

The Adiabatic Compressibility of Poly(acrylic Acid) and Polyacrylamide in Aqueous Solution

PHANIBHUSAN ROY-CHOWDHURY and KALIDAS M. KALE,
National Chemical Laboratory, Poona 8, India

Synopsis

The results of adiabatic compressibility measurements of poly(acrylic acid) and polyacrylamide along with their corresponding monomers and two poly(sodium acrylates) obtained by neutralizing the polyacid 25% and 100% with sodium hydroxide have been described. The total adiabatic compressibility of poly(acrylic acid) solution is higher than that of the corresponding salt solutions or of polyacrylamide solutions. The unneutralized acid does not dissociate much, even in dilute solution, and the magnitude of electrostriction in polyamide is greater than in acid. The ΦV_2 and ΦK_2 values for monomers and polymers are seen to be almost concentration independent, and so are the sodium salts of the polyacid. Poly(acrylic acid) and poly(acrylamide) are structurally closely related polymers, and water must be bound to them through polar groups either by hydrogen bonding or by dipole attraction. The hydrophobic part of the solute, because of compact orientation of water and solute in the boundary region, causes a decrease in solvent volume and therefore in the values of ΦV_2 and ΦK_2 . On the other hand, intermolecular hydrogen bonding between the polar groups increases the volume and counterbalances the hydrophobic effect. Because of these two counteracting effects, the observed ΦV_2 and ΦK_2 values are seen to be concentration independent. Contrary to the observation with poly(methacrylic acid)¹ and its sodium salts, the solvated counter-ions in case of poly(sodium acrylates) make no special contribution in the dilute region. In 100% neutralized polyacid, the dissociation of counterions is complete, and the magnitude of electrostriction is highest in this case. Accordingly, lowest ΦV_2 and ΦK_2 values (37.0 cc/mole and -5.50×10^{-3} cc bar⁻¹ mole⁻¹) are observed. However, the dissociation and therefore the magnitude of electrostriction are somewhat reduced in the presence of 1.0M NaCl solution; and, accordingly, the values increase to 42.80 cc/mole and -33.0×10^{-4} cc bar⁻¹ mole⁻¹, respectively. The limiting values for the apparent molal volume and the apparent molal compressibility for the polymers show a considerable decrease over those of the monomers. The values of ΦV_2^0 and ΦK_2^0 per methyl group are less in the polymers than in the monomers, and this has been attributed to water clusters that become stronger and better formed as the molecules grow larger and larger. The molal volumes of acrylic acid and methacrylic acid are decreased, while those of acrylamide and methacrylamide are increased when dissolved in water to form an infinitely dilute solution.

INTRODUCTION

In a program for the systematic study of adiabatic compressibility of polyelectrolytes in aqueous solution in this laboratory, the results for poly(methacrylic acid) and poly(methacrylamide) along with those for their monomers were reported in earlier papers.^{1,2} However, poly(methacrylic

acid), poly(methacrylamide), poly(acrylic acid), and polyacrylamide are structurally closely related and they have functional groups which can form a hydrogen-bonded structure. Silberberg and co-workers³ have studied the temperature dependence of the 90-degree scattering of light and of the viscosity of the dilute aqueous solutions of these four hydrogen-bonding polymers and observed that the results of poly(methacrylic acid) were at variance with those of the other three. Besides, the statistical chain element length for poly(methacrylic acid) and poly(methacrylamide) was found to be half that of poly(acrylic acid) under corresponding condition. It was explained that, because of the presence of a methyl group in the α -position, intramolecular hydrogen bonding may probably have taken place. Since the adiabatic compressibility data of the last two polymers, i.e., poly(acrylic acid) and polyacrylamide, and of their monomers have not been reported so far, the results obtained by us are reported in this paper.

EXPERIMENTAL

The apparatus and technique were essentially the same as previously described,¹ i.e., the ultrasonic velocities were measured by an ultrasonic interferometer and the density with Ostwald-type pycnometers. The adiabatic compressibility β_s of the liquid was obtained by the relation

$$\beta_s = \frac{1}{u^2 d}$$

where u and d are velocity and density, respectively.

