

Adiabatic Compressibility of Polyelectrolytes: Poly(N-dimethylaminoethyl Methacrylate) and its Copolymer with Acrylic Acid

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Synopsis

The adiabatic compressibility of poly(N-dimethylaminoethyl methacrylate) and of three copolymers of N-dimethylaminoethyl methacrylate and acrylic acid, ranging in composition from 33 to 58 mole-% amino groups, has been studied. The ϕV_2^0 of the polymer shows a slight decrease (2.4 cc/mole), while the ϕK_2^0 is found to have increased considerably (51×10^{-4} cc bar⁻¹ mole⁻¹) compared to that of the monomer. The latter is apparently due to the more compressible nature of the polymer than that of its monomer. The experimentally observed ϕK_2^0 and ϕV_2^0 values for the three copolymers containing 58%, 43%, and 33% amino groups are -2.5×10^{-4} cc bar⁻¹ mole⁻¹ and 164.5 cc/mole, -32×10^{-4} cc bar⁻¹ mole⁻¹ and 177.5 cc/mole, and -55×10^{-4} cc bar⁻¹ mole⁻¹ and 211.3 cc/mole, respectively, whereas the calculated values are less by 19.4×10^{-4} cc bar⁻¹ mole⁻¹ and 3.2 cc/mole, 49.5×10^{-4} cc bar⁻¹ mole⁻¹ and 19.9 cc/mole, and 73×10^{-4} cc bar⁻¹ mole⁻¹ and 16.4 cc/mole, respectively. This decrease is attributed to the interaction of acid and base groups in the molecules. The ϕK_2^0 and ϕV_2^0 values have been resolved into their ionic components ϕK_{2i}^0 and ϕV_{2i}^0 . Since the magnitude of electrostriction is higher in fully neutralized salt than in unneutralized salt, the ϕK_{2i}^0 and ϕV_{2i}^0 values are lower as expected. The difference in these values for the polybase and its salt is 23.7×10^{-4} cc bar⁻¹ mole⁻¹ and 7.5 cc/mole, respectively, which may be due to the electrostrictive effect. In excess NaCl (1.0M), the magnitude of electrostriction is somewhat reduced and ϕK_{2i}^0 and ϕV_{2i}^0 approach values more or less equal to those of the unneutralized polymer. The 100% neutralized hydrochloride salt of poly(N-dimethylaminoethyl methacrylate) shows greatly increased reduced viscosity over that of the feebly basic parent polymer due to the characteristic polyelectrolytic expansion in dilute aqueous solution. The copolymer containing excess amount of amino groups (58%) shows similar behavior, while the other two copolymers containing fewer amino groups (43% and 33%) show a contraction of chains, which may be ascribed in interaction of the carboxyl ions that are freshly formed on dilution with the amino groups in the copolymer chain.

INTRODUCTION

Considerable amount of work has been carried out on adiabatic compressibility^{1,2} and apparent molal volume^{3,4,5} of polyanions, but investigations on polycations^{6,7} are limited. Further, a study of adiabatic compressibility of anionic and cationic polymer separately and then in com-

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bination in the form of amphoteric polyelectrolyte may help to elucidate the nature of the interaction between the acid and base groups and the resultant molecular configuration when they are put together on the same polymer chain.

In this paper, the results of our study on the adiabatic compressibility of poly(*N*-dimethylaminoethyl methacrylate) and of a few copolymers made with acrylic acid are reported. Poly(acrylic acid) has been chosen as the anionic counterpart for synthesizing the amphoteric polyelectrolytes, as its adiabatic compressibility was studied earlier in this laboratory. Poly(*N*-dimethylaminoethyl methacrylate) is feebly basic in aqueous solution, but its hydrochloride shows the characteristic expansion and contraction in dilute aqueous solution. The copolymer containing excess amount of amine groups shows the polyelectrolytic expansion at the lower concentration, but as the amine groups in the chain are decreased, contraction of the chain instead of expansion is observed.

