Adiabatic Compressibility of
Some Amphoteric Polyelectrolytes

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Synopsis

The results of adiabatic compressibility measurements for two amphoteric polyelectrolytes, acrylic acid–4-vinyl-N-*n*-butylpyridinium bromide copolymer and methacrylic acid–4-vinyl-N-*n*-butylpyridinium bromide copolymer, and their completely neutralized potassium salts have been described. The two amphoteric polyelectrolytes are strongly acidic, and the strength of the acidic group has been increased by the presence of the neighboring basic group. The reduced viscosity for these polyampholytes is extremely low ($\sim$0.03–0.07 dl/g) which may be on account of the mutual interaction of acid and base groups making the polyelectrolyte chain highly coiled and compact. The apparent molal volume ΦV_2 and apparent molal compressibility ΦK_2 are concentration independent. Their potassium salts showed the lowest ΦV_2 and ΦK_2 values as the electrostriction is highest here; these values showed a slight increase in the presence of dilute KBr solution as the dissociation is somewhat reduced. However, in excess KBr solution, the acrylic acid-containing copolymer having comparatively more carboxyl groups (21.7%) behaves more or less similar to poly(acrylic acid), whereas the methacrylic acid-containing copolymer, with only 15.1% carboxyl groups, behaves closely to poly(4-vinyl-N-*n*-butylpyridinium bromide). These polyelectrolytes showed absorption in the 2700 to 3800 Å region in the presence of chloride, bromide, and iodide ions which are due to charge transfer complex formation between the halide ions and the polymer nucleus. The magnitude of extinction coefficient for these two polyampholytes is much less than that of poly(4-vinyl-N-*n*-butylpyridinium bromide). The limiting values of apparent molal volume, $\Phi V_2{}^0$, for acrylic acid- and methacrylic acid-containing copolymers are 183.9 and 184.6 cc/mole, respectively. These experimentally determined values fall short of 9.2 and 6.2 cc/mole compared to the calculated values (if there was no interaction between acid and base groups) which are definitely due to mutual interaction of acid and base groups in the polymer chain.

INTRODUCTION

Studies on adiabatic compressibility of some polymeric acids such as poly(acrylic acid)[1] and poly(methacrylic acid)[2] and polymeric base such as poly(4-vinyl-N-*n*-butylpyridinium bromide)[3] were reported earlier. The present paper is an extension of a similar study with synthetic polyelectrolytes and copolymers carrying both acid and base groups in the chain. The interest in studying synthetic amphoteric polyelectrolytes has been stimulated for the last two decades by the fact that these polymeric molecules are somewhat similar to many of the biologically important materials such as proteins. Proteins carry a variety of ionizable groups in their side

chains which may give rise to a net positive or negative charge depending on their state of ionization. We have synthesized two amphoteric copolymers of 4-vinyl-N-n-butylpyridinium bromide with acrylic acid or methacrylic acid, which are soluble in water. These copolymers and their fully neutralized potassium salts in aqueous solution show extremely low reduced viscosity ($\sim$0.03 dl/g) which may be ascribed to the interaction of the acid and base groups in the polymer chain, making the chain highly coiled and compact. The ultraviolet absorption measurements confirm that these amphoteric polymers in excess KBr solution absorb halide ions due to the formation of charge transfer complex between halogen ions and the zwitter ion. However, this effect is more prominent in adiabatic compressibility data for methacrylic acid-containing copolymer rather than in acrylic acid-containing copolymer.

EXPERIMENTAL

Synthesis and Purification of Amphoteric Polyelectrolytes

Acrylic Acid–4-Vinylpyridine (AA–ViPy) Copolymer. The copolymer was prepared by bulk polymerization of a mixture of freshly distilled monomers of acrylic acid (50 mole-% in the monomer) and 4-vinylpyridine without initiator at 55°C with constant stirring and bubbling of nitrogen for 1 hr. The reaction was very vigorous, and the product obtained after the reaction was a hard, solid mass. This was dissolved in a small amount of benzene–methyl alcohol mixture (40:60), precipitated with a large excess of ethyl acetate and finally dried in vacuo to constant weight. The conversion into polymer was about 82.5%. The copolymer was very hygroscopic.

Methacrylic Acid–4-Vinylpyridine (MAA–ViPy) Copolymer. This was prepared in a similar way by bulk polymerization of freshly distilled monomers of methacrylic acid (50 mole-% in monomer) and 4-vinylpyridine by treatment with 0.1% azobisisobutyronitrile at 70°C with constant stirring and bubbling of nitrogen for 6 hr. The product was purified by dissolving it into benzene–methyl alcohol mixture (40:60) and precipitating the polymer with large excess of ethyl acetate. Only 20% conversion into polymer was done, and the dried product was very hygroscopic. The pyridine groups in the two copolymers were further converted into stronger base by quaternization.

Quaternization of the Copolymers. The pyridine groups in the above two copolymers were quaternized with n-butyl bromide by the method of Fuoss and Edelson.[4] A 16-g sample of the finely powdered copolymer was suspended in dimethylformamide (400 cc) and treated with excess (9.65 moles) n-butyl bromide. The mixture was stirred for 50 hr at 55°C. After the reaction was over, the product was concentrated to a small volume by distilling out the liquid under reduced pressure, and the polymer was precipitated with dry dioxane. The product was further purified by redissolving in absolute alcohol and precipitating with dry dioxane, and

was finally dried to constant weight under vacuum. The two amphoteric polyelectrolytes thus obtained were acrylic acid–4-vinyl-N-n-butylpyridinium bromide (AA–ViBuPyBr) and methacrylic acid–4-vinyl-N-n-butyl-pyridinium bromide (MAA–ViBuPyBr) copolymers.

