

Adiabatic Compressibility of Polyelectrolytes in Aqueous Solutions: Poly(methacrylic Acid)*

PHANIBHUSAN ROY-CHOWDHURY,
National Chemical Laboratory, Poona, India

Synopsis

The adiabatic compressibility of dilute aqueous solutions of methacrylic acid, poly(methacrylic acid), and three poly(sodium methacrylates) obtained by neutralizing the polyacid with sodium hydroxide to different extents were determined from sound-velocity and density data. The ultrasonic velocity at 25°C. was measured by employing a precision ultrasonic interferometer, and the density was measured with Ostwald-type pycnometers. The plots of the decrease of compressibility per unit concentration, $(\beta_1 - \beta)/c$ versus c shows that there is a marked difference between the curves of monomer and of polymer solutions. In case of the monomer there is a proportional decrease with increase in concentration, whereas in polymer in the dilute region (0.1–0.5 g./dl.) the curve rises sharply, then slows down, and finally approaches a constant value at comparatively higher concentrations. The nature and number of the free counterions and the shape and the concentration of the polymer molecules are responsible for the compressibility of polymer solutions. However, the contribution of the size and shape and concentration of the polymer seem to be less than that of the nature and number of the counterions. The apparent molal volume ΦV_2 and apparent molal compressibility ΦK_2 for polymer repeat units show a sharp decrease with increase in concentration and finally attain a constant value at higher concentrations; this has been explained by the fact that in the dilute region the polymer, being extended by coulombic repulsion between similar charges situated on the side chain, enhances the formation of water clusters around it, and the free counterions are solvated, leading to a decrease to these values. The number of free counterions proportionately increases with concentration, causing a proportional decrease of the ΦV_2 and ΦK_2 values, until the concentration reaches a definite stage, above which the so-called condensation of ions occurs, and the number of free counterions does not increase further at higher concentrations.

Introduction

Ultrasonics is one of the powerful methods of studying the properties of solutions, such as adiabatic compressibility and ratio of specific heats, which *inter alia* are used for elucidating the structure and nature of molecular interaction in the liquid state. Recently some work on sound-velocity measurements in polymer solutions has been reported in the literature,¹⁻⁵ but it is confined mainly to the study of uncharged chain molecules in non-aqueous solvents. Apart from the work of Sohma³ no systematic study of adiabatic compressibility in dilute aqueous solutions of

* Communication No. 1105 from the National Chemical Laboratory, Poona, India.

polyelectrolytes seems to have been reported so far. The peculiar characteristics that a linear polyelectrolyte shows in aqueous solutions are due to the fact that these solutions possess both electrolytic as well as chain molecular properties. A coiled-up polymer molecule unfolds and expands because of the mutual repulsion between similarly charged groups in their chain. The extent of expansion depends on the intensity of the repulsive force and the characteristics of the polymer chain, which are generally manifested in the results of viscosity, electrometric titration, light scattering, osmotic pressure, and other measurements. It is presumed that the molecular properties such as the degree of extension of the polymer chain, may be related to the compressibility data, obtained by sound-velocity measurements. In an attempt at investigating this relationship poly(methacrylic acid) at different extensions, induced by controlled neutralization with sodium hydroxide, has been investigated and the preliminary results are reported in this paper.

Experimental

The ultrasonic velocities were determined by a precision ultrasonic interferometer⁶ developed in this laboratory. The path length of the cell was varied by movement of a reflector. The electrical reaction of the cell upon the oscillator was used for fixing standing-wave positions at a standard frequency (5 Mc./sec.), and their positions were determined accurately within $\pm 1 \mu$ with a suitable scale and microscope fitted with a micrometer eyepiece. The cell was kept immersed in a thermostatic water bath at $25 \pm 0.01^\circ\text{C}$. The measured half-wavelength was averaged out from 410 counts for each experiment. Two measurements of the wavelengths of sound were made in each instance, and the velocity of sound in liquid was computed as the product of frequency f and wavelength λ . The two values of the sound velocity agreed to within 0.05 m./sec. with no appreciable systematic difference between them.