EXPERIMENTAL

Poly(*N*-dimethylaminoethyl Methacrylate)

Poly(*N*-dimethylaminoethyl methacrylate), PDAM, was prepared by polymerizing freshly distilled monomer in dioxane solution (30% w/w) using 0.5% isobutyronitrile as initiator at 75°C with constant stirring in nitrogen atmosphere. The product was precipitated with petroleum ether (60–80°C fraction) and dried in vacuo to constant weight. The hydrochloride salt of the polymer was obtained by neutralizing it with a calculated amount of hydrochloric acid, predetermined by pH-metric titration.

Synthesis and Purification of Amphoteric Polyelectrolytes

Three amphoteric polyelectrolytes were prepared by copolymerizing varying proportions of *N*-dimethylaminoethyl methacrylate with acrylic acid^{8,9} in the following way:

Acrylic Acid-*N*-Dimethylaminoethyl Methacrylate (AA-DAM 58) Copolymer. This copolymer was prepared by polymerization of a mixture of freshly distilled monomers of *N*-dimethylaminoethyl methacrylate (DAM) (70 mole-% in the monomer) and acrylic acid (AA) in a 2*M* dioxane solution with 0.5% benzoyl peroxide at 70°C, with constant stirring and bubbling with nitrogen for 6 hr. The product was diluted with dioxane, precipitated with petroleum ether, and finally dried in vacuo to constant weight. The conversion into polymer was 75%, and the polymer was gummy in character.

Acrylic Acid-*N*-Dimethylaminoethyl Methacrylate (AA-DAM 43) Copolymer. This was prepared in a similar way by polymerization of a mixture of monomers of the amine (50 mole-% in the monomer) and the acid in 2*M* dioxane solution. The product was a white precipitate which was

washed several times with petroleum ether until it was free from monomer. Finally, it was dried in vacuo to constant weight. The conversion into polymer was 26%, and the product was obtained as white, fine powder.

Acrylic Acid-N-dimethylaminoethyl Methacrylate (AA-DAM 33) Copolymer. This was prepared in 2*M* aqueous solution with 30 mole-% amine in the mixture using potassium persulfate (0.1%) as initiator at 70°C. The polymerization was completed within 15 min. The product was precipitated with acetone and dried in vacuo over P₂O₅ to constant weight. The conversion into polymer was 50%, and the polymer was obtained as a hard mass.

Composition of Copolymers

Nitrogen content of the copolymers was determined by the Kjeldahl method and the equivalent weight was calculated on this basis. The acid and amine groups were estimated pH-metrically with 0.8*N* NaOH and HCl, respectively. The equivalent weights as obtained by the nitrogen estimation and pH-metric titration are given in Table I. The two sets of data are in close agreement.

All calculations regarding the compressibilities and apparent molal properties were made taking the equivalent weight determined on the basis of nitrogen content of the copolymer. However, other values, based on acid groups present, may be obtained by multiplying with the corresponding ratio of acid-to-base groups in the polymeric chain.

The adiabatic compressibility, β_s , was determined from the sound velocity and density data in the usual way.¹ The limiting values of apparent molal compressibility, ΦK_2^0 , and apparent molal volume, ϕV_2^0 , of the solute in aqueous solution were obtained by extrapolation of ϕK_2 - and ϕV_2 -versus-concentration curves to infinite dilution. These values are given in parenthesis in Tables II to VIII.

The viscosity of the solution was measured at 25°C with a Ubbelohde viscometer.

TABLE I
Composition of Acrylic Acid-N-Dimethylaminoethyl Methacrylate Copolymer (AA-DAM)

Copolymer	Amine in monomer mixture mole-%	Equivalent weight by nitrogen analysis		Equivalent weight on basis of pH-metric titration		Ratio of acid to base group in the co-polymer	Groups in polymer, mole-%	
		Acid	Amine	Acid	Base		Acid	Amine
AA-DAM 58	70	291	207	296	201	1:1.4	42	58
AA-DAM 43	50	188	254	190	254	1:0.74	57	43
AA-DAM 33	30	152	299	154	298	1:0.5	67	33