Determination of Composition of the Polyampholytes

The composition, i.e., the equivalent weight M_2 of the repeat unit of each of the copolymer, was determined by electrometric titration of the acid and base groups in the polymer. The acid groups present in the copolymer were estimated pH-metrically with $0.1N$ NaOH. Since it was not possible to locate the endpoint decisively at low pH by titration with $0.5N$ HCl, the base groups as bromide ions were estimated by titrating with $0.1M$ silver nitrate solution. A simple potentiometric method employing a silver wire as one electrode and a glass electrode,[5] as another was used to estimate the bromide ions. The equivalent weights of the copolymers as obtained by the bromide ions (base group) estimation and by acid group estimation are given in Table I. Comparing the two equivalent weights thus obtained for each amphoteric polyelectrolyte, it was found that the ratios of acid to base group were $1:3.6$ and $1:5.6$ for acrylic acid-containing and methacrylic acid-containing copolymers, respectively.

All calculations regarding the compressibilities and apparent molal properties of the amphoteric polyelectrolytes were made taking the equivalent weights determined by base group analysis. However, other values corresponding to acid group analysis may be obtained by multiplying those values (base) with the proper ratio of acid to base groups in the polymer chain.

The potassium salt (100% neutralized) of the two amphoteric polyelectrolytes were prepared by neutralizing the polymers with a calculated amount of KOH solution.

TABLE I
Composition of Copolymers: Equivalent Weight for
Copolymer Repeat Unit

Copolymer	Milliequivalent NaOH consumed per g copolymer	Acid equiv. weight	Milliequivalent of AgNO$_3$ soln. consumed per g copolymer	Base equiv. weight	Ratio of acid to base groups in polymer chain
Acrylic acid–4-vinyl-N-n-butylpyridinium bromide	1.06	943	3.81	262	1:3.6
Methacrylic acid–4-vinyl-N-n-butyl-pyridinium bromide	0.69	1449	3.88	258	1:5.6

The ultrasonic velocities were measured by an ultrasonic interferometer and the density, with an Ostwald-type pycnometers. The experimental details have been described earlier.[1-3] The adiabatic compressibility β_s, the apparent molal compressibility ΦK_2 of the solute, and the apparent molal volume ΦV_2 of the solute have been determined from the velocity and density data in the usual way.

The viscosity measurements were done with a Ubbelohde viscometer thermostated at $25 \pm 0.02°C$. The flow time of the solvents was more than 200 sec, and hence no kinetic energy correction was made.

Ultraviolet absorption measurements were carried out in a Spektromom 201 spectrophotometer (Hungarian) with 1-cm quartz cells. The "difference method" as proposed by Solough[6] was used for determining the interactions of chloride, bromide, and iodide ions with the copolymers. The polymer solution in the presence of chloride ($1.0M$ NaCl), bromide ($1.0M$ KBr), or iodide ($0.001M$ or $0.01M$ KI) ions was kept in one of the two cells, and the other cell contained the polymer of the same concentration in aqueous solution as blank. The concentration used for the copolymers was 0.02%, and for poly(4-vinyl-N-n-butylpyridinium bromide) it was 0.01%. Since the aqueous solution of NaCl, KBr, and KI showed negligible absorption in the range 2600 Å to 4000 Å, the absorption for polymers at this region has been attributed to the charge transfer complex between polymer and halide ions.

RESULTS AND DISCUSSION

The two amphoteric polyelectrolytes are seen strongly acidic. Before quaternization, the 0.2% aqueous solution of the two copolymers, AA–ViPy copolymer and MAA–ViPy copolymer, were found to have a pH of 4.8 and 5.2, respectively. The same copolymers after quaternization, at the same concentration (0.2%), showed a pH of 3.3 and 3.5, respectively. The pH's for 0.2% aqueous solution of poly(acrylic acid), poly(methacrylic acid), and poly(4-vinyl-N-n-butyl pyridinium bromide) were measured and found to be 3.6, 3.7, and 4.1, respectively, which are higher than those of the quaternary copolymers made with them. The strength of the acid group is increased by the presence of the base group neighbors, and this behavior was also observed by Alfrey et al.[7] in the study of a series of amphoteric polyelectrolytes made by copolymerizing N-dialkylaminoethyl acrylates and methacrylates with acrylic, methacrylic, and itaconic acids. During titration, the two polyampholytes show good buffer capacity (titration curves are not shown here), and the water solubility of the ampholytes, even in the isoelectric range, indicates that the polymers are zwitterionic since it is known that zwitterionic materials are much more water soluble than their uncharged isomers.[8]