The adiabatic compressibility β_s of the liquid was calculated by the equation of Newton and Laplace,

$$\beta_s = -(\delta \ln V / \delta P)_s = 1/u^2d$$

Here V , P , and S are volume, pressure, and entropy, respectively.

The density of each solution was determined as the mean of three measurements by 30 cm.³ Ostwald-type pycnometers, and the agreement between the measurements was ± 0.00002 or better. The densities were calculated from the mass of the solution, and the volumes were obtained from the mass of pure solvent they held at 25°C . and its density d . All weighings were reduced to the vacuum standard.

Poly(methacrylic acid) was prepared by polymerizing freshly distilled monomer (30% w/w) in dioxane solution by treatment with 0.5% benzoyl peroxide at 55°C . with constant stirring and bubbling of nitrogen. The product was dissolved in methanol, precipitated with ether, and dried *in vacuo* to constant weight. The molecular weight of this sample was

determined by esterifying with diazomethane in benzene and measuring the intrinsic viscosity $[\eta]$ of the resulting poly(methyl methacrylate) in chloroform solution at 25°C. by applying the relation⁷ $[\eta]_{25} = 3.4 \times 10^{-5} M_v^{0.83}$. The viscosity-average molecular weight thus calculated for poly(methacrylic acid) was 6.793×10^5 . Poly(sodium methacrylate) solutions with degrees of neutralization α of 0.05, 0.25, and 1.0 were prepared by adding a calculated amount of sodium hydroxide to the polyacid.

The flow times for the solvent and solution of different concentrations of polyelectrolytes were measured with an Ubbelohde-type viscometer, and η_{25} was determined by the use of the constants $A = 0.016687$ and $B = 13.7044$ in the equation: $\eta_{25} = At + B/t$. The symbols have the usual significance.

Double-distilled water, degassed by boiling so as to prevent formation of air bubbles on the interferometer transducer or reflector, was used for the preparation of all solutions. The polymer did not dissolve easily, and it was left for several days, to give clear solutions. The solutions were filtered before use, and the concentrations were determined by weighing the residue from evaporation.

Results and Discussion

The results of sound-velocity measurements of solutions of methacrylic acid, poly(methacrylic acid) (PMA), and the three poly(sodium methacrylates) (PSMA) obtained by neutralizing the polyacid to different extents are summarized in Tables I–VII. The apparent molal volume of solute, ΦV_2 , and apparent molal compressibility of solute, ΦK_2 , were computed from 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 I

Summary of Results for Methacrylic Acid in Aqueous Solution at 25°C. ($M_2 = 86.09$)

c , g./dl.	d , g./cm. ³	ΦV_2 , cm. ³ /mole	u , m./sec.	β , bar ⁻¹ ($\times 10^6$)	ΦK_2 , cm. ³ /bar/ mole ($\times 10^3$)
0.0000	0.99704 ₆	(78.60) ^a	1496.05	44.812	(0.680) ^a
0.1008	0.99714	78.635	1496.53	44.779	0.692
0.2015	0.99723	78.632	1497.08	44.742	0.538
0.3022	0.99732	78.631	1497.50	44.713	0.703
0.4029	0.99739	78.058	1497.99	44.680	0.719
0.5039	0.99751	78.463	1498.43	44.649	0.730
1.0026	0.99797	78.422	1500.82	44.486	0.714
2.0052	0.99896	78.121	1505.36	44.174	0.762
2.9556	0.99989	78.048	1509.19	43.910	0.870
4.0304	1.00091	78.076	1513.20	43.633	0.980

^a Extrapolated value.

TABLE II
Summary of Results for Poly(methacrylic Acid) in Aqueous Solution at 25°C.
($M_2 = 86.09$)

c , g./dl.	d , g./cm. ³	ΦV_2 , cm. ³ /mole	u , m./sec.	β , bar ⁻¹ ($\times 10^6$)	ΦK_2 , cm. ³ /bar/ mole ($\times 10^3$)
0.0000	0.99704 ₆	—	1496.05	44.812	—
0.1122	0.99727	69.414	1496.17	44.794	1.734
0.2158	0.99764	62.738	1496.46	44.761	0.773
0.3415	0.99795	62.578	1496.80	44.724	0.579
0.5460	0.99860	61.833	1497.41	44.661	0.390
0.8830	0.99966	60.823	1498.43	44.553	0.196
1.7425	1.00233	60.182	1500.85	44.291	0.120
2.5093	1.00476	59.815	1503.65	44.019	0.040
3.3370	1.00734	59.720	1506.00	43.770	-0.012
4.1478	1.00980	59.803	1508.65	43.510	-0.023