TABLE II

Summary of Results for N-Dimethylaminoethyl Methacrylate in Aqueous Solution at 25°C ($M_2 = 157.2$)

c , g/dl	d , g/cc	ϕ/V_2 , cc/mole	u , m/sec	β , bar ⁻¹ $\times 10^6$	ϕK_2 , (cc bar ⁻¹ mole ⁻¹) $\times 10^4$
0.0000	0.99705	(136.7)	1496.05	44.812	(-35.0)
0.1000	0.99718	137.2	1496.98	44.750	-35.7
0.2000	0.99732	136.4	1497.89	44.689	-35.7
0.3000	0.99745	136.6	1498.75	44.632	-33.1
0.4000	0.99758	136.8	1499.79	44.565	-35.7
0.5000	0.99772	136.5	1500.66	44.507	-34.7
0.7500	0.99805	136.6	1502.98	44.355	-34.7
1.0000	0.99839	136.5	1505.40	44.197	-35.5
1.5000	0.99906	136.5	1510.09	43.894	-35.0
2.0000	0.99972	136.6	1514.65	43.601	-34.0

TABLE III

Summary of Results for Poly(N-dimethylaminoethyl Methacrylate) in Aqueous Solution at 25°C ($M_2 = 157.2$)

c , g/dl	d , g/cc	ϕV_2 , cc/mole	u , m/sec	β , bar ⁻¹ $\times 10^6$	ϕK_2 , (cc bar ⁻¹ mole ⁻¹) $\times 10^4$
0.0000	0.99705	(134.3)	1496.05	44.812	(16.0)
0.0994	0.99720	133.9	1496.40	44.784	15.4
0.1987	0.99734	134.6	1496.75	44.757	16.8
0.2981	0.99749	134.4	1497.10	44.729	16.5
0.3975	0.99764	134.3	1497.46	44.701	16.2
0.4969	0.99779	134.2	1497.81	44.673	16.2
0.7453	0.99815	134.4	1498.73	44.602	15.9
0.9937	0.99852	134.3	1499.59	44.535	16.4
1.4906	0.99926	134.3	1501.30	44.400	16.7
1.9875	1.00001	134.2	1503.00	44.267	17.0

TABLE IV

Summary of Results for Poly(N-dimethylaminoethyl Methacrylate) Hydrochloride Salt in Aqueous Solution at 25°C ($M_2 = 193.7$)

c , g/dl	d , g/cc	ϕV_2 , cc/mole	u , m/sec	β , bar ⁻¹ $\times 10^6$	ϕK_2 , (cc bar ⁻¹ mole ⁻¹) $\times 10^4$
0.0000	0.99705	(144.9)	1496.05	44.812	(-15.0)
0.0995	0.99730	145.5	1496.55	44.770	-15.0
0.1989	0.99755	145.4	1497.06	44.729	-15.5
0.2984	0.99781	144.8	1497.57	44.687	-16.2
0.3979	0.99807	144.5	1498.07	44.645	-16.6
0.4973	0.99831	145.0	1498.56	44.605	-15.6
0.7460	0.99895	144.8	1499.86	44.499	-16.4
0.9947	0.99957	145.0	1501.10	44.398	-15.6
1.4920	1.00084	144.9	1503.68	44.190	-15.8
1.9894	1.00210	144.9	1506.16	43.989	-14.9

RESULTS AND DISCUSSION

The results of adiabatic compressibility for N-dimethylaminoethyl methacrylate in aqueous solution are summarized in Table II; while those of the corresponding polymer (PDAM) and the salt formed by neutralizing it with HCl, both in aqueous solution and in the presence of 1.0M NaCl solution, are given in Tables III to V. The plots of ϕK_2 and ϕV_2 as a function of concentration are shown in Figures 1 and 2. The ϕK_2 and ϕV_2 values for the monomer, polymer, and its hydrochloride salt are found to be concentration independent. The limiting values, ϕK_2^0 and ϕV_2^0 , are given in Table IX. The ϕV_2^0 for the cationic polymer shows a slight decrease (2.4 cc/mole), whereas the ϕK_2^0 shows a considerable increase (51×10^{-4} cc bar $^{-1}$ mole $^{-1}$) compared to that of the monomer. Such increased ϕK_2^0 value implies that the cationic polymer is apparently more compressible than its monomer. The electrostrictive N center may have been blocked