The most interesting point that may be noted here is that the reduced viscosity of these amphoteric polyelectrolytes are extremely low, i.e., in the range of 0.03 to 0.07 dl/g. The reduced viscosity-versus-concentration
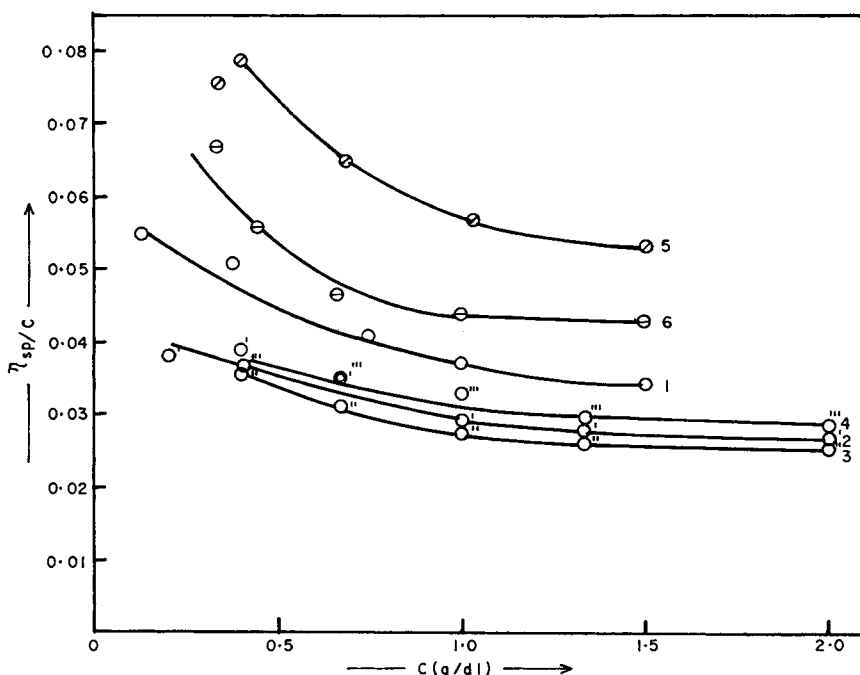
Fig. 1. Plots of reduced viscosity as a function of concentration: (1) AA–ViBuPyBr copolymer in aqueous solution; (2) PoA–ViBuPyBr copolymer in aqueous solution; (3) PoA–ViBuPyBr copolymer in 0.1M KBr solution; (4) PoA–ViBuPyBr copolymer in 1.0M KBr solution; (5) MAA–ViBuPyBr copolymer in aqueous solution; (6) PoMA–ViBuPyBr in aqueous solution.

curves are shown in Figure 1. In case of globular proteins, such as glycogen or albumin, the intrinsic viscosity is very low ($\sim$0.03–0.06 dl/g). Similar to that of globular macromolecules, the reduced viscosity changed very little with dilution. However, even if there is an increase at lower dilution, this cannot be decisively measured with our viscometer, as the difference of flow time between the solvent and solution was negligibly small. This abnormal decrease of reduced viscosity and insensitivity with dilution may be due to mutual interaction of acid and base groups making the polyelectrolyte chain highly coiled and compact, with no effective change in volume with dilution similar to the behavior of well-defined globular proteins. Contrary to polyacids and polybases, the potassium salts of these two polyampholytes show comparatively lower reduced viscosity than that of the corresponding unneutralized polyampholytes. Probably some carboxyl ions which were freshly formed by the neutralization of acids interacted with the pyridinium ions present in the polymer chain and effected further coiling of the molecules.

The results for adiabatic compressibility of the two amphoteric polyelectrolytes in aqueous solution are summarized in Tables II and III, while the data for the corresponding potassium salts obtained by 100%

TABLE II

Summary of Results for Copolymer of Acrylic Acid and 4-Vinyl-N-n-butylpyridinium Bromide in Aqueous Solution at 25°C (M_2 = 262)

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	183.9[a]	1496.05	44.812	−7[a]
0.1000	0.99735	183.9	1496.40	44.777	−9
0.2000	0.99765	183.9	1496.75	44.743	−8
0.3000	0.99796	183.1	1497.07	44.710	−7
0.4000	0.99826	183.3	1497.41	44.676	−7
0.5000	0.99856	183.4	1497.79	44.640	−8
0.7500	0.99930	183.9	1498.61	44.558	−6
1.0000	1.00005	183.9	1499.50	44.472	−7
1.5000	1.00154	184.1	1501.29	44.300	−7
2.0000	1.00302	184.3	1503.03	44.132	−6

[a] Extrapolated value.

TABLE III

Summary of Results for Copolymer of Methacrylic Acid and 4-Vinyl-N-n-butylpyridinium Bromide in Aqueous Solution at 25°C (M_2 = 258)

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	184.6[a]	1496.05	44.182	−3[a]
0.1030	0.99734	185.9	1496.40	44.778	−2
0.2060	0.99764	184.6	1496.76	44.743	−4
0.3090	0.99794	184.2	1497.12	44.708	−4
0.4028	0.99820	184.9	1497.43	44.677	−3
0.5035	0.99849	184.8	1497.79	44.643	−4
0.7552	0.99922	184.4	1498.65	44.559	−4
1.0299	0.99999	184.9	1499.56	44.471	−3
1.4876	1.00132	184.5	1501.12	44.320	−3
2.0189	1.00279	185.2	1503.01	44.143	−2

[a] Extrapolated value.