TABLE III
Summary of Results for Poly(methacrylic Acid) in 0.1M Acetic Acid Solution
at 25°C. ($M_2 = 86.09$)

c , g./dl.	d , g./cm. ³	ΦV_2 , cm. ³ /mole	u , m./sec.	β , bar ⁻¹ ($\times 10^6$)	ΦK_2 , cm. ³ /bar/ mole ($\times 10^3$)
0.0000	0.99791 ₆	—	1497.98	44.657	—
0.1021	0.99818	64.301	1498.20	44.362	0.765
0.2042	0.99845	63.878	1498.53	44.601	0.482
0.3268	0.99880	63.039	1498.91	44.562	0.311
0.4357	0.99913	62.312	1499.19	44.531	0.297
0.5810	0.99954	62.215	1499.72	44.481	0.173
0.7747	1.00011	61.881	1500.25	44.425	0.185
1.0329	1.00088	61.547	1500.86	44.354	0.220
2.0658	1.00399	60.921	1503.92	44.037	0.138
3.3053	1.00765	60.874	1507.41	43.674	0.158
4.1316	1.01009	60.858	1510.03	43.418	0.136

TABLE IV
Summary of Results for Poly(sodium Methacrylate) ($\alpha = 1/20$) in Aqueous Solution
at 25°C. ($M_2 = 87.19$)

c , g./dl.	d , g./cm. ³	ΦV_2 , cm. ³ /mole	u , m./sec.	β , bar ⁻¹ ($\times 10^6$)	ΦK_2 , cm. ³ /bar/ mole ($\times 10^3$)
0.0000	0.99704 ₆	—	1496.05	44.812	—
0.1315	0.99739	64.838	1496.32	44.780	0.769
0.2630	0.99780	62.511	1496.77	44.735	0.249
0.4625	0.99845	60.982	1497.42	44.667	-0.000 ₃
0.9240	0.99993	60.191	1498.81	44.518	-0.077
1.8425	1.00283	60.016	1501.70	44.219	-0.117
2.9720	1.00633	60.142	1505.18	43.861	-0.095

TABLE V

Summary of Results for Poly(sodium Methacrylate) ($\alpha = 1/4$) in Aqueous Solution at 25°C. ($M_2 = 91.59$)

c , g./dl.	d , g./cm. ³	ΦV_2 , cm. ³ /mole	u , m./sec.	β , bar ⁻¹ ($\times 10^6$)	ΦK_2 , cm. ³ /bar/ mole ($\times 10^3$)
0.0000	0.99704 ₆	—	1496.05	44.812	—
0.0946	0.99732	65.643	1496.31	44.784	0.212
0.1892	0.99768	61.273	1496.66	44.747	-0.396
0.3028	0.99808	60.614	1497.20	44.697	-0.763
0.3945	0.99841	60.193	1497.46	44.666	-0.690
0.5390	0.99895	59.480	1498.24	44.596	-1.001
1.0640	1.00089	58.708	1500.37	44.383	-1.060
2.1115	1.00473	58.449	1504.71	43.959	-1.081
2.8153	1.00728	58.482	1507.69	43.674	-1.082

TABLE VI

Summary of Results for Poly(sodium Methacrylate) ($\alpha = 1$) in Aqueous Solution at 25°C. ($M_2 = 108.075$)

c , g./dl.	d , g./cm. ³	ΦV_2 , cm. ³ /mole	u , m./sec.	β , bar ⁻¹ ($\times 10^6$)	$-\Phi K_2$, cm. ³ /bar/ mole ($\times 10^3$)
0.0000	0.99704 ₆	—	1496.05	44.812	—
0.1068	0.99756	56.633	1496.72	44.749	3.849
0.2044	0.99807	54.304	1497.39	44.686	4.217
0.3204	0.99867	53.588	1498.17	44.612	4.333
0.4088	0.99913	53.242	1498.91	44.548	4.596
0.5140	0.99968	52.932	1499.65	44.479	4.631
1.0318	1.00232	53.031	1503.42	44.140	4.662
2.0637	1.00765	52.719	1510.92	43.472	4.654