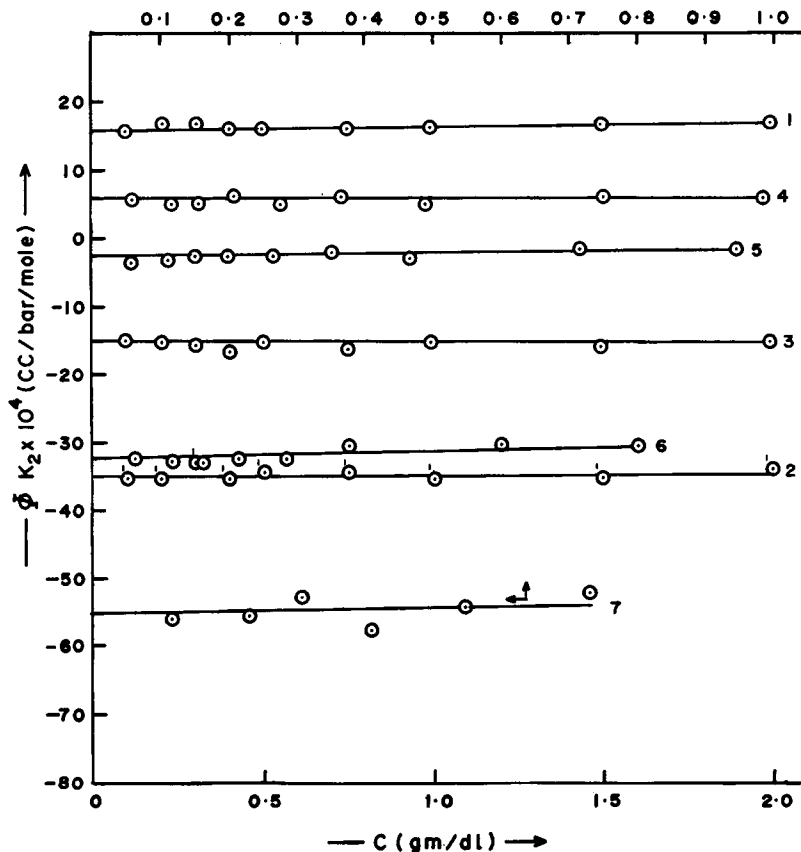


Fig. 1. Plots of apparent molal compressibility as a function of concentration: (1) PDAM; (2) DAM; (3) hydrochloride of PDAM; (4) hydrochloride of PDAM in 1.0M NaCl solution; (5) AA-DAM 58; (6) AA-DAM 43; (7) AA-DAM 33.

