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The Adiabatic Compressibility of Polyelectrolytes: Sodium and Hydrochloride Salts of Acrylic Acid–N-Dimethylaminoethyl Methacrylate Copolymer

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Synopsis

The results of adiabatic compressibility measurement for the 100% neutralized sodium and hydrochloride salts of three copolymers of acrylic acid and N-dimethylaminoethyl methacrylate, namely, AA-DAM 58, AA-DAM 43, and AA-DAM 33, are discussed. Similar to three unneutralized amphoteric polyelectrolytes, the ϕK_2 and ϕV_2's for these salts are found to be concentration independent. Since in the former both anionic and cationic groups are present, fully neutralized sodium salts and hydrochloride salts of these polyelectrolytes are expected to show a decrease in ϕK_{2i}^0 and ϕV_{2i}^0 values due to maximum electrostriction. In fact, in case of AA-DAM 58 with excess amino group in the chain (58%), the experimentally obtained values are found to be -9.6×10^{-4} cc/bar/mole and 159.6 cc/mole, and -3.3×10^{-4} cc/bar/mole and 164.4 cc/mole for sodium and hydrochloride salts, respectively, which corresponds to a decrease of 7.1×10^{-4} cc/bar/mole and 4.9 cc/mole for the sodium salt and 0.8×10^{-4} cc/bar/mole and 0.1 cc/mole for the hydrochloride salt. In contrast, the hydrochloride salt of AA-DAM 43 shows an increase of 6.2×10^{-4} cc/bar/mole and 2.2 cc/mole, respectively, while in case of AA-DAM 33, both the hydrochloride salt (56.2×10^{-4} cc/bar/mole and 24.7 cc/mole) and the sodium salt (6.2×10^{-4} cc/bar/mole and 6.2 cc/mole) show an increase. This increase has been ascribed to suppression of dissociation of carboxyl groups by the hydrochloric acid (common ion effect) added for neutralization. However, in all the three amphoteric copolymers, when neutralized with NaOH solution or HCl acid, the viscosity increases over that of the unneutralized copolymer.

INTRODUCTION

In an earlier paper,[1] we described the adiabatic compressibility of poly(N-dimethylaminoethyl methacrylate) and of its three copolymers with acrylic acid. In this present paper, similar studies of fully neutralized sodium and hydrochloride salts of the same three copolymers, namely, AA-DAM 58, AA-DAM 43, and AA-DAM 33, ranging in composition from 33 to 58 mole-% amino groups, will be discussed.

EXPERIMENTAL

Experimental procedures and preparation of the copolymers were given in the preceding paper.[1] 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 fully neutralized salts were prepared by adding calculated amount of NaOH solution of HCl to the copolymers. The salts were soluble in water, and the solutions showed increased viscosity.

RESULTS AND DISCUSSION

The results of adiabatic compressibility measurements are summarized in Tables I to VI. The density and ultrasonic velocity for the sodium and hydrochloride salts of the three copolymers increase linearly, and accordingly, the adiabatic compressibility decrease with increasing concentration. The decrease in compressibility per unit concentration, $(\beta_1 - \beta)/c$, is a measure of the change of compressibility of the molecules. The $(\beta_1 - \beta)/c$ values are shown in column 6 in each table. Similar to three unneutralized amphoteric polyelectrolytes, the ϕK_2 and ϕV_2 values for the corresponding sodium and hydrochloride salts are found to be concentration independent. The limiting values, ϕK_2^0 and ϕV_2^0, are given in parenthesis in Tables I to VI. The ϕK_2^0 and ϕV_2^0 values have been resolved into their ionic components, ϕK_{2i}^0 and ϕV_{2i}^0, as described earlier.[1,2] The values are listed in Table VII.

In amphoteric polyelectrolytes, both anionic and cationic groups are present and therefore the fully neutralized salts prepared either with NaOH solution or with HCl are expected to give electrostriction in either case; and, accordingly, a decrease in ϕK_{2i}^0 and ϕV_{2i}^0 values may be observed. However, in case of AA-DAM 58 with excess amino groups (58%), this expectation proved to be true. The experimentally obtained values are -9.6×10^{-4} cc/bar/mole and 159.6 cc/mole, and -3.3×10^{-4} cc/bar/mole and 164.4 cc/mole for sodium and hydrochloride salts, respectively. This shows a decrease of 7.1×10^{-4} cc/bar/mole and 4.9 cc/mole for sodium salt and 0.8×10^{-4} cc/bar/mole and 0.1 cc/mole (extremely small) for hydrochloride salt from that of the unneutralized copolymer.