neutralization with KOH in aqueous solution are given in Tables IV and V. As usual, the total adiabatic compressibility for the potassium salts are lower than those of the corresponding acids. Tables VI and VII give compressibility data for the potassium salt of the copolymers in 0.1M KBr solution, while Tables VIII and IX give data for the same in 1.0M KBr solution. The decrease in compressibility per unit concentration, $(\beta_1 - \beta)/c$, is a measure of the change in compressibility of the molecules. As the compressibility of the molecules decreases, the $(\beta_1 - \beta)/c$ values increase, and vice versa. In polyampholytes, these values are found to be fairly constant throughout the concentration range (0.1–2.0 g/dl). The plots of $(\beta_1 - \beta)/c$ versus concentration are shown in Figure 2. In aqueous solution, the H$^+$ ions of the polyampholytes do not dissociate completely, even in dilute region, but dissociation is completed when the H$^+$ ions are

TABLE IV

Summary of Results for Potassium Salt of Acrylic Acid–4-Vinyl-
N-n-butylpyridinium Bromide Copolymer in Aqueous Solution
at 25°C (M_2 = 273)

| 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	184.4[a]	1496.05	44.812	−23[a]
0.1000	0.99738	183.4	1496.45	44.773	−24
0.2000	0.99770	184.8	1496.85	44.734	−23
0.3000	0.99803	184.4	1497.25	44.696	−23
0.4000	0.99836	184.1	1497.63	44.658	−22
0.5000	0.99868	184.5	1498.04	44.620	−22
0.7500	0.99950	184.4	1499.04	44.524	−22
1.0000	1.00032	184.3	1499.67	44.450	−16
1.5000	1.00191	185.1	1501.91	44.247	−20
1.9941	1.00346	185.8	1503.64	44.077	−17

[a] Extrapolated value.
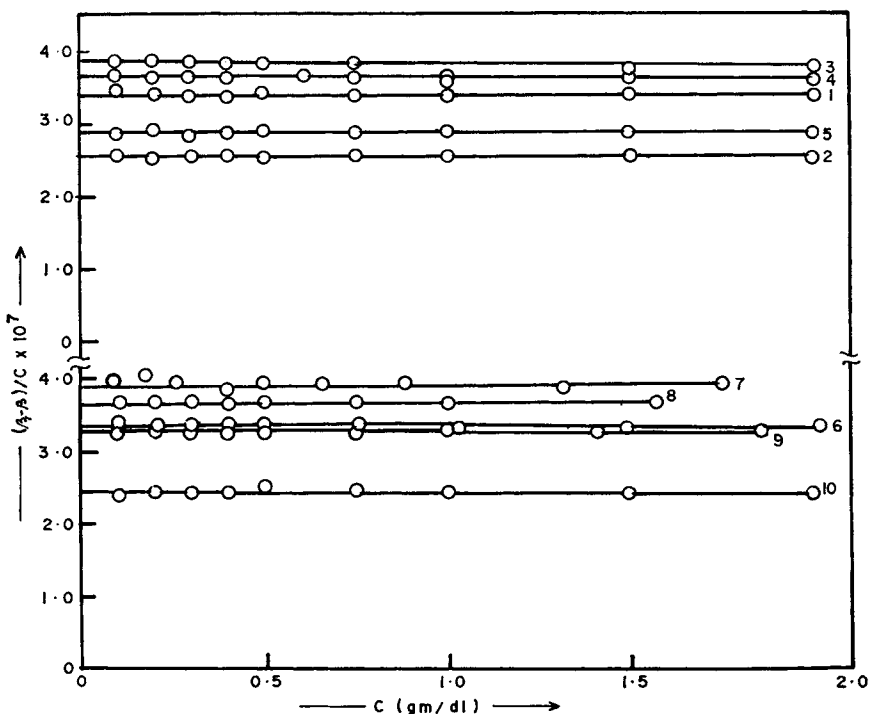
Fig. 2. Plots of adiabatic compressibility decrement per unit concentration as a function of concentration: (1) AA–ViBuPyBr copolymer in aqueous solution; (2) AA–ViBuPyBr copolymer in 1.0M KBr solution; (3) PoA–ViBuPyBr copolymer in aqueous solution; (4) PoA–ViBuPyBr copolymer in 0.1M KBr solution; (5) PoA–ViBuPyBr copolymer in 1.0M KBr solution; (6) MAA–ViBuPyBr copolymer in aqueous solution; (7) MAA–ViBuPyBr copolymer in 1.0M KBr solution; (8) PoMA–ViBuPyBr copolymer in 0.1M KBr solution; (10) PoMA–ViBuPyBr copolymer in 1.0M KBr solution.

TABLE V
Summary of Results for Potassium Salt of Methacrylic Acid–4-
Vinyl-N-n-butylpyridinium Bromide Copolymer in Aqueous
Solution at 25°C (M_2 = 265)

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	176.6[a]	1496.05	44.812	−24[a]
0.0876	0.99734	177.8	1496.41	44.777	−26
0.1753	0.99764	176.3	1496.78	44.741	−29
0.2630	0.99793	176.8	1497.13	44.707	−26
0.3944	0.99837	176.8	1497.61	44.659	−24
0.4931	0.99870	176.8	1498.04	44.619	−24
0.6574	0.99927	176.0	1498.68	44.555	−25
0.8765	1.00000	176.3	1499.57	44.470	−24
1.3148	1.00142	177.4	1501.31	44.304	−23
1.7530	1.00284	178.0	1503.34	44.122	−24

[a] Extrapolated value.