Poly(acrylic acid) was prepared by polymerizing freshly distilled monomer (30% w/w) in dioxane solution using 0.5% benzoyl peroxide as initiator at 55°C with constant stirring in nitrogen atmosphere. The product was dissolved in methanol, precipitated with ether, and dried in vacuo to constant weight. The unfractionated sample was used for adiabatic compressibility measurements; it had a molecular weight of 1.504×10^4 as determined from the intrinsic viscosity data of the sodium salt in 1.0M NaCl solution.⁴

Poly(sodium acrylate) solutions with different degrees (25% and 100%) of neutralized products were prepared by adding calculated amounts of sodium hydroxide to the polyacid.

Polyacrylamide was prepared by polymerizing the monomer (10% solution) in ethanol solution using azobisisobutyronitrile (0.5%) as initiator at 60°C with constant stirring and bubbling nitrogen throughout. The polymer precipitated out, was washed with fresh alcohols several times, and was dried in vacuo over P_2O_5 to constant weight. This polymer was very hygroscopic. The molecular weight of the sample was 2.423×10^4 as obtained by measuring the intrinsic viscosity in aqueous solution.⁵

RESULTS AND DISCUSSION

The results of the adiabatic compressibility measurements are summarized in Tables I to VIII. The materials used were the two monomers, acrylic acid (AA) and acrylamide (AAM), with their corresponding polymers, poly(acrylic acid) (PAA) and polyacrylamide (PAAM), and two sodium salts of poly(acrylic acid) (PSA) obtained by neutralizing the polyacid to different extents. Tables I and II give the data for acrylic acid and acrylamide, while Tables III and IV give similar data for the corresponding polymers in aqueous solution. It is observed that the total adiabatic

TABLE I
Summary of Results for Acrylic Acid in Aqueous Solution
at 25°C ($M_2 = 72.06$)

c , g/dl	d , g/cm ³	ΦV_2 , cm ³ /mole	u , m/sec	β , bar ⁻¹ $\times 10^6$	$(\beta_1 - \beta)/c$ $\times 10^7$	ΦK_2 , cm ³ bar ⁻¹ mole ⁻¹ $\times 10^4$
0.0000	0.99705	61.70 ^a	1496.05	44.812	—	6.00 ^a
0.1028	0.99720	61.728	1496.42	44.783	2.811	7.257
0.2056	0.99735	61.728	1496.84	44.751	2.952	6.315
0.3084	0.99750	61.728	1497.30	44.717	3.080	5.478
0.4112	0.99765	61.728	1497.63	44.690	2.952	6.394
0.5140	0.99778	62.009	1498.04	44.660	2.951	6.503
0.7437	0.99810	61.778	1498.92	44.593	2.937	6.682
1.0280	0.99855	61.728	1500.08	44.504	2.990	6.127
1.4875	0.99912	62.216	1501.88	44.372	2.954	6.575
1.9833	0.99984	62.106	1503.69	44.234	2.914	6.825

^a Extrapolated value.

TABLE II
Summary of Results for Acrylamide in Aqueous Solution
at 25°C ($M_2 = 71.08$)

c , g/dl	d , g/cm ³	ΦV_2 , cm ³ /mole	u , m/sec	β , bar ⁻¹ $\times 10^6$	$(\beta_1 - \beta)/c$ $\times 10^7$	ΦK_2 , cm ³ bar ⁻¹ mole ⁻¹ $\times 10^4$
0.0000	0.99705	65.50 ^a	1496.05	44.812	—	5.00 ^a
0.10005	0.99713	65.600	1496.57	44.777	3.488	5.480
0.2001	0.99722	65.233	1497.10	44.741	3.523	4.864
0.3001	0.99729	65.589	1497.56	44.711	3.365	5.522
0.4000	0.99738	65.409	1498.19	44.669	3.572	3.919
0.5002	0.99747	65.304	1498.59	44.630	3.624	3.421
1.0001	0.99790	65.231	1500.51	44.484	3.276	5.925
1.5001	0.99832	65.255	1503.61	44.305	3.374	5.277
2.0001	0.99877	65.160	1505.97	44.147	3.321	5.603

^a Extrapolated value.

