Adiabatic Compressibility of Polyelectrolytes: The Influence of Solvents on Ionic and Nonionic Polymers*

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Synopsis

The adiabatic compressibility of two ionic polymers; namely, poly(acrylic acid) (PAA) and poly(N-dimethylaminoethyl methacrylate) (PDAM) in methanol and dioxane solutions and of a nonionic polymer, poly(vinyl pyrrolidone) (PVP) in aqueous, methanol, and dioxane solutions has been studied. The ϕV_2 and ϕK_2 values for the three polymers and their corresponding monomers in methanol and dioxane solutions are found to be concentration independent. There is a marked difference in ϕK_2^0 and ϕV_2^0 values between monomer and polymer in all three solvents. In aqueous solution, the difference in ϕV_2^0 is, on an average, 16.1 cm³/mol, while in methanol and dioxane solution, the same is 24.0 and 20.5 cm³/mol (average), respectively. All three monomers in dilute aqueous solution show a contraction of volume and decrease of adiabatic compressibility which are comparatively small in methanol and dioxane solutions. The ϕV_2^0 for PAA, PDAM, and PVP were found to have increased by 0.8, 11.0, and 1.5 cm³/mol, respectively, in dioxane solution over that of the value of the aqueous solution. It is interesting to note that in methanol solution, PAA, PDAM, and PVP show a decrease of ϕK_2^0 and ϕV_2^0 values by 68.8 cm³/bar/mol and 8.2 cm³/mol, 32.7 cm³/bar/mol, and 4.3 cm³/mol, and 36.6 cm³/bar/mol and 5.8 cm³/mol, respectively, compared to the values obtained from aqueous solution. This has been ascribed to geometric effect since the void space around the molecules is smaller in methanol than in water.

INTRODUCTION

There has been a large number of studies dealing with adiabatic compressibility and apparent molal volume of polyelectrolytes in aqueous solution.[1-10] In aqueous solution there are three types of solute–solvent interaction: (1) the electrostrictional hydration by the electric charges of gegenions and macroions, i.e., the charge effect; (2) the hydrophobic structural enhancement or "iceberg" formation by the hydrophobic parts of the electrolyte, i.e., the hydrophobic effect; and (3) the intermolecular hydrogen bonding between the polar groups. Both the electrostrictional effect and the hydrophobic effect cause a decrease in the limiting values of the apparent molal adiabatic compressibility, ϕK_2^0 and volume, ϕV_2^0, whereas hydrogen bonding brings about an increase in those values. However, the study of adiabatic compressibility of some ionic polymers as well as some nonionic polymers in different solvent media (aqueous and nonaqueous), where the structural hydration effect (hydrophobic bonding and hydrogen bonding) and electrostrictional hydration effect are suppressed either partially or completely, may help one to differentiate between the two effects separately so that greater insight into the problem of solvent–solute interaction may be made. The difficulty in such a study is the limitations of the solubility of ionic polymers in nonpolar solvents and nonionic polymers in polar solvents. However, we have studied the solvent effect on two ionic polymers, namely poly(ac-

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

c, g/dl	d, g/cm^3	ϕV_2, cm^3/mol	u, m/sec	β, bar$^{-1} \times 10^6$	ϕK_2, (cm^3 bar^{-1} mol^{-1}) $\times 10^4$
0.0000	0.78664	(63.6)	1102.49	104.587	(11.0)
0.1287	0.78703	63.8	1102.74	104.487	11.5
0.2574	0.78743	63.5	1102.99	104.387	10.6
0.4348	0.78797	63.6	1103.34	104.249	10.5
0.5798	0.78841	63.6	1103.62	104.138	10.8
0.7703	0.78903	63.3	1103.92	104.000	11.5
1.2312	0.79039	63.7	1104.89	103.639	11.1
1.6416	0.79164	63.7	1105.72	103.319	11.0
2.1888	0.79331	63.7	1106.80	102.900	11.1

rylic acid) and poly(N-dimethylaminoethyl methacrylate), and a nonionic polymer, poly(vinyl pyrrolidone), in three different solvents: water, methanol, and dioxane having a high-to-low dielectric constant and the results have been reported in this article. The dielectric constant of the solvents at 25°C are 78.6, 32.6, and 2.2, respectively. The former two solvents are polar and preferentially interact with the polar groups in the polymer, whereas the latter is nonpolar and is not capable of forming hydrogen bonds with the polar groups of the polymers. Our choice of poly(acrylic acid) and poly(N-dimethylaminoethyl methacrylate) was governed by the fact that they are soluble both in aqueous and non-aqueous solvents (methanol and dioxane). Moreover, they were studied earlier in aqueous solution in this laboratory. Poly(vinyl pyrrolidone) was chosen as nonionic polymer because of the fact that it is a water-soluble polymer having both polar groups and hydrophobic groups similar to those of the ionic polymers chosen by us. Further, this polymer is unique in that it is readily soluble in many organic solvents.