TABLE VI
Summary of Results for Potassium Salt of Acrylic Acid–4-Vinyl-
N-n-butylpyridinium Bromide Copolymer in 0.1M KBr Solution
at 25°C (M_2 = 273)

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	1.00552	184.6[a]	1497.94	44.322	−18[a]
0.1000	1.00584	184.6	1498.32	44.285	−20
0.2000	1.00616	184.6	1498.70	44.249	−18
0.3000	1.00648	184.6	1499.08	44.212	−18
0.4000	1.00680	184.6	1499.48	44.175	−18
0.6136	1.00749	184.3	1500.28	44.097	−18
0.7500	1.00793	184.3	1500.78	44.049	−18
1.0000	1.00872	184.6	1501.74	43.958	−17
1.5000	1.01030	185.0	1503.63	43.779	−17
2.0000	1.01188	185.2	1505.60	43.596	−17

[a] Extrapolated value.

converted into the potassium salts, which causes a further decrease of compressibility due to an increase in electrostriction. Accordingly, (β_1 − β)/c values are seen highest in potassium salt solutions. In KBr solution, the counterions are suppressed, and the values are found to decrease and approach values corresponding to acids. However, in excess KBr solution, not only the dissociation of K$^+$ ions but also the dissociation of the Br$^-$ ions is suppressed (there is also the effect of charge transfer complex formation by the Br$^-$ ions and the heterocyclic π-system in the polymer nucleus, which will be discussed later). Accordingly, the (β_1 − β)/c values are found to decrease beyond the acid values.

The plots of ΦK_2 and ΦV_2 versus concentration are shown in Figures 3 and 4. The ΦK_2 and ΦV_2 values for these polyampholytes are found to be

TABLE VII
Summary of Results for Potassium Salt of Methacrylic Acid–4-Vinyl-N-n-butylpyridinium Bromide Copolymer in 0.1M KBr Solution at 25°C (M_2 = 265)

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	1.00552	179.5[a]	1497.94	44.322	−18[a]
0.1013	1.00584	180.3	1498.33	44.285	−18
0.2027	1.00617	179.0	1498.72	44.247	−19
0.3040	1.00649	179.4	1499.11	44.210	−18
0.4028	1.00680	179.8	1499.49	44.174	−18
0.5067	1.00713	179.8	1499.90	44.136	−18
0.7506	1.00791	179.6	1500.82	44.047	−18
1.0008	1.00873	179.0	1501.79	43.955	−18
1.5687	1.01056	178.9	1504.11	43.740	−19

[a] Extrapolated value.

TABLE VIII
Summary of Results of Potassium Salt of Acrylic Acid–4-Vinyl-N-n-butylpyridinium Bromide Copolymer in 1.0M KBr Solution at 25°C (M_2 = 273)

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	1.08054	184.8[a]	1513.80	40.385	−4[a]
0.1000	1.08081	184.4	1514.15	40.356	−5
0.2000	1.08108	184.4	1514.53	40.326	−6
0.3000	1.08134	185.3	1514.86	40.299	−3
0.4000	1.08162	184.4	1515.20	40.270	−4
0.5000	1.08188	184.9	1515.56	40.241	−4
0.7500	1.08255	184.9	1516.47	40.168	−4
1.0000	1.08321	185.2	1517.37	40.096	−4
1.5000	1.08454	185.3	1519.17	39.952	−4
2.0000	1.08578	186.4	1521.00	39.811	−3

[a] Extrapolated value.

TABLE IX
Summary of Results for Potassium Salt of Methacrylic Acid–4-Vinyl-N-n-butylpyridinium Bromide Copolymer in 1.0M KBr Solution at 25°C (M_2 = 265)

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	1.08054	165.5[a]	1513.80	40.385	−20[a]
0.1000	1.08087	164.3	1514.20	40.352	−21
0.2000	1.08119	165.5	1514.59	40.319	−20
0.3000	1.08152	165.1	1514.99	40.285	−22
0.4000	1.08184	165.5	1515.38	40.253	−20
0.5000	1.08217	165.3	1515.78	40.219	−21
0.7500	1.08298	165.5	1516.68	40.141	−19
1.0002	1.08380	165.3	1517.73	40.055	−21
1.4128	1.08514	165.4	1519.21	39.928	−19
1.8543	1.08658	165.4	1520.91	39.786	−19

[a] Extrapolated value.

TABLE X

Summary of Results for Acrylic Acid–4-Vinyl-N-n-butylpyridinium
Bromide Copolymer in 1.0M KBr Solution at 25°C (M_2 = 262)

| 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	1.08054	184.3[a]	1513.80	40.385	7[a]
0.1000	1.08078	184.3	1514.13	40.359	7
0.2000	1.08102	184.3	1514.42	40.334	8
0.3000	1.08126	184.3	1514.76	40.307	6
0.4000	1.08151	183.7	1515.08	40.281	6
0.5000	1.08176	183.3	1515.36	40.257	7
0.7500	1.08237	183.3	1516.16	40.191	6
1.0000	1.08293	184.5	1516.97	40.128	7
1.5000	1.08411	184.8	1518.60	39.998	7
2.0000	1.08522	185.7	1520.17	39.875	8