TABLE III
Summary of Results for Poly(acrylic Acid) in Aqueous
Solution at 25°C ($M_2 = 72.06$)

c , g/dl	d , g/cm ³	ΦV_2 , cm ³ /mole	u , m/sec	β , bar ⁻¹ $\times 10^6$	$(\beta_1 - \beta)/c$ $\times 10^7$	ΦK_2 , cm ³ bar ⁻¹ mole ⁻¹ $\times 10^4$
0.0000	0.99705	46.70*	1496.05	44.812	—	0.85*
0.0942	0.99737	47.722	1496.26	44.785	2.866	0.850
0.1884	0.99773	46.571	1496.41	44.759	2.813	0.850
0.3015	0.99813	46.864	1496.64	44.728	2.687	0.792
0.4020	0.99847	46.744	1496.84	44.701	2.761	1.059
0.5034	0.99885	46.430	1497.01	44.673	2.761	1.083
0.8054	0.99993	46.429	1497.69	44.585	2.817	0.512
1.2886	1.00169	46.193	1498.59	44.453	2.786	0.687
1.7182	1.00326	46.109	1499.33	44.340	2.747	0.888

* Extrapolated value.

TABLE IV
Summary of Results for Polyacrylamide in Aqueous Solution
at 25°C ($M_2 = 71.08$)

c , g/dl	d , g/cm ³	ΦV_2 , cm ³ /mole	u , m/sec	β , bar ⁻¹ $\times 10^6$	$(\beta_1 - \beta)/c$ $\times 10^7$	ΦK_2 , cm ³ bar ⁻¹ mole ⁻¹ $\times 10^4$
0.0000	0.99705	50.90*	1496.05	44.812	—	-3.00*
0.1035	0.99735	50.627	1496.46	44.774	3.652	-3.445
0.2670	0.99764	50.971	1496.88	44.735	3.691	-3.599
0.3105	0.99793	51.086	1497.25	44.700	3.581	-2.727
0.4140	0.99825	50.627	1497.67	44.661	3.638	-3.137
0.5175	0.99855	50.627	1498.14	44.620	3.708	-3.691
0.7752	0.99925	51.058	1498.95	44.540	3.505	-2.075
1.0336	1.00000	51.288	1500.10	44.438	3.613	-2.846
1.5493	1.00149	50.860	1502.13	44.252	3.609	-2.860
2.0657	1.00297	51.032	1504.15	44.069	3.597	-2.763

* Extrapolated value.

compressibility of poly(acrylic acid) solution is higher than that of the corresponding salt solutions or of polyacrylamide solutions. The data for 25% and 100% neutralized poly(acrylic acid) solutions are given in Tables V and VI, respectively. The decreased compressibility of electrolytes is due to the action on water of the electric field around each ion; the electrostatic pressure causes an additional contraction of the water in the same way as is caused by increasing external pressure. However, the comparatively larger decrease in compressibility in case of polyamide with respect to polyacid may be due to the presence of amphoteric $-\text{CONH}_2$ groups in the polymer chain. The unneutralized acid does not dissociate much, even in

TABLE V
Summary of Results for Poly(sodium Acrylate), $\alpha = 0.25$,
in Aqueous Solution at 25°C ($M_2 = 77.56$)

c , g/dl	d , g/cm ³	ΦV_2 , cm ³ /mole	u , m/sec	β , bar ⁻¹ $\times 10^6$	$(\beta_1 - \beta)/c$ $\times 10^7$	ΦK_2 , cm ³ bar ⁻¹ mole ⁻¹ $\times 10^4$
0.0000	0.99705	45.50 ^a	1496.05	44.812	—	-14.00 ^a
0.0949	0.99743	46.658	1496.61	44.761	5.329	-20.41
0.1899	0.99783	45.839	1496.74	44.735	4.018	-10.53
0.3165	0.99836	45.593	1497.55	44.663	4.689	-15.87
0.4114	0.99876	45.461	1497.77	44.632	4.361	-13.38
0.6330	0.99970	45.224	1498.83	44.527	4.493	-14.61
0.7815	1.00032	45.241	1499.31	44.471	4.357	-13.48
1.0159	1.00141	44.403	1500.62	44.345	4.591	-15.71
1.5630	1.00366	44.893	1502.84	44.115	4.455	-14.42

^a Extrapolated value.

