the methyl group. Using the formulas of the thermal expansion of ice[24] and unbound liquid water,[20] the difference between the molar volumes of the two states was calculated at 25°, from which the volume increase by the formation of a hydrogen bond times N_A was found to be 0.78 ml. If we take an average value of −17.5 ml monomole^{-1} for P_{2p} of PAA ions, its difference with the P_{2p} of PMA is −9.1 − (−17.5) = 8.4 ml monomole^{-1}, which can be ascribed to the increase of hydrogen bonds by one CH_3 group. This increase is calculated to be 11 (= 8.4/0.78) monomole^{-1}.

(24) N. E. Dorsey, "Properties of Ordinary Water-Substance," ACS Monograph No. 81, Reinhold Publishing Corp., New York, N. Y., 1940.

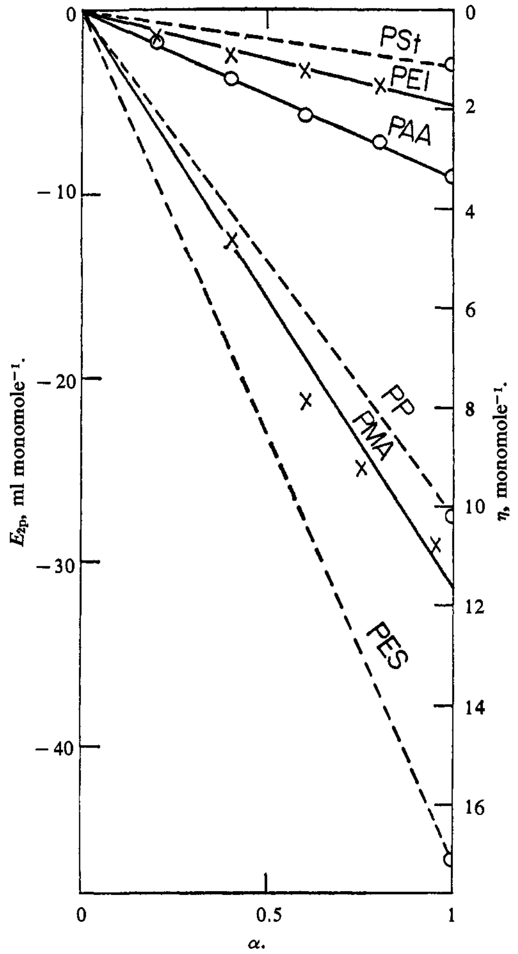

Figure 7. Electrostriction by macroions.

in the calculation was 3.0 Å for both PES and PSt, and a was 3.0 and 4.4 Å for PES and PSt, respectively. The $\bar{V}_{2p}^0$ values obtained for lithium, sodium, and potassium tetraalkylammonium polystyrenesulfonates were 115.2, 117.5, 115.7, and 116.0 ml monomole^{-1}, respectively.[19] We again note the constancy of the $\bar{V}_{2p}^0$ values. The $\bar{V}_{2p}^0$ for PES ions was estimated to be −4.9 ml monomole^{-1} from Figure 6.

Assuming further that $V_{\text{int},2p}$ and P_{2p} are not dependent on the degree of neutralization, or on the change of the macroion charge, we proceed to the evaluation of the E_{2p} term. The results are given in Tables II and III and in Figure 7.

It is seen that E_{2p} is negative in all cases, as it should be. Another point to be mentioned is the enhanced macroion specificity in E_{2p}. The magnitude of E_{2p} (*i.e.*, the strength of the electrostriction) increases in the order

$$\text{PSt} < \text{PEI} < \text{PAA} < \text{PP} < \text{PMA} < \text{PES} \qquad \text{(A)}$$