[a] Extrapolated value.
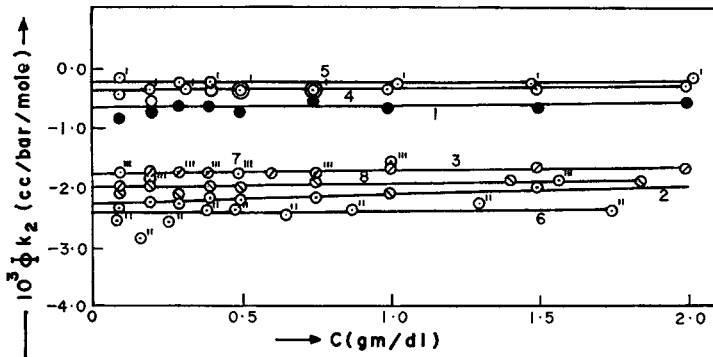
Fig. 3. Plots of apparent molal compressibility as a function of concentration: (1) AA–ViBuPyBr copolymer in aqueous solution; (2) PoA–ViBuPyBr copolymer in aqueous solution; (3) PoA–ViBuPyBr copolymer in 0.1M KBr solution; (4) PoA–ViBuPyBr copolymer in 1.0M KBr solution; (5) MAA–ViBuPyBr copolymer in aqueous solution; (6) PoMA–ViBuPyBr copolymer in aqueous solution; (7) PoMA–ViBuPyBr copolymer in 0.1M KBr solution; (8) PoMA–ViBuPyBr copolymer in 1.0M KBr solution.

concentration independent. The dissociation of Br$^-$ ions and H$^+$ ions (only those which were free) were suppressed in excess KBr solution, and hence the ΦK_2 and ΦV_2 values for the two amphoteric copolymers were found to have increased (Tables X and XI). Since the magnitude of electrostriction is highest in potassium salts, the lowest ΦK_2 and ΦV_2 values are obtained. The ΦV_2 and ΦK_2 values are seen to increase a little in dilute KBr solution as the dissociation is somewhat suppressed. On the other hand, in excess KBr solution (1.0M), the ΦV_2 and ΦK_2 values for the potassium salt of the methacrylic acid-containing copolymer (PoMA–ViBuPyBr) are seen lower than those of the values in 0.1M KBr solution. This indicates that instead of decreasing, the electrostriction has increased, and this is probably due to binding of more Br$^-$ ions in the system. It may be noted that Strauss et al.[9] observed a similar effect in electrophoresis

Summary of Results for Methacrylic Acid–4-Vinyl-N-n-butyl-
pyridinium Bromide Copolymer in 1.0M KBr Solution
at 25°C ($M_2 = 258$)

| c, g/dl	d, m/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	1.08054	188.6[a]	1513.80	40.385	13[a]
0.1000	1.08075	188.6	1514.11	40.361	15
0.2000	1.08096	188.6	1514.42	40.336	13
0.3000	1.08117	188.6	1514.74	40.311	13
0.4000	1.08137	189.2	1515.07	40.287	13
0.5000	1.08159	188.6	1515.41	40.260	12
0.7500	1.08214	187.8	1516.14	40.201	12
1.0000	1.08263	188.9	1516.87	40.144	14
1.5000	1.08370	188.5	1518.41	40.023	14
2.0000	1.08476	188.4	1520.00	39.901	14

[a] Extrapolated value.
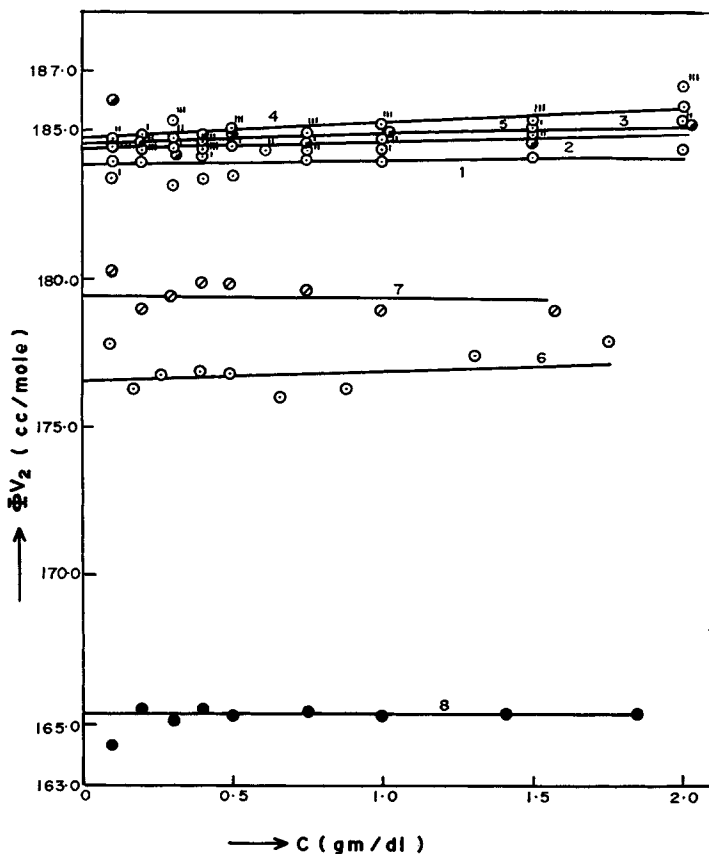
Fig. 4. Plots of apparent molal volume as a function of concentration: (1) AA–
ViBuPyBr copolymer in aqueous solution; (2) PoA–ViBuPyBr copolymer in aqueous
solution; (3) PoA–ViBuPyBr copolymer in 0.1M KBr solution; (4) PoA–ViBuPyBr
copolymer in 1.0M KBr solution (5) MAA–ViBuPyBr copolymer in aqueous solution;
(6) PoMA–ViBuPyBr copolymer in aqueous solution; (7) PoMA–ViBuPyBr copolymer
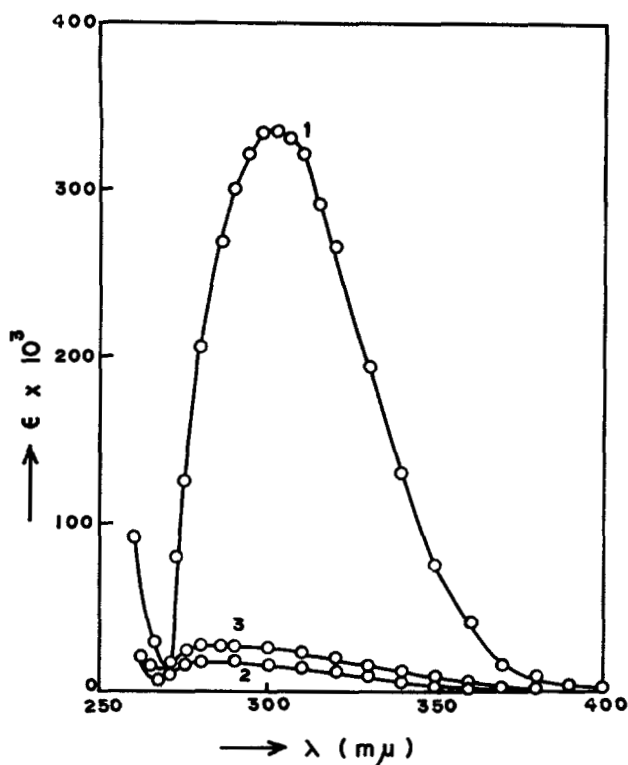in 0.1M KBr solution; (8) PoMA–ViBuPyBr copolymer in 1.0M KBr solution.