EXPERIMENTAL

Poly(acrylic acid) (PAA) and poly(N-dimethylaminoethyl methacrylate) (PDAM) were prepared by polymerizing freshly distilled monomers in dioxane solution with initiators as described earlier.[6,9] The products were washed and dried *in vacuo* to constant weight. They were further dried in an oven overnight at 110°C and stored over P_2O_5 under vacuum for several weeks. The sample

TABLE II
Summary of Results for Acrylic Acid in Dioxane at 25°C ($M_2 = 72.06$)

c, g/dl	d, g/cm^3	ϕV_2, cm^3/mol	u, m/sec	β, bar$^{-1} \times 10^6$	ϕK_2, (cm^3 bar^{-1} mol^{-1}) $\times 10^4$
0.0000	1.02801	(67.5)	1345.09	53.765	(39.0)
0.1518	1.02806	67.7	1344.99	53.770	38.4
0.3036	1.02811	67.7	1344.88	53.777	39.2
0.6072	1.02823	67.5	1344.61	53.792	39.5
0.8941	1.02833	67.5	1344.46	53.799	39.0
1.1922	1.02841	67.7	1344.23	53.813	39.3
1.5898	1.02857	67.5	1343.83	53.837	39.6
2.0588	1.02869	67.7	1343.66	53.844	39.2

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

c, g/dl	d, g/cm^3	ϕV_2, cm^3/mol	u, m/sec	β, bar$^{-1} \times 10^6$	ϕK_2, (cm^3 bar^{-1} mol^{-1}) $\times 10^4$
0.0000	0.78664	(38.5)	1102.49	104.587	(−68.0)
0.1000	0.78722	38.5	1102.88	104.436	−68.5
0.2001	0.78780	38.5	1103.27	104.285	−68.1
0.2846	0.78829	38.5	1103.60	104.158	−68.1
0.5691	0.78994	38.5	1104.71	103.732	−67.9
0.7588	0.79104	38.5	1105.48	103.443	−68.3
1.1242	0.79316	38.5	1106.87	102.908	−67.4
1.4990	0.79530	38.7	1108.30	102.366	−66.3
1.9987	0.79820	38.6	1110.20	101.645	−65.6

of poly(vinyl pyrrolidone) (PVP) was obtained from General Aniline and Film Corp., New York, and used without purification. The viscosity of PVP in aqueous solution at 25°C was found to be 150.5 ml/g, and the average molecular weight was computed[11] as 1.69×10^6. All the monomers, acrylic acid (AA), N-dimethylaminoethyl methacrylate (DAM), and N-vinyl-2-pyrrolidone (VP) used in this work were freshly distilled.

The solvents, methanol and dioxane, used were carefully dried and freed from the last trace of water. Methanol was dried first with calcium hydride and finally by means of magnesium ribbons activated with iodine.[12] Dioxane was refluxed with sodium and the distillate was stored under sodium wires. All precautions

TABLE IV
Summary of Results for Poly(Acrylic Acid) in Dioxane Solution at 25°C ($M_2 = 72.06$)

c, g/dl	d, g/cm^3	ϕV_2, cm^3/mol	u, m/sec	β, bar$^{-1} \times 10^6$	ϕK_2, (cm^3 bar^{-1} mol^{-1}) $\times 10^4$
0.0000	1.02801	(47.5)	1345.09	53.765	(0.3)
0.1264	1.02841	47.8	1345.37	53.721	0.3
0.2528	1.02881	47.8	1345.69	53.676	0.4
0.3738	1.02921	47.5	1345.95	53.634	0.3
0.5056	1.02964	47.4	1346.27	53.586	−0.01
0.7476	1.03040	47.6	1346.81	53.503	0.4
1.0113	1.03130	47.2	1347.45	53.406	−0.2
1.4951	1.03279	47.6	1348.53	53.244	0.5
2.0227	1.03450	47.5	1349.48	53.081	1.2