The smallest electrostriction of PSt ions can be accounted for by the large intrinsic volume ($V_{\text{int},2p}$) of the macroion, which amounts to 125 ml monomole^{-1} (Table III). The strong interaction between π electrons and water molecules,[25] which would interfere with the orientation of water molecules favorable to the hydration, may be another factor. The likewise high E_{2p} values of PEI ion are believed to be associated with the position of the electric charges confined to the main polymer chain, not to the side chain. In the case of PAA ions, the charges are on the side chain, so that the hydration takes place with a greater ease than for PEI ions. Accordingly, E_{2p} of the former ions is smaller than that of the latter. The PMA ion, on the other hand, has methyl groups at the α position which, as is reflected in the P_{2p} value, promote the hydrophobic iceberg formation more strongly than in the PAA case. Without additional experimental evidence, we suggest that a portion of the water molecules in the inner shell of the iceberg can participate in the electrostrictional hydration by the ionized groups. The transfer of the water molecules into the electrostricted region from the iceberg may take place easily because the water molecules in the iceberg have lower translational energy. Thus the E_{2p} values of PMA ion are considerably lower than those of PAA ion. For the low E_{2p} values of PP and PES ions, no plausible explanation is available at present. In this respect, however, it would be useful to remark that some water molecules cannot be removed from polyethylenesulfonate[5,26,27] even by a thorough drying.

The electrostriction per mole of water in the primary hydration shell was reported as 2.7 ml mole^{-1} by Conway, *et al.*,[10a] and 2.0 ml mole^{-1} by Yasunaga and Sasaki.[28] Using Conway's data and the E_{2p} values given in Tables II and III and Figure 7, the number of electrostrictionally hydrated water molecules per repeating unit (n) was estimated and is shown on the right coordinate of Figure 7. At the full degree of neutralization, PSt, PEI, PAA, PP, PMA, and PES ions were found to be hydrated by 1, 2, 3, 10, 12, and 17 water molecules, respectively. We note that the corresponding hydration number of Li^+, the smallest alkali ion under consideration, is found to be 4.9 and that of I^-, the largest halogen ion, 1.4 by using eq 6.

Table III indicates that the E_{2p} value of NaPP increases with increasing degree of polymerization. E_{2p} was further calculated at various temperatures for NaPAA. It appears to increase slightly with rising temperature from −11.1 (15°) to −9.4 (35°) ml monomole^{-1}. The hydration becomes more unstable with increasing temperature.

When water molecules are immobilized in the vicinity of macroions by hydrophobic or electrostrictional influences, the thermodynamic activity of water in the solution should be affected. The osmotic coefficients of sodium salts of polyelectrolytes were found to increase in the order

$$\text{PES}^{5} \approx \text{PAA}^{1} < \text{PMA}^{29} < \text{PP}^{6} < \text{PSt}^{4} \qquad \text{(B)}$$

If the electrostrictional hydration is a major factor determining water activity, the inequality B should coincide with (A) mentioned above. This is not the case, however. According to Tables II and III, the magnitude of P_{2p} decreased in the order

$$\text{PES} > \text{PAA} > \text{PMA} > \text{PSt} > \text{PP} \qquad \text{(C)}$$

Excepting the PP–PSt sequence, the inequalities B and C are consistent. This indicates that the osmotic coefficient is almost solely determined by the P_{2p} term for the anionic polyelectrolytes under consideration. This

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(25) I. M. Goldman and R. O. Crisler, *J. Org. Chem.*, 23, 751 (1958); M. Oki and H. Iwamura, *Bull. Chem. Soc. Japan*, 33, 717 (1960).

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(28) T. Yasunaga and T. Sasaki, *Nippon Kagaku Zasshi*, 72, 87 (1951).

(29) N. Ise and F. Matsui, unpublished data.

situation is in marked contrast with the ordinary simple electrolyte cases, in which the electrostrictional factor is concluded to be most important in determining the thermodynamic properties.[10a,30] The reversal of the PP–PSt sequence may be due to the rather arbitrary choice of the P_{2p} value for PP.

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(30) W. F. McDevit and F. A. Long, *J. Amer. Chem. Soc.*, **74**, 1773 (1952).