TABLE VII

Summary of Results for Poly(sodium Methacrylate) ($\alpha = 1$) in 0.1M NaCl Solution at 25°C. ($M_2 = 108.075$)

c , g./dl.	d , g./cm. ³	ΦV_2 , cm. ³ /mole	u , m./sec.	β , bar ⁻¹ ($\times 10^6$)	$-\Phi K_2$, cm. ³ /bar/ mole ($\times 10^3$)
0.0000	1.00112 ₅	—	1502.27	44.260	—
0.1000	1.00161	55.056	1502.89	44.202	3.784
0.2000	1.00214	52.897	1503.66	44.134	4.478
0.2812	1.00255	53.056	1504.28	44.079	4.612
0.5625	1.00397	53.257	1506.22	43.904	4.483
1.1250	1.00683	53.162	1510.31	43.542	4.542
2.2500	1.01255	53.113	1518.29	42.842	4.461
3.0000	1.01634	53.186	1523.85	42.372	4.447
4.1275	1.02215	52.950	1532.51	41.656	4.476

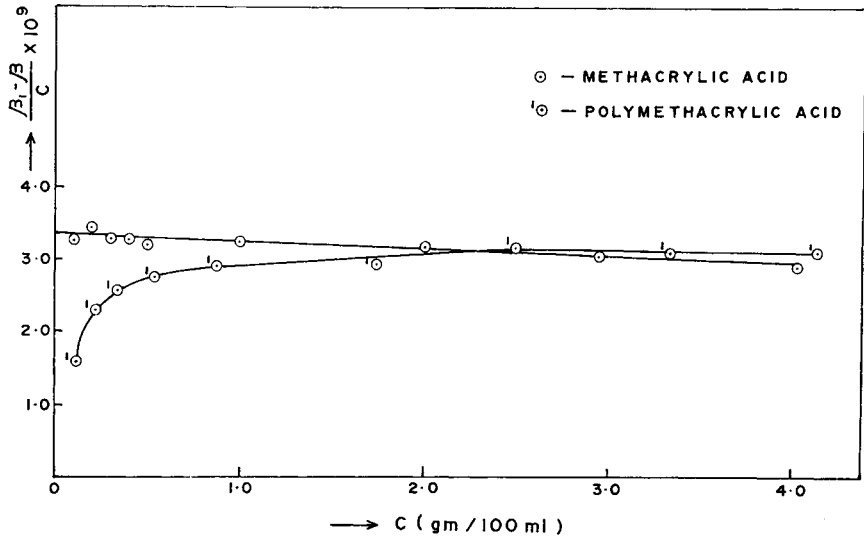


Figure 1.