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

c, g/dl	d, g/cm^3	ϕV_2, cm^3/mol	u, m/sec	β, bar$^{-1} \times 10^6$	ϕK_2, (cm^3 bar^{-1} mol^{-1}) $\times 10^4$
0.0000	0.78664	(157.0)	1102.49	104.587	(43.0)
0.1686	0.78700	157.2	1102.93	104.455	41.3
0.3870	0.78747	157.0	1103.48	104.289	43.3
0.5364	0.78779	157.0	1103.87	104.173	43.2
0.7152	0.78820	156.9	1104.33	104.032	41.7
1.0731	0.78894	157.0	1105.25	103.776	45.5
1.4307	0.78972	156.8	1106.20	103.480	42.4
1.9075	0.79074	156.9	1107.37	103.130	44.4

TABLE VI

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

c, g/dl	d, g/cm^3	ϕV_2, cm^3/mol	u, m/sec	β, bar$^{-1} \times 10^6$	ϕK_2, (cm^3 bar^{-1} mol^{-1}) $\times 10^4$
0.0000	1.02801	(169.0)	1345.09	53.765	(114.0)
0.2710	1.02773	168.7	1344.78	53.804	113.1
0.5421	1.02744	169.0	1344.47	53.844	113.7
0.7224	1.02725	169.0	1344.26	53.871	113.8
1.0776	1.02688	168.9	1343.85	53.924	114.0
1.4367	1.02647	169.3	1343.57	53.968	113.2
1.9156	1.02600	169.0	1342.89	54.051	114.3

TABLE VII

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

c, g/dl	d, g/cm^3	ϕV_2, cm^3/mol	u, m/sec	β, bar$^{-1} \times 10^6$	ϕK_2, (cm^3 bar^{-1} mol^{-1}) $\times 10^4$
0.0000	0.78664	(130.0)	1102.49	104.587	(−16.7)
0.1099	0.78702	130.7	1102.79	104.479	−16.9
0.2197	0.78741	129.8	1103.08	104.372	−17.5
0.4394	0.78818	129.8	1103.68	104.157	−18.1
0.5858	0.78869	129.9	1104.07	104.017	−16.9
0.7810	0.78937	130.0	1104.60	103.827	−16.9
1.1500	0.79066	130.0	1105.59	103.472	−16.5
1.5333	0.79201	129.8	1106.63	103.102	−16.4
2.0445	0.79376	130.2	1108.01	102.618	−15.1

were taken that the methanol and dioxane solutions were not exposed to moist air. Dry box with gloves was used for preparation of solution, fill up of ultrasonic cell and pycnometers, and for storage of solvents and solutions.

The dioxane and methanol solutions for PAA and PDAM were prepared by stirring the solutions with a magnetic stirrer under closed container at 40°C for 4–6 hr and then filtering with a sintered-glass funnel in the dry box. Once the solution was prepared, it was found that no precipitation occurred even at room temperature, 23–25°C, although 30°C was reported as the theta temperature

TABLE VIII

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

c, g/dl	d, g/cm^3	ϕV_2, cm^3/mol	u, m/sec	β, bar$^{-1} \times 10^6$	ϕK_2, (cm^3 bar^{-1} mol^{-1}) $\times 10^4$
0.0000	1.02801	(145.3)	1345.09	53.765	(64.3)
0.1023	1.02806	145.4	1345.17	53.756	64.0
0.2047	1.02811	145.4	1345.25	53.747	64.4
0.4094	1.02821	145.4	1345.42	53.728	63.8
0.5125	1.02828	144.9	1345.50	53.719	63.6
0.8189	1.02841	145.4	1345.73	53.693	64.2
1.0250	1.02855	144.9	1345.88	53.674	63.9
1.6378	1.02883	145.3	1346.26	53.629	64.5
2.0500	1.02905	145.2	1346.69	53.583	64.1

TABLE IX
Summary of Results for N-Vinyl 2-Pyrrolidone in Aqueous Solution at 25°C ($M_2 = 111.14$)

c, g/dl	d, g/cm^3	ϕV_2, cm^3/mol	u, m/sec	β, bar$^{-1} \times 10^6$	ϕK_2, (cm^3 bar^{-1} mol^{-1}) $\times 10^4$
0.0000	0.99705	(101.9)	1496.29	44.797	(2.2)
0.1286	0.99716	101.9	1497.05	44.747	2.7
0.2573	0.99727	101.9	1497.82	44.696	2.1
0.5146	0.99747	102.4	1499.35	44.596	2.5
1.0722	0.99797	101.9	1502.66	44.377	2.1
1.5317	0.99837	101.9	1505.38	44.199	2.2
2.0423	0.99877	102.1	1508.43	44.003	2.5

for PAA in pure dioxane.[13]   In this connection, it should be mentioned that Morcellet and Loucheux[14] have reported that PAA is soluble in dioxane, even in room temperature, when a drop of water was added; otherwise, it is insoluble at room temperature.   It is not known whether the solubility of our sample in dioxane was due to the presence of a trace of moisture in the sample.   The exact concentration of each stock solution was determined by an acid-base titration.