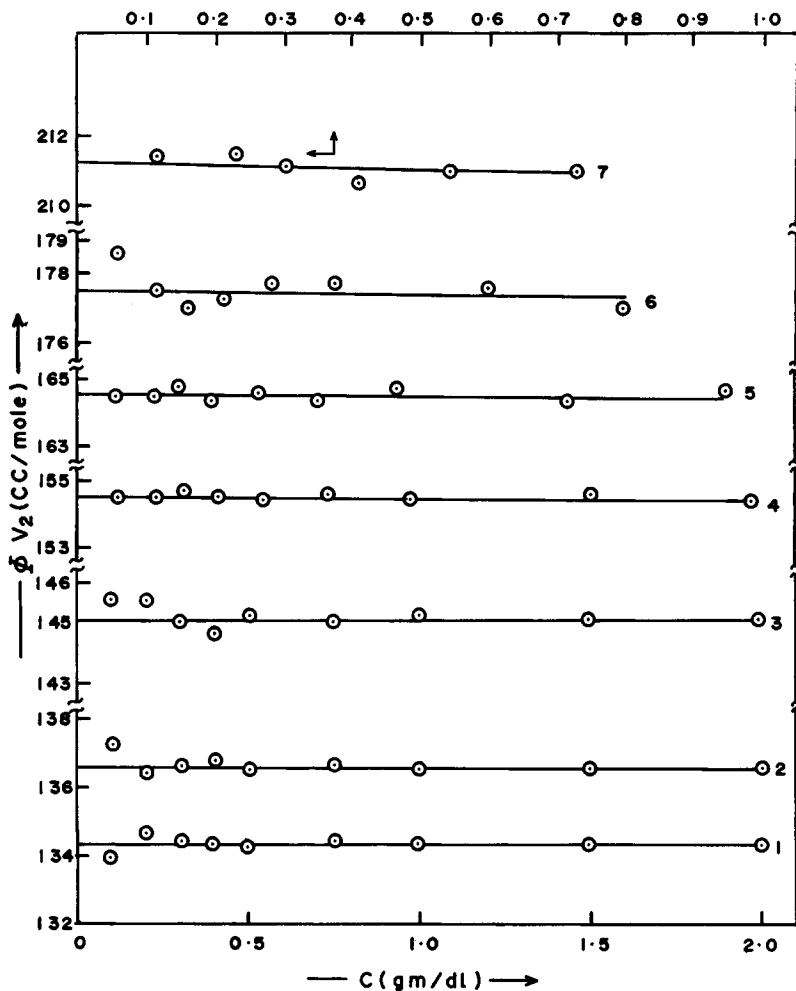


Fig. 2. Plots of apparent molal volume as a function of concentration: (1) PDAM; (2) DAM; (3) hydrochloride of PDAM; (4) hydrochloride of PDAM in 1.0M NaCl solution; (5) AA-DAM 58; (6) AA-DAM 43; (7) AA-DAM 33.

up interaction with the solvent and facilitated by an orderly arrangement of the amino groups in the polymer chain. Further, the monomer is a liquid at room temperature, and its molar volume, 169.7 cc, decreases by 33.0 cc when dissolved to infinite dilution. This is much higher than that found in acrylic acid and methacrylic acid¹ (~6-7 cc).

The results for the three copolymers (AA-DAM 58, AA-DAM 43, and AA-DAM 33) are summarized in Tables VI to VIII. All three copolymers are soluble throughout the pH ranges. The basicity of the copolymer decreases as the mole per cent of the amino groups in the amphoteric polyelectrolyte decreases. The compressibility measurement for copolymer containing 33% amino groups was restricted to 1% concentration, as the

TABLE V
Summary of Results for Poly(N-dimethylaminoethyl Methacrylate)
Hydrochloride Salt in 1.0M NaCl Solution ($M_2 = 193.7$)

c , g/dl	d , g/cc	ϕV_2 , cc/mole	u , m/sec	β , bar ⁻¹ $\times 10^6$	ϕK_2 , (cc bar ⁻¹ mole ⁻¹) $\times 10^4$
0.0000	1.03709	(154.5)	1557.30	39.759	(6.0)
0.1157	1.03729	154.5	1557.80	39.726	6.4
0.2313	1.03749	154.5	1558.31	39.692	5.3
0.3084	1.03762	154.7	1558.67	39.669	5.1
0.4113	1.03780	154.5	1559.09	39.641	5.9
0.5489	1.03804	154.4	1559.71	39.600	5.2
0.7312	1.03835	154.6	1560.48	39.549	5.9
0.9750	1.03878	154.4	1561.62	39.475	5.0
1.5000	1.03967	154.6	1563.82	39.331	6.1
1.9753	1.04051	154.4	1565.84	39.197	6.2

TABLE VI
Summary of Results for Acrylic Acid-N-Dimethylaminoethyl Methacrylate
Copolymer AA-DAM 58 in Aqueous Solution at 25°C ($M_2 = 207$)

c , g/dl	d , g/cc	ϕV_2 , cc/mole	u , m/sec	β , bar ⁻¹ $\times 10^6$	ϕK_2 , (cc bar ⁻¹ mole ⁻¹) $\times 10^4$
0.0000	0.99705	(164.5)	1496.05	44.812	(-2.5)
0.1106	0.99728	164.4	1496.56	44.771	-3.4
0.2212	0.99751	164.4	1497.09	44.729	-3.8
0.2950	0.99766	164.7	1497.41	44.703	-2.5
0.3934	0.99787	164.3	1497.86	44.667	-2.7
0.5245	0.99814	164.5	1498.50	44.616	-2.6
0.6993	0.99851	164.3	1499.24	44.556	-2.1
0.9324	0.99898	164.6	1500.39	44.467	-2.8
1.4344	1.00004	164.3	1502.59	44.290	-1.7
1.8886	1.00096	164.6	1504.67	44.127	-1.3