Fig. 5. Ultraviolet absorption curves: (1) poly(4-vinyl-N-n-butylpyridinium bromide) in KI solution; (2) PoA–ViBuPyBr copolymer in KI solution; (3) PoMA–ViBuPyBr copolymer in KI solution.

measurements for poly(4-vinyl-N-n-butylpyridinium bromide) in excess KBr solution, where the polycation, being effectively negatively charged, moved to the anode. Contrary to this copolymer, the ΦV_2 and ΦK_2 values for potassium salt of acrylic acid-containing copolymer (PoA–ViBuPyBr) showed an increase as if supression of dissociation of K^+ ions and Br^- ions had only taken place. Two points emerge from these observations: the acrylic acid-containing copolymer, having comparatively more carboxyl groups in the chain (21.7%), behaves more or less like poly(acrylic acid),[1] whereas methacrylic acid-containing copolymer, where the carboxyl groups are comparatively less (15.1%), behaves like poly(4-vinyl-N-n-butylpyridinium bromide).[3] In fact, in excess KBr solution, the suppression of dissociation of both K^+ ions and Br^- ions has taken place. In addition to those, charge transfer complex between the bromide ions and the zwitterions has taken place. In methacrylic acid-containing copolymer, the effect of charge transfer complex is more prominent as the pyridinium groups are comparatively more, whereas this effect is overshadowed by the suppression of charge effect found in acrylic acid-containing copolymer, where the carboxyl groups are comparatively more.
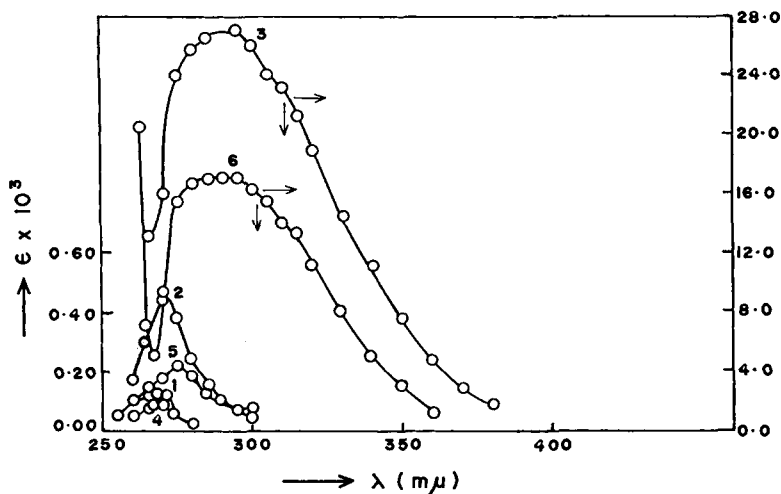
Fig. 6. Ultraviolet absorption curves: (1) PoMA–ViBuPyBr copolymer in NaCl solution; (2) PoMA–ViBuPyBr copolymer in KBr solution; (3) PoMA–ViBuPyBr copolymer in KI solution; (4) PoA–ViBuPyBr copolymer in NaCl solution; (5) PoA–ViBuPyBr copolymer in KBr solution; (6) PoA–ViBuPyBr copolymer in KI solution.