TABLE VI
Summary of Results for Poly(sodium Acrylate), $\alpha = 1.0$,
in Aqueous Solution at 25°C ($M_2 = 94.04$)

c , g/dl	d , g/cm ³	ΦV_2 , cm ³ /mole	u , m/sec	β , bar ⁻¹ $\times 10^6$	$(\beta_1 - \beta)/c$ $\times 10^7$	ΦK_2 , cm ³ bar ⁻¹ mole ⁻¹ $\times 10^4$
0.0000	0.99705	37.00 ^a	1496.05	44.812	—	-50.50 ^a
0.1024	0.99769	35.369	1496.82	44.739	7.305	-52.80
0.2049	0.99832	37.240	1497.57	44.664	7.213	-51.72
0.3013	0.99888	37.032	1498.28	44.596	7.142	-50.46
0.3964	0.99945	37.213	1499.00	44.528	7.149	-50.65
0.4955	1.00005	37.213	1499.76	44.456	7.169	-50.69
0.7743	1.00174	37.189	1501.70	44.267	7.036	-49.49
1.0188	1.00325	36.920	1503.86	44.073	7.247	-51.59
1.4982	1.00624	36.463	1507.09	43.754	7.058	-50.02
1.9976	1.00914	37.234	1511.10	43.397	7.077	-49.88
2.6635	1.01331	36.740	1516.26	42.925	7.083	-50.13

^a Extrapolated value.

dilute solution, and the magnitude of electrostriction in polyamide is greater than in acid. Accordingly, the apparent molal compressibility of polyamide is slightly negative, in contrast to that of the polyacid, which is positive in dilute solution.

The apparent molal volume of the solute, ΦV_2 , and its apparent molal compressibility, ΦK_2 , have been computed by the following equations:

$$\Phi V_2 = (M_2/d_1)[1 - (100/c)(d - d_1)]$$

$$\Phi K_2 = M_2\beta_1\{(100/c)[(\beta/\beta_1) - (d/d_1)] + (1/d_1)\}$$

TABLE VII
Summary of Results for Poly(sodium Acrylate), $\alpha = 1.0$,
in 0.1M NaCl Solution at 25°C ($M_2 = 94.04$)

c , g/dl	d , g/cm ³	ΦV_2 , cm ³ /mole	u , m/sec	β , bar ⁻¹ $\times 10^6$	$(\beta_1 - \beta)/c$ $\times 10^7$	ΦK_2 , cm ³ bar ⁻¹ mole ⁻¹ $\times 10^4$
0.0000	1.00115	37.10 ^a	1502.30	44.257	—	-49.50 ^a
0.0877	1.00170	35.023	1503.01	44.191	7.537	-55.24
0.1755	1.00222	36.663	1503.76	44.124	7.578	-55.18
0.2581	1.00272	36.794	1504.29	44.071	7.210	-51.63
0.3396	1.00322	36.677	1504.87	44.015	7.140	-50.83
0.5306	1.00435	37.282	1506.37	43.878	7.145	-50.75
0.7185	1.00551	36.932	1507.58	43.757	6.959	-49.04
0.9580	1.00691	37.259	1509.43	43.590	6.972	-48.97
1.4739	1.01003	37.340	1512.57	43.275	6.668	-46.19
2.2109	1.01442	37.553	1518.64	42.744	6.847	-47.77

^a Extrapolated value.