Conformational Stability of Phenylalanine in Aqueous Solution by Nuclear Magnetic Resonance[1]

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Abstract: The nmr spectral parameters for the aliphatic protons of the phenylalanine anion and cation in aqueous solution have been obtained as a function of both temperature and concentration. The temperature variation of the vicinal coupling constants for the anion depends critically on the concentration: at low concentration, the coupling constants diverge with increasing temperature; at high concentrations, they converge. The results for the anion are inconsistent with the interpretation that the anomalous behavior may arise from nonstaggered conformations. It appears that deviations from the staggered conformations are small but that the anion rotamer energies vary with both temperature and concentration, the two less favorable conformations gaining enhanced stability at low temperatures and concentrations. This variation can be related to changes in the dielectric constant of the aqueous solution but may be indicative of specific solute–solvent interactions. The spectral parameters corresponding to the vicinal coupling constants for the cation exhibit little variation either with temperature or concentration. These results suggest that the rotational isomerism for the cation may be interpreted in terms of staggered conformations whose relative energies are independent of temperature and concentration.

In a previous investigation,[3] the temperature variations of the vicinal coupling constants for the phenylalanine anion and dipolar ion in aqueous solution were found to be anomalous. For the anion, the coupling constants diverge with increasing temperature; for the dipolar ion, the larger coupling is constant over the measured temperature range. Two interpretations are consistent with these data. If the potential energy curve for the internal rotation about the C_α–C_β bond is assumed to be temperature independent, the potential energy minima do not correspond to the staggered conformations. On the other hand, if the rotational isomers do correspond to the staggered conformations, then the potential energies of the rotamers must vary with temperature. It is the purpose of the present communication to establish the proper interpretation from additional data on the concentration dependence of the spectrum and to examine the implications thereof.

Experimental Section

The nmr spectra were recorded on a Varian Associates DA-60-IL spectrometer,[4] equipped with a variable-temperature probe and operated at 60 MHz in the internal-lock, frequency-sweep mode. The frequency sweep was calibrated in the vicinity of each resonance peak by counting the frequency difference between fixed and swept oscillators. The line positions were calculated as the averages of at least four recordings taken with alternating upfield and downfield sweep. Reproducibility of the measurements was better than 0.1 Hz for most resonances (see below). The variable-temperature apparatus was calibrated using the internal chemical shifts of ethylene glycol and methanol as standards for the high- and low-temperature scales, respectively. Accuracy of the settings was ±1°.

L-Phenylalanine was obtained from a commercial source and was of the highest purity. The anion was prepared by dissolving the amino acid in NaOH solution in D_2O, containing a slight excess of an equivalent amount of NaOH; the cation, in HCl solution in D_2O, containing a slight excess of an equivalent amount of HCl. Concentrations are reported in moles of phenylalanine/liter of solvent. *t*-Butyl alcohol and acetic acid (2%) were added as internal references for the anion and cation, respectively.

Results and Discussion

Analysis of the Spectra. The general features of the proton spectrum of phenylalanine in aqueous solution have been discussed previously.[5] The spectral analyses for the anion are straightforward; the chemical shifts

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(1) Presented in part at the 155th National Meeting of the American Chemical Society, San Francisco, Calif., March 31–April 5, 1968.

(2) Eastern Utilization Research and Development Division, Agricultural Research Service, U. S. Department of Agriculture.

(3) J. R. Cavanaugh, *J. Am. Chem. Soc.*, **89**, 1558 (1967).

(4) Mention of commercial products does not constitute an endorsement by the U. S. Department of Agriculture over others of a similar nature not mentioned.

(5) *Cf.* ref 3 and references quoted therein. In addition, it is to be noted that the line widths (full width at half-height) for the anion proton resonances increase substantially with concentration at low sample temperatures, with a value of ~2.5 Hz for the most concentrated sample at 15°.