TABLE VII
Summary of Results for Acrylic Acid-N-Dimethylaminoethyl Methacrylate
Copolymer AA-DAM 43 in Aqueous Solution at 25°C ($M_2 = 254$)

c , g/dl	d , g/cc	ϕV_2 , cc/mole	u , m/sec	β , bar ⁻¹ $\times 10^6$	ϕK_2 , (cc bar ⁻¹ mole ⁻¹) $\times 10^4$
0.0000	0.99705	(177.5)	1496.05	44.812	(-32.0)
0.1171	0.99740	178.6	1496.65	44.760	-32.6
0.2343	0.99776	177.5	1497.24	44.708	-33.0
0.3180	0.99802	177.0	1497.68	44.671	-33.3
0.4240	0.99834	177.2	1498.20	44.625	-32.4
0.5653	0.99876	177.7	1498.94	44.562	-32.6
0.7537	0.99933	177.7	1499.82	44.485	-30.7
1.2060	1.00070	177.6	1502.09	44.290	-30.3
1.6080	1.00196	177.0	1504.09	44.116	-30.6

TABLE VIII
Summary of Results for Acrylic Acid-N-Dimethylaminoethyl Methacrylate
Copolymers AA-DAM 33 in Aqueous Solution at 25°C ($M_2 = 299$)

c , g/dl	d , g/cc	ϕV_2 , cc/mole	u , m/sec	β , bar ⁻¹ $\times 10^6$	ϕK_2 , (cc bar ⁻¹ mole ⁻¹) $\times 10^4$
0.0000	0.99705	(211.3)	1496.05	44.812	(-55.0)
0.1153	0.99739	211.4	1496.76	44.754	-56.2
0.2306	0.99773	211.4	1497.47	44.696	-55.6
0.3076	0.99796	211.1	1497.90	44.660	-53.0
0.4100	0.99827	210.6	1498.62	44.603	-57.8
0.5467	0.99867	211.0	1499.40	44.539	-54.6
0.7290	0.99921	211.0	1500.42	44.455	-52.0

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

Materials	M_2	Molar volume, cc/mole	ϕV_{2i}^0 , cc/mole	ϕV_{2i}^0 , cc/mole	ϕK_{2i}^0 , (cc bar ⁻¹ mole ⁻¹) $\times 10^4$	ϕK_{2i}^0 , (cc bar ⁻¹ mole ⁻¹) $\times 10^4$
N-Dimethylaminoethyl methacrylate	157.2	169.7 ^a	136.7	137.7	-35.0	-35.0
Poly(N-dimethylamino- ethyl methacrylate)	157.2		134.3	134.3	16.0	16.0
Poly(N-dimethylamino- ethyl methacrylate) hydrochloride	193.7		144.9	126.8	-15.0	-6.8
Poly(N-dimethylamino- ethyl methacrylate) hydrochloride in 1.0M NaCl solution	193.7		154.5	136.4	6.0	14.2
Copolymers						
AA-DAM 58	207		164.5	164.5	-2.5	-2.5
AA-DAM 43	254		177.5	177.5	-32.0	-32.0
AA-DAM 33	299		211.3	211.3	-55.0	-55.0
Poly(acrylic acid) ^b	72.06		46.7	46.7	0.86	0.86
Poly(sodium acrylate), $\alpha = 1^b$	94.04		37.0	38.4	-50.5	-7.9
Poly(sodium acrylate), $\alpha = 1$, in 1.0M NaCl solution ^b	94.04		42.80	44.3	-33.0	9.63

^a Density obtained from Alfrey and Pinner.¹³

^b Data from Roy-Chowdhury and Kale.¹

viscosity of the solution is very high. Similar to the cationic and anionic polymers, the ϕK_2 and ϕV_2 for the copolymers are found to be concentration independent (Figs. 1 and 2, curves 5, 6, and 7 in both figures).