TABLE VIII
Summary of Results for Poly(sodium Acrylate), $\alpha = 1.0$,
in 1.0M NaCl Solution at 25°C ($M_2 = 94.04$)

c , g/dl	d , g/cm ³	ΦV_2 , cm ³ /mole	u , m/sec	β , bar ⁻¹ $\times 10^6$	$(\beta_1 - \beta)/c$ $\times 10^7$	ΦK_2 , cm ³ bar ⁻¹ mole ⁻¹ $\times 10^4$
0.0000	1.03709	42.80 ^a	1557.30	39.759	—	-33.00 ^a
0.1059	1.03765	42.727	1558.06	39.699	5.685	-36.68
0.2118	1.03820	43.154	1558.65	39.648	5.255	-32.26
0.3025	1.03870	42.416	1559.26	39.598	5.335	-33.29
0.4033	1.03923	42.562	1559.99	39.541	5.420	-34.03
0.5378	1.03992	42.961	1560.84	39.471	5.351	-33.26
0.7683	1.04125	41.580	1562.07	39.359	5.210	-32.47
1.0976	1.04302	41.687	1564.54	39.168	5.385	-34.09
1.6886	1.04614	42.079	1568.43	38.858	5.338	-33.47

^a Extrapolated value.

where M_2 is the molecular weight of the monomer as well as the polymer repeat unit; c is the concentration expressed in g/dl; and d , d_1 , β , and β_1 are the density and compressibility of the solution and solvent, respectively.

The plots of ΦV_2 and ΦK_2 versus concentration are shown in Figures 1 and 2, respectively. The ΦV_2 and ΦK_2 values for monomers and polymers are seen to be almost concentration independent. The insensitivity of the ΦV_2 and ΦK_2 values toward concentration are also seen for the sodium salt of poly(acrylic acid). According to Wen and Saito,⁶ the hydrophobic effect tends to lower ΦV_2 with concentration, while the charge effect tends to increase ΦV_2 with concentration, especially with smaller electrolytes;⁷ the