In the case of poly(vinyl pyrrolidone) solutions, it was observed in the preliminary experiment that the values of concentration obtained by nitrogen content determined using the Kjeldhal method, as well as weighing the residue after evaporation, were within the limits of experimental error.   Hence, concentration of stock solutions was determined by evaporation to dryness and storage of the residue under P_2O_5 in vacuum for several days.

The ultrasonic velocity, u, was measured at a frequency of 5 MHz employing

TABLE X
Summary of Results of N-Vinyl-2-Pyrrolidone in Methanol Solution at 25°C ($M_2 = 111.14$)

c, g/dl	d, g/cm^3	ϕV_2, cm^3/mol	u, m/sec	β, bar$^{-1} \times 10^6$	ϕK_2, (cm^3 bar^{-1} mol^{-1}) $\times 10^4$
0.0000	0.78664	(101.0)	1102.49	104.587	(−14.0)
0.2664	0.78740	101.0	1103.47	104.300	−14.1
0.5329	0.78816	101.0	1104.46	104.013	−14.1
1.0658	0.78968	101.0	1106.43	103.443	−13.6
2.1316	0.79271	101.1	1110.43	102.307	−13.2

TABLE XI
Summary of Results of N-Vinyl-2-Pyrrolidone in Dioxane Solution at 25°C ($M_2 = 111.14$)

c, g/dl	d, g/cm^3	ϕV_2, cm^3/mol	u, m/sec	β, bar$^{-1} \times 10^6$	ϕK_2, (cm^3 bar^{-1} mol^{-1}) $\times 10^4$
0.0000	1.02801	(106.5)	1345.09	53.765	(40.8)
0.2013	1.02804	106.5	1345.45	53.735	40.6
0.4027	1.02808	106.2	1345.82	53.704	40.2
0.5240	1.02809	106.5	1345.99	53.689	41.0
0.8055	1.02814	106.4	1346.49	53.647	40.8
1.0580	1.02818	106.4	1346.94	53.609	40.8
1.4505	1.02824	106.4	1347.63	53.551	40.8
2.1161	1.02835	106.4	1348.79	53.453	40.8

TABLE XII

Summary of Results for Poly(N-Vinyl Pyrrolidone) in Aqueous Solution at 25°C (M_2 = 111.14)

c, g/dl	d, g/cm^3	ϕV_2, cm^3/mol	u, m/sec	β, bar$^{-1} \times 10^6$	ϕK_2, (cm^3 bar^{-1} mol^{-1}) $\times 10^4$
0.0000	0.99705	(87.0)	1496.29	44.797	(−0.35)
0.1762	0.99743	87.4	1497.04	44.735	−0.06
0.3525	0.99782	87.1	1497.79	44.673	−0.2
0.4701	0.99808	87.0	1498.29	44.631	−0.4
0.6267	0.99843	86.9	1498.96	44.576	−0.3
0.8355	0.99890	86.8	1499.84	44.503	−0.3
1.1140	0.99950	86.9	1501.04	44.405	−0.2
1.4853	1.00031	87.0	1502.63	44.275	−0.1
1.9804	1.00142	86.9	1504.75	44.102	−0.1

a precision ultrasonic interferometer, and the density with an Ostwald-type pycnometers at 25°C. The experimental details have been described earlier.[5,6] The adiabatic compressibility, β_s, the apparent molal adiabatic compressibility, ϕK_2, and the apparent molal volume, ϕV_2, of solute have been computed by the following equations:

$$\beta_s = 1/(u^2 d)$$
$$\phi K_2 = M_2 \beta_1 [(100/c)(\beta/\beta_1 - d/d_1) + 1/d_1]$$
$$\phi V_2 = M_2/d_1 [1 - (100/c)(d - d_1)]$$

where M_2 is the molecular weight of the monomer as well as the polymer repeat unit, c is the concentration expressed in g/100 ml, and d, d_1, and β, and β_1 are