In case of AA-DAM 43 with 43% amino groups in the polymer chain, the decrease of ϕK_{2i}^0 and ϕV_{2i}^0 values for the sodium salt is found to be 35.0×10^{-4} cc/bar/mole and 19.7 cc/mole, respectively, but the hydrochloride salt shows an increase of 6.2×10^{-4} cc/bar/mole and 2.2 cc/mole, respectively; while in case of AA-DAM 33 containing a still lesser amount of amino groups (33%) in the chain, instead of a decrease, a large increase of ϕK_{2i}^0 and ϕV_{2i}^0 values for both sodium salt (6.2×10^{-4} cc/bar/mole and 6.2 cc/mole, respectively) and hydrochloride salt (56.2×10^{-4} cc/bar/mole and 24.7 cc/mole, respectively) is observed. It may be pointed out that, due to mutual interaction of the acid and base groups, the dissociation of carboxyl groups occurs and the neighboring amino groups accept the protons as a result of which the amphoteric polymer chain is comprised of both positive and negatively charged groups as indicated below:

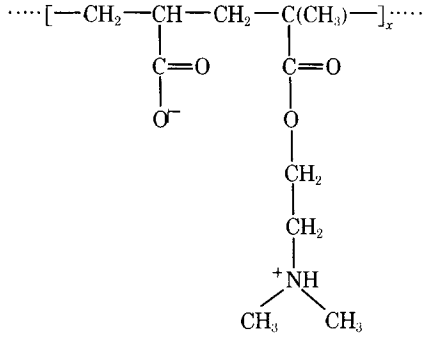

TABLE I
Summary of Results for Sodium Salt (100% Neutralized) of AA-DAM 58 Copolymer in Aqueous Solution at 25°C (M_2 = 223)

c, g/dl	d, g/cc	ϕV_2, cc/mole	u, m/sec	$\beta \times 10^6$, bar^{-1}	$(\beta_1 - \beta)/c \times 10^7$	$\phi K_2 \times 10^4$, cc/bar/mole
0.0000	0.99705	(158.6)	1496.05	44.812	—	(−40.0)
0.1154	0.99738	159.7	1496.76	44.754	5.0	−40.9
0.2307	0.99772	158.7	1497.47	44.697	5.0	−40.1
0.3296	0.99801	158.5	1498.10	44.646	5.0	−41.4
0.4394	0.99833	158.5	1498.75	44.593	5.0	−40.1
0.5493	0.99865	158.5	1499.47	44.536	5.0	−40.9
0.8239	0.99945	158.5	1501.13	44.402	5.0	−40.0
1.0986	1.00024	158.7	1502.84	44.266	5.0	−39.8
1.6479	1.00184	158.6	1506.23	43.997	5.0	−39.2
2.1971	1.00342	158.8	1509.57	43.733	4.9	−38.4

TABLE II
Summary of Results for the Hydrochloride Salt (100% Neutralized) of AA-DAM 58 Copolymer in Aqueous Solution at 25°C (M_2 = 243)

c, g/dl	d, g/cc	ϕV_2, cc/mole	u, m/sec	$\beta \times 10^6$, bar^{-1}	$(\beta_1 - \beta)/c$, $\times 10^7$	$\phi K_2 \times 10^4$, cc/bar/mole
0.0000	0.99705	(182.5)	1496.05	44.812	—	(−11.5)
0.1297	0.99737	183.6	1496.64	44.762	3.8	−11.7
0.2594	0.99770	182.6	1497.23	44.712	3.8	−11.7
0.3705	0.99798	182.5	1497.73	44.669	3.9	−11.9
0.4940	0.99829	182.5	1498.30	44.622	3.9	−11.6
0.6176	0.99860	182.5	1498.85	44.575	3.8	−11.4
0.9501	0.99944	182.4	1500.36	44.448	3.8	−11.4
1.2667	1.00024	182.3	1501.82	44.326	3.8	−11.5
1.8096	1.00160	182.4	1504.28	44.121	3.8	−11.0
2.4128	1.00313	182.3	1507.03	43.893	3.8	−10.8