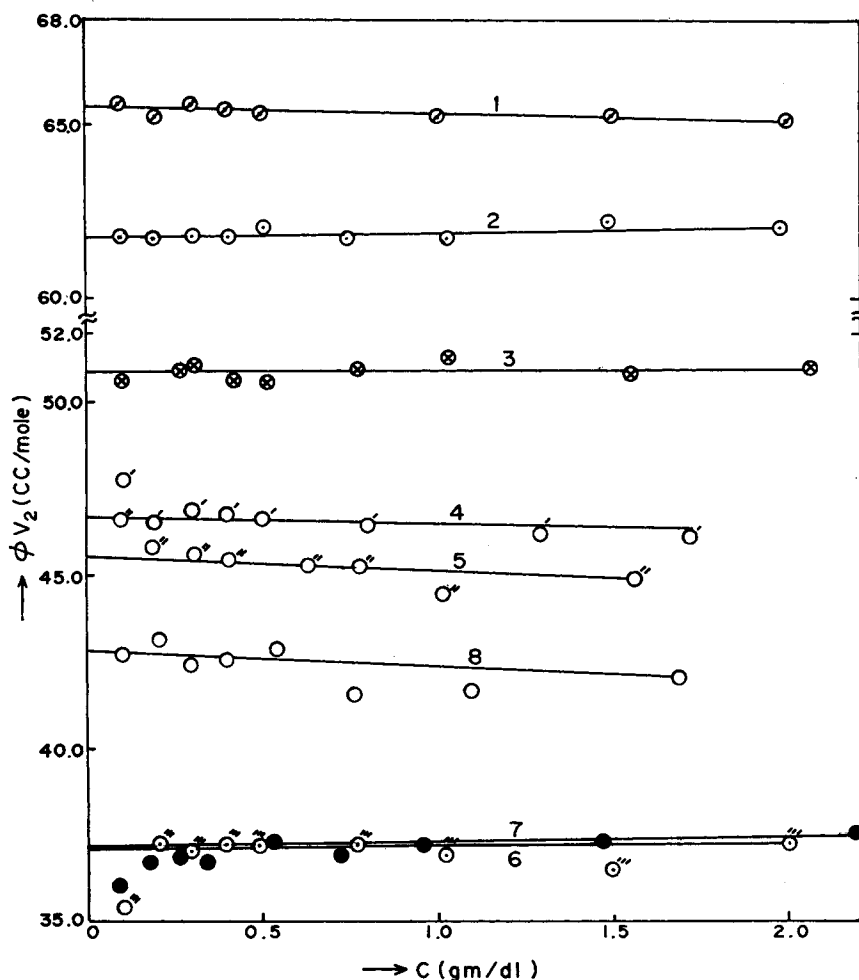


Fig. 1. Plots of apparent molal volume as a function of concentration: (1) acrylamide; (2) acrylic acid; (3) polyacrylamide; (4) poly(acrylic acid); (5) poly(sodium acrylate), $\alpha = 0.25$; (6) poly(sodium acrylate), $\alpha = 1.0$; (7) poly(sodium acrylate), $\alpha = 1.0$ in $0.1M$ NaCl solution; (8) poly(sodium acrylate), $\alpha = 1.0$ in $1.0M$ NaCl solution.

insensitivity toward concentration in case of some large tetraalkylammonium salts was described as a delicate balancing between these two effects. In fact, Ise and Okubo⁸ have explained the observed insensitivity of ΦV_2 toward concentration in case of poly(acrylic acid) and other poly(sodium acrylates) as the result of balancing of two opposite effects, i.e., hydrophobic effect and charge effect. However, the insensitivity of ΦV_2 and ΦK_2 toward concentration in case of uncharged polyamides (and also the polyacid and its partially and fully neutralized sodium salts) may be explained in the following way: poly(acrylic acid) and polyacrylamide are structurally closely related polymers, and water must be bound to them

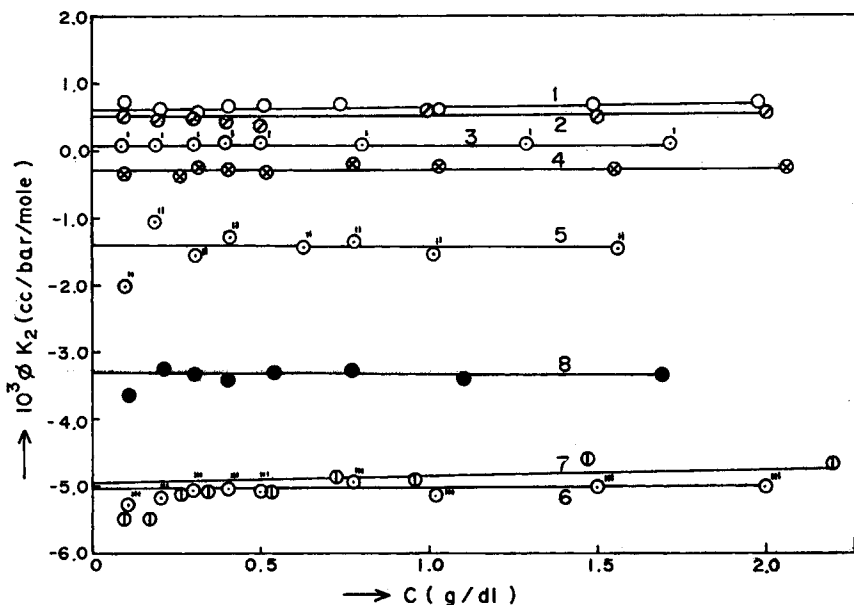


Fig. 2. Plots of apparent molal compressibility as a function of concentration: (1) acrylic acid; (2) acrylamide; (3) poly(acrylic acid); (4) polyacrylamide; (5) poly(sodium acrylate), $\alpha = 0.25$; (6) poly(sodium acrylate), $\alpha = 1.0$; (7) poly(sodium acrylate), $\alpha = 1.0$ in $0.1M$ NaCl solution; (8) poly(sodium acrylate), $\alpha = 1.0$ in $1.0M$ NaCl solution.