These points have been further substantiated by the ultraviolet absorption study of these compounds in chloride, bromide, and iodide solutions. The absorption curves for poly(4-vinyl-N-n-butylpyridinium bromide) and for the potassium salt of two amphoteric polyelectrolytes in KI solution are shown in Figure 5. The poly(4-vinyl-N-n-butylpyridinium bromide) in KI solution showed absorption in the region 2700 to 3800 Å, with a maximum at 3000 Å, and this is definitely due to the formation of charge transfer complex between the iodide ions and polycation.[6] Poly(sodium acrylate) and poly(sodium methacrylate) do not show any absorption in this region in the presence of chloride, bromide, and iodide ions. In KI solution, the polyampholytes also show absorption in the same region, 2700 to 3800 Å, but with greatly reduced extinction coefficient. The extinction coefficients are found to be in the order of ViBuPyBr > PoMa–ViBuPyBr copolymer > PoA–ViBuPyBr copolymer. The ultraviolet absorption curves for the potassium salts of the two polyampholytes in chloride, bromide, and iodide solutions are shown in Figure 6. Absorption does occur for each of the polyampholytes due to charge transfer complex formation in the region 2700 to 3800 Å in chloride, bromide, and iodide ions. The absorption increases in intensity in the order $Cl^- < Br^- < I^-$, which is expected on the basis of the polarizability.

The limiting values of apparent molal compressibility ΦK_2^0 and apparent molal volume ΦV_2^0 of solutes in aqueous solution are listed in Table XII. The limiting values of poly(acrylic acid), poly(methacrylic acid), and poly(4-vinyl-N-n-butylpyridinium bromide) have been listed for comparison. It is observed that the equivalent weight of the repeat unit

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TABLE XII

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

Materials	M_2	$\Phi V_2{}^0$, cc/mole	$\Phi K_2{}^0$, cc bar^{-1} mole$^{-1} \times 10^4$
Acrylic acid–4-vinyl-N-*n*-butyl-pyridinium bromide copolymer	262	183.9	−7
Acrylic acid–4-vinyl-N-*n*-butyl-pyridinium bromide copolymer in 1.0M KBr solution	262	184.3	7
Potassium salt of acrylic acid 4-vinyl-N-*n*-butylpyridinium bromide copolymer	273	184.4	−23
Potassium salt of acrylic acid–4-vinyl-N-*n*-butylpyridinium bromide copolymer in 0.1M KBr solution	273	184.6	−18
Potassium salt of acrylic acid–4-vinyl-N-*n*-butylpyridinium bromide copolymer in 1.0M KBr solution	273	184.8	−4
Methacrylic acid–4-vinyl-N-*n*-butylpyridinium bromide copolymer	258	184.6	−3
Methacrylic acid–4-vinyl-N-*n*-butylpyridinium bromide copolymer in 1.0M KBr solution	258	188.6	13
Potassium salt of methacrylic acid–4-vinyl-N-*n*-butylpyridinium bromide copolymer	265	176.6	−24
Potassium salt of methacrylic acid–4-vinyl-N-*n*-butylpyridinium bromide copolymer in 0.1M KBr solution	265	179.5	−18
Potassium salt of methacrylic acid–4-vinyl-N-*n*-butylpyridinium bromide copolymer in 1.0M KBr solution	265	165.5	−20
Poly(acrylic acid)[1]	72.06	46.7	0.85
Poly(methacrylic acid)[10]	86.09	60.0	1.1
Poly(4-vinyl-N-*n*-butylpyridinium bromide)[3]	242.17	180.1	5.0

of acrylic acid-containing copolymer and methacrylic acid-containing copolymer have increased from the value of the poly(4-vinyl-N-*n*-butyl-pyridinium bromide) by 19.8 and 15.8, respectively. If there had been no interaction between acid and base groups, the apparent molal volume would accordingly have been 193.1 and 190.8 cc/moles for the acrylic acid- and methacrylic acid-containing copolymers, respectively. However, we have obtained experimental values of 183.9 and 184.6 cc/mole, respectively, which show a decrease of 9.2 and 6.2 cc/mole, respectively. This decrease

is definitely due to the mutual interaction of the acid and base groups in the molecules.

References

1. P. Roy-Chowdhury and K. M. Kale, *J. Appl. Polym. Sci.*, **14**, 2937 (1970).
2. P. Roy-Chowdhury, *J. Appl. Polym. Sci.*, **12**, 751 (1968).
3. P. Roy-Chowdhury, *J. Polym. Sci. A-2*, **7**, 1451 (1969).
4. R. M. Fuoss and D. Edelson, *J. Polym. Sci.*, **6**, 767 (1951).
5. R. M. Fuoss and G. I. Cathers, *J. Polym. Sci.*, **4**, 97 (1949).
6. W. Slough, *Trans. Faraday Soc.*, **55**, 1030 (1959).
7. T. Alfrey and S. H. Pinner, *J. Polym. Sci.*, **23**, 533 (1957).
8. E. J. Cohn and J. T. Edsall, *Proteins, Amino Acids and Peptides*, Reinhold, New York, 1943, Chap. 8.
9. U. P. Strauss, N. L. Gershfeld, and H. Spiera, *J. Amer. Chem. Soc.*, **76**, 5909 (1954).
10. P. Roy-Chowdhury, *Indian J. Chem.*, **7**, 692 (1969).