TABLE III
Summary of Results for Sodium Salt (100% Neutralized) of AA-DAM 43 Copolymer in Aqueous Solution at 25°C (M_2 = 284)

c, g/dl	g, g/cc	ϕV_2, cc/mole	u, m/sec	$\beta \times 10^6$, bar^{-1}	$(\beta_1 - \beta)/c$, $\times 10^7$	$\phi K_2 \times 10^4$, cc/bar/mole
0.0000	0.99705	(155.8)	1496.05	44.812	—	(−124.5)
0.1013	0.99751	155.5	1496.87	44.742	6.9	−126.1
0.2026	0.99797	155.5	1497.67	44.673	6.9	−124.9
0.3117	0.99846	156.0	1498.55	44.599	6.8	−123.9
0.4156	0.99893	156.0	1499.40	44.528	6.8	−124.1
0.5196	0.99941	155.5	1500.24	44.456	6.8	−125.1
0.7422	1.00041	155.9	1502.03	44.306	6.8	−123.6
1.0603	1.00185	155.9	1504.58	44.093	6.8	−122.7
1.4138	1.00346	155.7	1507.44	43.855	6.8	−122.4
1.7673	1.00509	155.3	1510.27	43.620	6.7	−121.5

TABLE IV
Summary of Results for Hydrochloride Salt (100% Neutralized) of AA-DAM 43 Copolymer in Aqueous Solution at 25°C (M_2 = 290)

c, g/dl	d, g/cc	ϕV_2, cc/mole	u, m/sec	$\beta \times 10^6$, bar^{-1}	$(\beta_1 - \beta)/c$, $\times 10^7$	$\phi K_2 \times 10^4$, cc/bar/mole
0.0000	0.99705	(197.8)	1496.05	44.812	—	(−34.0)
0.1060	0.99739	197.6	1496.54	44.767	4.2	−35.2
0.2120	0.99773	197.6	1497.02	44.723	4.2	−33.3
0.3028	0.99802	197.7	1497.47	44.683	4.3	−34.9
0.4038	0.99834	197.8	1497.93	44.641	4.2	−34.1
0.5047	0.99867	197.5	1498.41	44.598	4.2	−34.4
0.7210	0.99937	197.3	1499.42	44.507	4.2	−34.4
1.0820	1.00053	197.3	1501.08	44.357	4.2	−33.5

TABLE V
Summary of Results for Sodium Salt (100% Neutralized) of AA-DAM 33 Copolymer in Aqueous Solution at 25°C (M_2 = 343)

c, g/dl	d, g/cc	ϕV_2, cc/mole	u, m/sec	$\beta \times 10^6$, bar^{-1}	$(\beta_1 - \beta)/c$, $\times 10^7$	$\phi K_2 \times 10^4$, cc/bar/mole
0.0000	0.99705	(214.6)	1496.05	44.812	—	(−134.0)
0.1106	0.99746	216.6	1496.98	44.737	6.8	−134.9
0.2211	0.99788	214.9	1497.91	44.663	6.7	−135.0
0.2949	0.99816	214.5	1498.53	44.614	6.7	−134.1
0.3932	0.99853	214.5	1499.34	44.549	6.7	−133.1
0.5242	0.99903	214.1	1500.46	44.460	6.7	−134.4
0.6989	0.99969	214.1	1501.91	44.345	6.7	−133.3
0.9310	1.00057	214.1	1503.88	44.190	6.7	−133.0

TABLE VI
Summary of Results for the Hydrochloride Salt (100% Neutralized) of the AA-DAM 33 Copolymer in Aqueous Solution at 25°C (M_2 = 335)

c, g/dl	d, g/cc	ϕV_2, cc/mole	u, m/sec	$\beta \times 10^6$, bar^{-1}	$(\beta_1 - \beta)/c$, $\times 10^7$	$\phi K_2 \times 10^4$, cc/bar/mole
0.0000	0.99705	(254.1)	1496.05	44.812	—	(−7.0)
0.1247	0.99735	255.1	1496.57	44.767	3.6	−7.1
0.2495	0.99766	253.8	1497.09	44.722	3.6	−7.1
0.3327	0.99786	254.2	1497.45	44.692	3.6	−6.9
0.4436	0.99813	254.2	1497.91	44.652	3.6	−6.8
0.5914	0.99850	253.2	1498.53	44.599	3.6	−6.8
0.7886	0.99898	253.8	1499.36	44.528	3.6	−6.9
1.0514	0.99963	253.8	1500.46	44.434	3.6	−6.9

When HCl is added for neutralization, especially in case of AA-DAM 43 and AA-DAM 33 copolymers, it acts effectively to suppress the dissociation of carboxyl groups also (due to common ion effect); and, accordingly, $\phi K_{2i}{}^0$ and $\phi V_{2i}{}^0$'s are found to have increased values over those of the unneutralized product. It may be mentioned that the viscosity of all the three amphoteric copolymer solutions when neutralized with NaOH or HCl increases over that