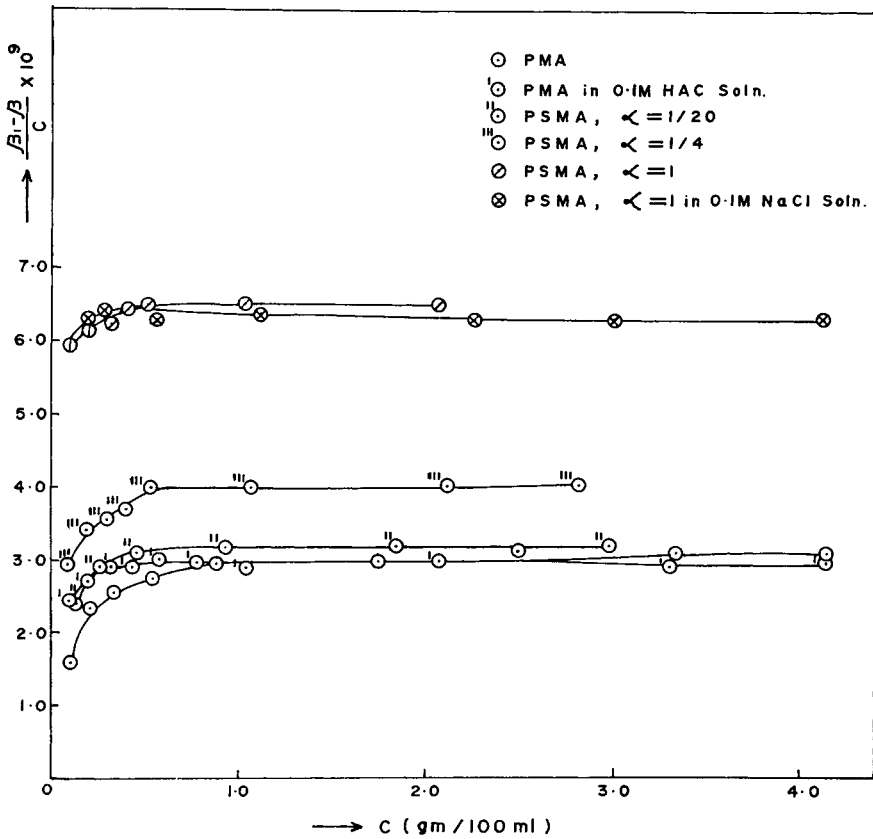


Figure 2.

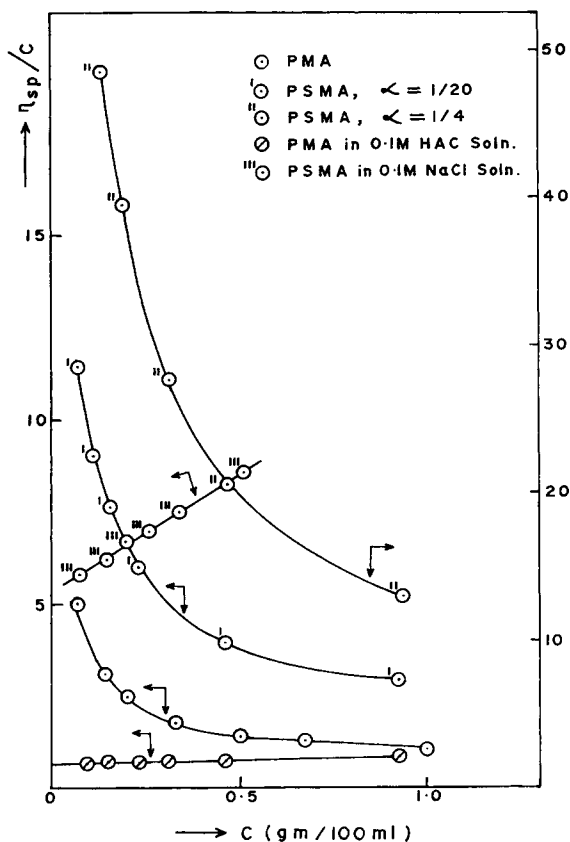


Figure 3.

Here M_2 is the molecular weight of the monomer as well as the polymer repeat unit, c is the concentration, expressed in grams per deciliter, and d , d_1 , β , and β_1 are the density and compressibility of the solution and solvent, respectively. From the experimental data it is observed that the density and sound velocity increase as the concentration increases. Accordingly the compressibility β_s decreases with increase in concentration. It is considered that the coulombic force or other intermolecular forces influence the structure of the liquid and also the association of the ions and so affect the compressibility of the solutions.

The plots of the decrease of compressibility per unit of concentration, $(\beta_1 - \beta)/c$ versus c , are shown in Figures 1 and 2. There is a marked difference between the curves of monomer and of polymer solutions. A steady decrease of $(\beta_1 - \beta)/c$ with increase in concentration is seen for methacrylic acid (Fig. 1), whereas for poly(methacrylic acid) the curve rapidly rises in the very dilute region (0.1–0.5 g./dl.), then slows down, and finally approaches to a constant value at comparatively higher concentrations. In the dilute methacrylic acid solutions the compressibility may be determined