through polar groups such as $-\text{COOH}$ or $-\text{CONH}_2$ either by hydrogen bonding or by dipole attraction. The hydrophobic part of the solute must give rise to an increase in volume of the solvent, but this volume increase will be outweighed by a large decrease in volume caused by the compact orientation of water and solute in the boundary region so that the net result is a decrease in ΦV_2 and ΦK_2 values. On the other hand, polar groups in the polymer chain bind the water molecules through hydrogen bridges, and the increase in volume due to this intermolecular hydrogen bonding counterbalances the hydrophobic effect. Because of these two counteracting effects, the observed ΦV_2 and ΦK_2 values are seen to be concentration independent. This assumption is further substantiated by the experimental observation that in case of polyacid and its salts, the water clusters around the polyions are not disturbed appreciably by a variation in charge intensity caused by dissociation of ionic groups with concentration variation upon dilution. Contrary to the observations with poly(methacrylic acid) and its sodium salt, the solvated counterions in poly(acrylic acid) or poly(sodium acrylate) make no special contribution in dilute regions. Perhaps a methyl group in the α -position is responsible for these peculiarities. Both the ion-solvent interactions (electrostrictive effect) and the effect of the water structure due to solute addition (structural effect) must influence the adiabatic compressibility—the two effects generally cause a reduction in volume

and therefore in compressibility. In 100% neutralized polyacid, the dissociation of counterions is complete and the magnitude of electrostriction is highest, so that lowest ΦV_2 and ΦK_2 values (~ 37.0 cc/mole and -50.5×10^{-4} cc bar $^{-1}$ mole $^{-1}$, respectively) are observed in this case. By suppression of dissociation of counterions, as was produced effectively with 1.0M NaCl solution (in 0.1M NaCl, the suppression of dissociation was marginal), the magnitude of electrostriction was somewhat reduced, and accordingly the values were increased to 42.80 cc/mole and -33.0×10^{-4} cc bar $^{-1}$ mole $^{-1}$, respectively. The data for 100% neutralized poly(acrylic acid) in 0.1M and 1.0M NaCl solution are given in Tables VII and VIII, respectively.

At infinite dilution, the apparent molal volume ΦV_2^0 and the compressibility ΦK_2^0 of the solute and the partial molal volume \bar{V}_2^0 and the compressibility \bar{K}_2^0 of the solute are identical. The limiting values for solutes at 25°C are listed in Table IX. The limiting values for methacrylic acid and methacrylamide along with their corresponding polymers² are listed in the same table for comparison. The values for the polymer are found to differ widely from that of the corresponding monomer. The polymers show a decrease of ~ 15.0 – 19.5 cc/mole for ΦV_2^0 and of $\sim 5.15 \times 10^{-4}$ – 8.0×10^{-4} cc bar $^{-1}$ mole $^{-1}$ for ΦK_2^0 over the monomer values.

TABLE IX
Limiting Values of Apparent Molal Compressibility and
Apparent Molal Volume of Solutes in Aqueous Solution at 25°C

Materials	M_2	Molar volume, cc/mole	ΦV_2^0 , cc/mole	ΦK_2^0 , cc bar $^{-1}$ mole $^{-1}$ $\times 10^4$
Acrylic acid	72.06	68.56 ^a	61.7	6.00
Poly(acrylic acid)	72.06		46.7	0.85
Acrylamide	71.08	63.35 ^a	65.5	5.00
Polyacrylamide	71.08		50.9	-3.00
Poly(sodium acrylate), $\alpha = 0.25$	77.56		45.5	-14.00
Poly(sodium acrylate), $\alpha = 1.0$	94.04		37.0	-50.50
Poly(sodium acrylate), $\alpha = 1.0$, in 0.1M NaCl solution	94.04		37.1	-49.50
Poly(sodium acrylate), $\alpha = 1.0$, in 1.0M NaCl solution	94.04		42.80	-33.00
Methacrylic acid ^b	86.09	84.79 ^a	78.6	6.80
Poly(methacrylic acid) ^b	86.09		60.0	1.10
Methacrylamide ^b	86.116	76.75 ^a	82.0	4.50
Poly(methacrylamide) ^b	86.116		62.5	-2.87

^a Density obtained from Brandrup and Immergut.¹⁰

^b Data from Roy-Chowdhury.²

^c Density of methacrylamide was not available in literature; therefore value determined in this laboratory was used, 1.122 g/cc at 25°C.