TABLE VII
Macroionic Volumes and Compressibilities in Aqueous Solution at 25°C

Copolymers	ϕV_{2i}^0, cc/mole	$\phi K_{2i}^0 \times 10^4$, cc/bar/mole
AA-DAM 58[a]	164.5	−2.5
AA-DAM 58 (Na salt)	159.6	−9.6
AA-DAM 58 (HCl salt)	164.4	−3.3
AA-DAM 43[a]	177.5	−32.0
AA-DAM 43 (Na salt)	157.8	−67.0
AA-DAM 43 (HCl salt)	179.7	−25.8
AA-DAM 33[a]	211.3	−55.0
AA-DAM 33 (Na salt)	217.5	−48.0
AA-DAM 33 (HCl salt)	236.0	1.3

[a] Data from Roy-Chowdhury and Dewhare.[1]

of the unneutralized copolymers. However, the increase for sodium salts are more than that of the hydrochloride salts (Fig. 1), especially when the mole-% of amino groups in the chain is less than 50. According to Tanford[3] also the amphoteric polymers are expected to behave like ordinary polyelectrolytes

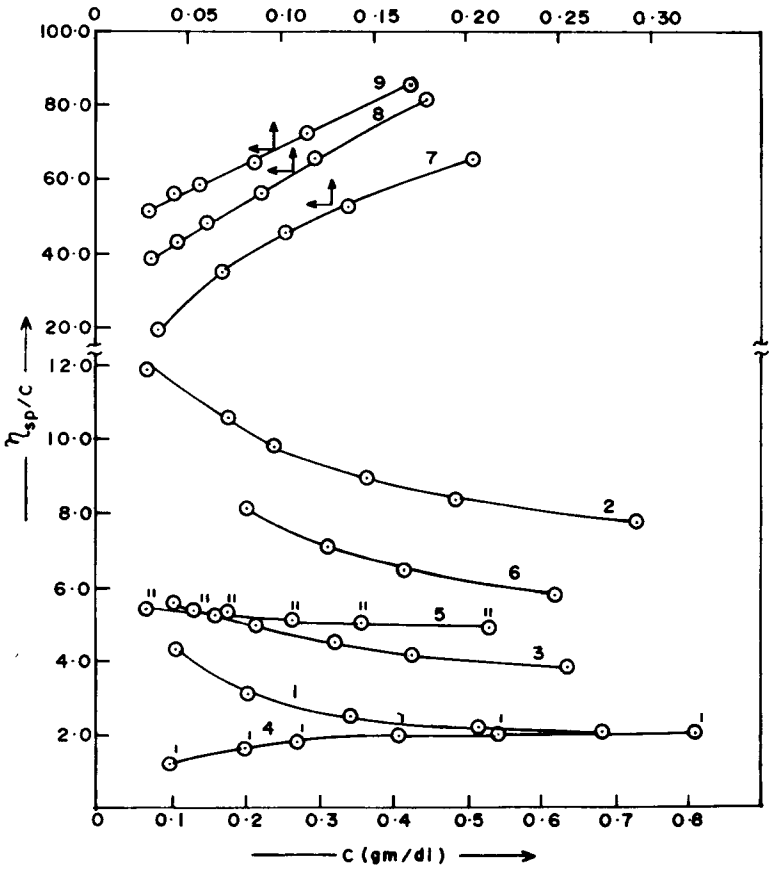

Fig. 1. Plots of reduced viscosity as a function of concentration: (1) AA-DAM 58; (2) AA-DAM 58 (HCl salt); (3) AA-DAM 58 (Na salt); (4) AA-DAM 43; (5) AA-DAM 43 (HCl salt); (6) AA-DAM 43 (Na salt); (7) AA-DAM 33; (8) AA-DAM 33 (HCl salt); (9) AA-DAM 33 (Na salt).

(i.e., they will expand more) when they are far from the isoelectric points as the interaction between oppositely charged ions are much reduced.

When the interactions between the acidic and basic groups in the chain are absent, the ϕK_{2i}^0 and ϕV_{2i}^0 values for three unneutralized copolymers AA-DAM 58, AA-DAM 43, and AA-DAM 33 as reported earlier are 16.9×10^{-4} cc/bar/mole and 167.7 cc/mole, 17.5×10^{-4} cc/bar/mole and 197.4 cc/mole, and 18.0×10^{-4} cc/bar/mole and 227.7 cc/mole, respectively. Comparing these values with the corresponding hydrochloride salts as recorded in Table VII, it is observed that the values for salts approach more or less the values computed on the basis of noninteraction.

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