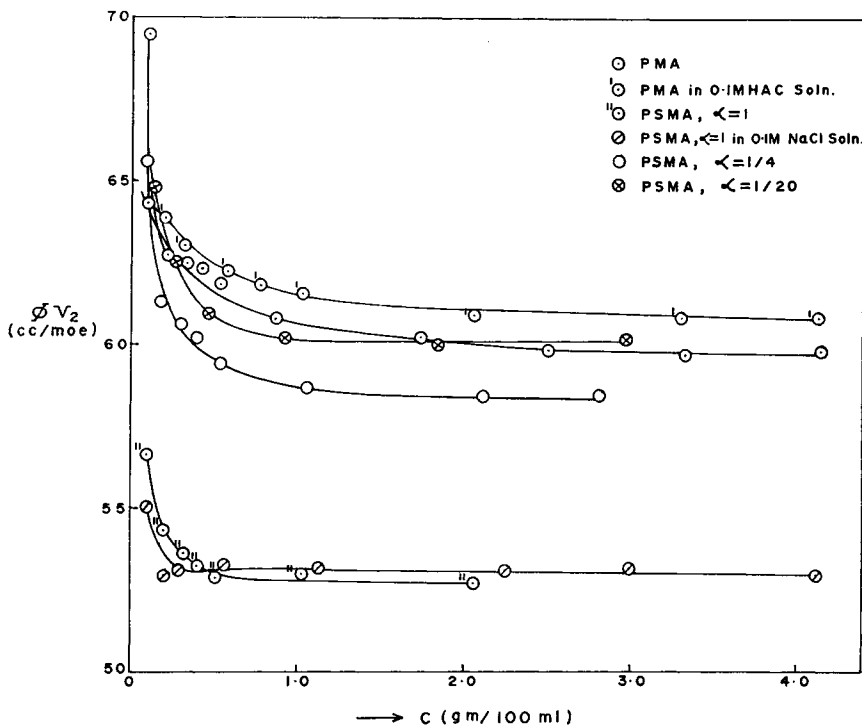


Figure 4.

mainly by the number of ions which increases proportionately with an increase in concentration throughout, whereas in polymer solutions, besides the number of ions, the size and shape of the polymer chain in addition to concentration influences the structure of the media appreciably. It is observed that the general shapes of the curves for poly(methacrylic acid) and its three products of different degrees of neutralization (Fig. 2) are more or less similar. However, the main point that emerges from these observations is that the number and nature of the counterions contribute more to the compressibility data than the shape and concentration of the polymer molecule. The decrement of compressibility per unit concentration increases proportionately as the degree of neutralization of the polyacid increases and more H^+ ions are replaced with Na^+ ions. Suppression of the dissociation of counterions, as in the case of poly(methacrylic acid) with $0.1M$ acetic acid or of poly(sodium methacrylate), $\alpha = 1$, with $0.1M$ sodium chloride solution, makes the curves of $(\beta_1 - \beta)/c$ versus c flattened in the very dilute region, but the same is not as distinct as is seen in the results of viscosity measurements. For comparison, the plots of reduced viscosity η_{sp}/c versus c for the same polyelectrolyte solutions are shown in Figure 3.

The plots of apparent molal volume of solute (polymer repeat unit) ΦV_2 versus concentration are shown in Figure 4. In the very dilute region ΦV_2 decreases sharply as the concentration increases, then slows down, and