It is interesting to note (Table IX) that ΦV_2^0 and ΦK_2^0 per methyl group are decreased as the molecules grew in size on polymerization. For example, in the case of monomers at 25°C, ΦV_2^0 and ΦK_2^0 per methyl group are 16.9 cc/mole and 0.8×10^{-4} cc bar⁻¹ mole⁻¹, respectively, in going from acrylic to methacrylic acid and are 16.5 cc/mole and -0.50×10^{-4} cc bar⁻¹ mole⁻¹, respectively, in going from acrylamide to methacrylamide; while for polymers, ΦV_2^0 and ΦK_2^0 per methyl group are 13.3 cc/mole and 0.25×10^{-4} cc bar⁻¹ mole⁻¹ in going from polyacrylic to poly(methacrylic acid) and are 11.6 cc/mole and -0.13×10^{-4} cc bar⁻¹ mole⁻¹ in going from polyacrylamide to poly(methylacrylamide). The lower values of ΦV_2^0 and ΦK_2^0 per methyl group in the case of polymers (average $\Phi V_2^0 = 12.45$ cc/mole) compared to monomers (average $\Phi V_2^0 = 16.7$ cc/mole) further substantiate the observation made by Wen and Saito⁶ that water clusters become stronger and better formed as the molecules grow larger and larger. They observed, in the case of five tetraalkylammonium salts (methyl to pentyl) at 25°C, that ΦV_2^0 per methyl group is an average of 15.7 cc/mole compared to the average of 23.75 cc/mole obtained by Masterlon⁹ for aliphatic hydrocarbons in water at 23°C.

Acrylic acid and methacrylic acid (both liquids at room temperature) with molar volumes of 68.56 and 84.79 cc, respectively,¹⁰ when dissolved to form an infinitely dilute solution are found (Table IX) to decrease in volume by 6.86 and 6.19 cc, respectively. This decrease is due to electrostriction. Uncharged molecules, such as acrylamide and methacrylamide (both solids at room temperature) with molar volumes 63.35 and 76.75 cc, respectively, when dissolved to form an infinitely dilute solution are found to increase in volume by 2.15 and 5.25 cc, respectively, which corresponds to the expansion of solids on melting to some extent. Considering the usual expansion on melting as 10%, the observed lesser volume increase may be partly due to electrostrictional decrease because of the presence of amphoteric —CONH₂ groups.

Sincerest thanks are due to Professor A. B. Biswas, Indian Institute of Technology, Bombay, for encouragement and helpful suggestions.

References

1. P. Roy-Chowdhury, *J. Appl. Polym. Sci.*, **12**, 751 (1968).
2. P. Roy-Chowdhury, *Indian J. Chem.*, **7**, 692 (1969).
3. A. Silberberg, J. Eliassaf, and A. Katchalsky, *J. Polym. Sci.*, **23**, 259 (1957).
4. A. Takahashi, N. Hayashi, and I. Kagawa, *Kogyo Kagaku Zasshi*, **60**, 1059 (1957).
5. W. Scholtan, *Makromol. Chem.*, **14**, 169 (1954).
6. Wen-Yang Wen and S. Saito, *J. Phys. Chem.*, **68**, 2639 (1964).
7. O. Redlich and D. M. Meyer, *Chem. Rev.*, **64**, 221 (1964).
8. N. Ise and T. Okubo, *J. Amer. Chem. Soc.*, **90**, 4527 (1968).
9. W. L. Masterlon, *J. Chem. Phys.*, **22**, 1830 (1954).
10. J. Brandrup and E. H. Immergut, *Polymer Handbook*, Interscience, New York, 1966, p. VIII 1-27.

Received May 6, 1970