From Table IX, it is observed that the equivalent weight of the repeat unit of the three copolymers has increased over that of PDAM by 49.8,

96.8, and 141.8, respectively. If there were no interaction between the acidic and basic groups in the chain, the ϕK_2^0 and ϕV_2^0 values would have been 16.9×10^{-4} cc bar⁻¹ mole⁻¹ and 167.7 cc/mole, 17.5×10^{-4} cc bar⁻¹ mole⁻¹ and 197.4 cc/mole, and 18.0×10^{-4} cc bar⁻¹ mole⁻¹ and 227.7 cc/mole, respectively. However, the experimentally obtained values are -2.5×10^{-4} cc bar⁻¹ mole⁻¹ and 164.5 cc/mole, -32.0×10^{-4} cc bar⁻¹ mole⁻¹ and 177.5 cc/mole, and -55.0×10^{-4} cc bar⁻¹ mole⁻¹ and 211.3 cc/mole, respectively. Thus, a decrease in ϕK_2^0 and ϕV_2^0 values by 19.4×10^{-4} cc bar⁻¹ mole⁻¹ and 3.2 cc/mole, 49.5×10^{-4} cc bar⁻¹ mole⁻¹ and 19.9 cc/mole, and 73.0×10^{-4} cc bar⁻¹ mole⁻¹ and 16.4 cc/mole, respectively, may be considered as due to the interaction of acidic and basic groups in the molecules. Copolymers containing 43% and 33% amino groups show more pronounced interaction than those containing 58% amino groups. The viscosity data also show a similar type of behavior.

Viscosity

The viscosity data for the three copolymers along with PDAM and its 100% neutralized hydrochloride salt are given in Figure 3. The reduced viscosity of PDAM is very low (~ 0.2 dl/g). The reduced viscosity of the hydrochloride salt has increased considerably (~ 5.5 dl/g) in the dilute region owing to polyelectrolytic expansion. The copolymer containing 58% amino groups shows a similar behavior at the dilute region, but the reduced viscosity is somewhat lower (~ 4 dl/g). Contrary to this observation, AA-DAM 43 and AA-DAM 33 show a lower reduced viscosity. On dilution, probably some carbonyl ions are freshly formed and interact with the amino groups present in the chain causing a coiling of the molecule and a lowering of the viscosity. It may be pointed out that the reduced viscosity of 100% neutralized potassium salt of the copolymers of 4-vinyl-N-n-butylpyridinium bromide with acrylic and methacrylic acids was found to be lower than that of the corresponding unneutralized copolymers.¹⁰ This is also attributed to the same type of interaction. However, in all the three copolymers, when fully neutralized with HCl or NaOH solution, the viscosity increases (plots are not shown) considerably over that of the unneutralized copolymers. Ehrlich and Doty⁹ and Alfrey et al.⁸ have also observed a similar type of chain expansion with a change of pH, away from the isoionic point in the copolymers of methacrylic acid and N-dimethyl-aminoethyl methacrylate.

Separation of Ionic Compressibility and Volume

The resolution of the ϕK_2^0 and ϕV_2^0 values of the polyelectrolytes into separate anionic and cationic values is necessary to explain the discrepancy that is observed in cationic and anionic polymers. Further, this will also help to ascertain the contribution of electrostrictive hydration effect in the macroion. However, strictly speaking, this additivity as in the case of simple electrolytes may not hold. Some counterions may remain bound to the polyanion even at infinite dilution.^{5,11,12}