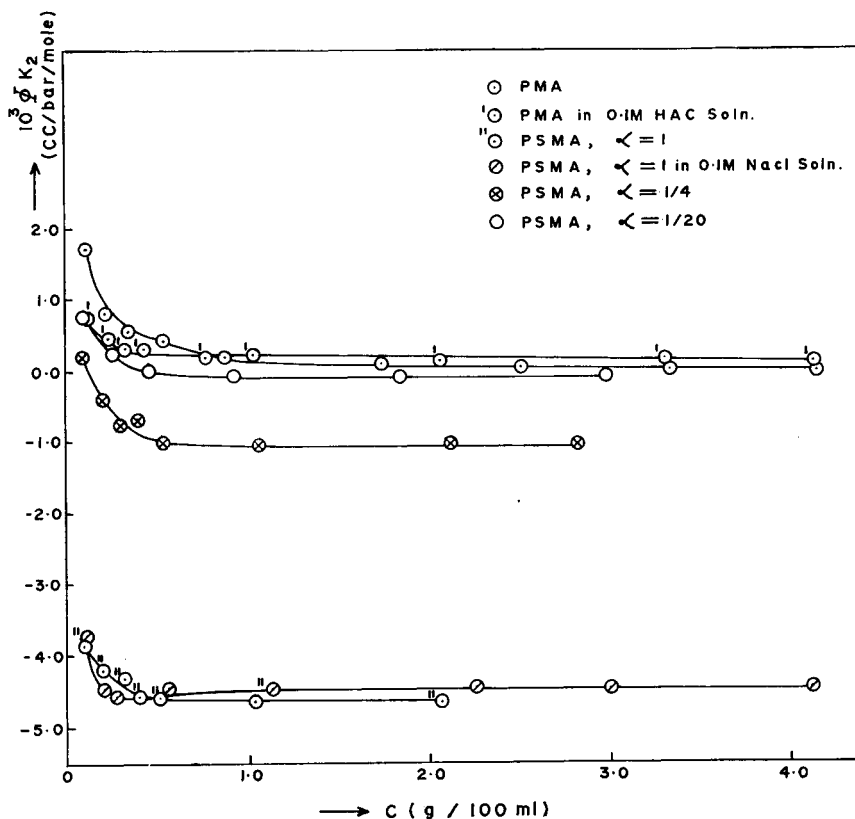


Figure 5.

ultimately approaches to a constant value at comparatively higher concentrations. The decrease of the ΦV_2 value for monomer is small and is within about $0.6 \text{ cm.}^3/\text{mole}$ for the entire range of concentration (0.1 to 4.0 g./dl.) studied. The decrease of apparent molal volume for the polyelectrolytes in this dilute range may be explained by the fact that at infinite dilution the dissociation of the counterions is complete, the large polyanion and the rather free counterions are far apart from each other, affecting the surrounding water structure in a unique way, the polyion enhances clustering of water around it through dipole-dipole interaction, and the free counterions are also solvated. This would cause the decrease of ΦV_2 values. In the dilute region the number of free counterions increases in proportion to the concentration, causing the proportional decrease of ΦV_2 values, until the concentration reaches a definite stage, above which the so-called condensation of ions occurs, and the number of free counterions does not increase further at higher concentrations. However, as the degree of neutralization of poly(methacrylic acid) is increased, the degree of dissociation of counterions increases accordingly, leading to a proportional decrease of the ΦV_2 values. In 100% neutralized polyacid solutions the

dissociation of counterions is almost complete, so that a maximum decrease of the ΦV_2 values is observed in this case.

The apparent molal compressibilities ΦK_2 versus the concentration curves (Fig. 5) for the polyelectrolytes studied are similar to the curves of ΦV_2 versus c , and this may also be explained in a similar way. It is interesting to note that the ΦK_2 values are positive in methacrylic acid and poly(methacrylic acid) solutions, contrary to what is observed in the case of dilute aqueous solutions of electrolytes, which is usually negative. However, at comparatively higher concentrations the polyacid and its salts show negative values. In dilute solutions ΦK_2 decreases with increase in concentration, giving a negative gradient, unlike the case of an electrolyte, in which generally only a positive gradient of ΦK_2 versus c is observed.

Sincere thanks are due A. B. Biswas for many helpful suggestions.

References

1. G. Natta and M. Baccaredda, *J. Polymer Sci.*, **3**, 829 (1948); *idem*, **4**, 533 (1949).
2. Y. Wada and S. Shimbo, *J. Phys. Soc. Japan*, **9**, 78 (1954).
3. J. Sohma, *J. Polymer Sci.*, **35**, 429 (1959).
4. P. R. K. L. Padmini, *Indian J. Pure Appl. Phys.*, **1**, 66 (1963).
5. W. R. Moore and B. M. Tidswell, *Makromol. Chem.*, **81**, 1 (1965).
6. P. Roy-Chowdhury, *Indian J. Pure Appl. Phys.*, **5**, 123 (1967).
7. S. N. Chinai, J. D. Matlack, A. L. Resnick, and R. J. Samuels, *J. Polymer Sci.*, **17**, 391 (1955).

Received August 2, 1967