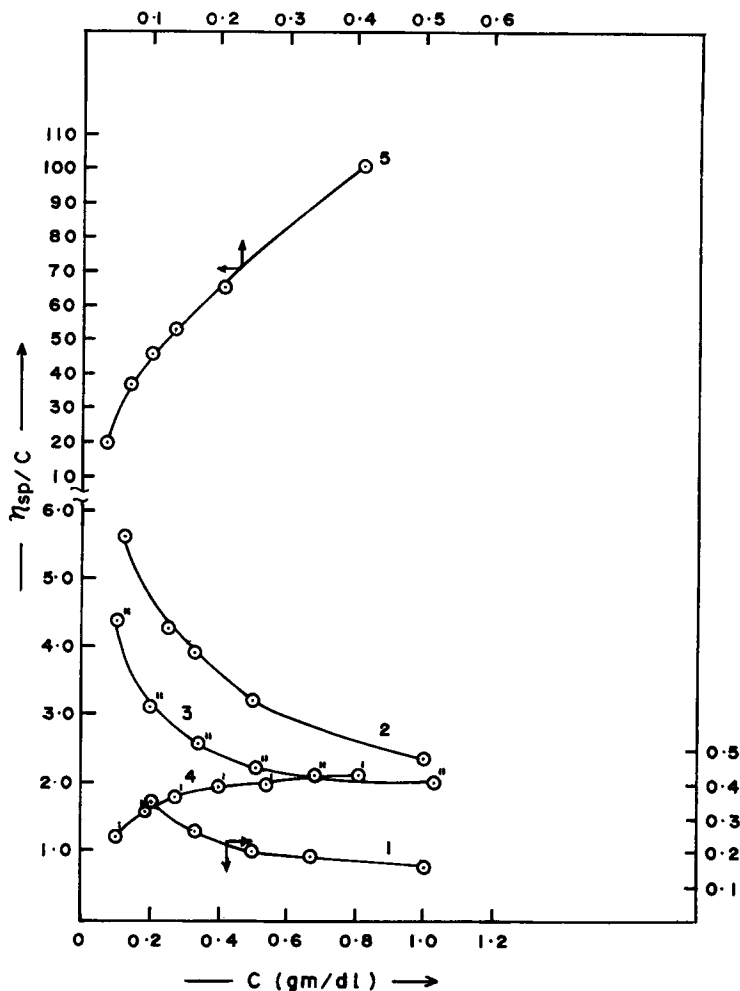


Fig. 3. Plots of reduced viscosity as a function of concentration: (1) PDAM; (2) hydrochloride of PDAM; (3) AA-DAM 58; (4) AA-DAM 43; (5) AA-DAM 33.

Contrary to the anionic polymers and their sodium salts, the ϕV_2^0 values of the hydrochloride salt of the cationic polymer increase compared to that of the unneutralized polymer. The limiting values, ϕK_2^0 and ϕV_2^0 , are related to the structural hydration and electrostrictive hydration effects. Considering that a polybase or polyacid and its salt are subjected to similar type of structural hydration effect, the difference in data for polyacid or polybase and its salt is due to the electrostrictive effect. Using the conventional reference values¹⁴ $\phi K_{2(H^+)}^0 = 0$ and $\phi V_{2(H^+)}^0 = 0$, the values of macroions (ϕK_{2i}^0 and ϕV_{2i}^0) were computed¹² and recorded in Table IX (columns 5 and 7).

Since the magnitude of electrostriction of fully neutralized salt is higher than that of the unneutralized one, the ϕK_{2i}^0 and ϕV_{2i}^0 values are found to

be lower in salts, similar to that of anionic polymers. Comparing the salt and polymer, the difference in ϕK_{2i}^0 and ϕV_{2i}^0 is found to be 23.7×10^{-4} cc bar⁻¹ mole⁻¹ and 7.5 cc/mole, respectively, which may be considered as a contribution of the electrostrictive effect. By suppression of the dissociation with NaCl solution (1.0*M*), the magnitude of electrostriction has been reduced, and accordingly the ϕK_{2i}^0 and ϕV_{2i}^0 values have increased to 14.2×10^{-4} cc bar⁻¹ mole⁻¹ and 136.4 cc/mole, respectively, which are more or less equal to that of the unneutralized polybase. These values were calculated considering that full suppression has been effected in the presence of NaCl solution.

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