TABLE XIII

Summary of Results for Poly(N-Vinyl Pyrrolidone) in Methanol Solution at 25°C (M_2 = 111.14)

c, g/dl	d, g/cm^3	ϕV_2, cm^3/mol	u, m/sec	β, bar$^{-1} \times 10^6$	ϕK_2, (cm^3 bar^{-1} mol^{-1}) $\times 10^4$
0.0000	0.78664	(81.2)	1102.49	104.587	(−37.0)
0.1192	0.78715	80.8	1102.83	104.455	−38.5
0.3180	0.78799	81.3	1103.39	104.237	−37.5
0.5031	0.78878	81.2	1103.90	104.037	−36.6
1.0062	0.79091	81.3	1105.32	103.490	−36.1
1.4626	0.79286	81.3	1160.60	102.998	−35.7
1.9500	0.79499	80.8	1108.02	102.457	−36.9

TABLE XIV

Summary of Results for Poly(N-Vinyl Pyrrolidone) in Dioxane Solution at 25°C (M_2 = 111.14)

c, g/dl	d, g/cm^3	ϕV_2, cm^3/mol	u, m/sec	β, bar$^{-1} \times 10^6$	ϕK_2, (cm^3 bar^{-1} mol^{-1}) $\times 10^4$
0.0000	1.02801	(88.5)	1345.09	53.765	(18.0)
0.1306	1.02824	89.1	1345.37	53.731	19.2
0.2612	1.02848	88.6	1345.65	53.696	18.1
0.3828	1.02870	88.6	1345.91	53.663	18.0
0.5224	1.02896	88.4	1346.21	53.626	18.0
0.7656	1.02941	88.3	1346.76	53.559	17.6
1.0335	1.02988	88.5	1347.31	53.491	18.1
1.5312	1.03082	88.3	1348.39	53.356	17.8

TABLE XV
Values of Huggins Constant K' and Intrinsic Viscosity of Polymers in Different Solvents at 25°C

Polymer	Solvent	$[\eta]$, dl/g	K'
PVA	water	1.56	0.15
	methanol	2.00	0.11
	dioxane	0.78	0.15
PDAM	methanol	0.44	0.52
	dioxane	0.39	0.38
PAA	dioxane	0.55	0.62

the densities and compressibilities of solution and solvent, respectively. The limiting values of apparent molal adiabatic compressibility, ϕK_2^0, and apparent molal volume, ϕV_2^0, of solute in different solvents were obtained by extrapolation of ϕK_2 and ϕV_2 versus concentration curves to infinite dilution. These values are given in parenthesis in Tables I–XIV.

The viscosity of the solutions was measured at $25 \pm 0.02°C$ with a Ubbelohde viscometer. Intrinsic viscosity, $[\eta]$, was obtained by extrapolation to infinite dilution, where possible, according to the relation $\eta_{sp}/c = [\eta] + K'[\eta]^2c$, where K' is the Huggins constant. The data for intrinsic viscosity and Huggins constant are given in Table XV.

RESULTS AND DISCUSSION

The results of adiabatic compressibility measurements are summarized in Tables I–XIV. Poly(acrylic acid), poly(N-dimethylaminoethyl methacrylate) and their monomers were studied in nonaqueous media, namely in methanol and dioxane, while poly(vinyl pyrrolidone) and its monomer were studied both in aqueous and in nonaqueous solutions. From the viscosity study (Fig. 1, reduced viscosity versus concentration curves), it is observed that poly(acrylic acid) dissociates both in aqueous and methanol solutions, but much less in methanol solution than that in aqueous solution. The polymer PDAM is feebly basic in aqueous solution and shows its characteristic expansion and contraction, while in methanol and dioxane solutions its basicity (dissociation) appears to be completely absent (curves 8 and 9). In dioxane solution, since dissociation for ionic polymers is arrested, they behave like nonionic polymers.

The plots of ϕK_2 and ϕV_2 as a function of concentration are shown in Figures 2–7. It is interesting to note that similar to aqueous solution, ϕK_2 and ϕV_2 values for the three polymers, PAA, PDAM, and PVP and their monomers in methanol and dioxane solutions, are found to be concentration independent. It may be stated here that the studies are generally made in dilute solutions, and in such solutions only the solvent–solute interactions are involved; the solute–solute interactions are negligible. The volume and compressibility of the nonionic solutes do not depend much on concentration because solvent–solute interactions due to the absence of charge groups are very weak and restricted to the first layer of the hydrating water molecules. The ϕV_2 is found to be independent in the case of a very large number of nonionic solutes in water and also in organic solvents,[15–19] where there are no strong solute–solute interactions. Further, in the case of ionic polymers even at the lowest concentration investigated, the ion-
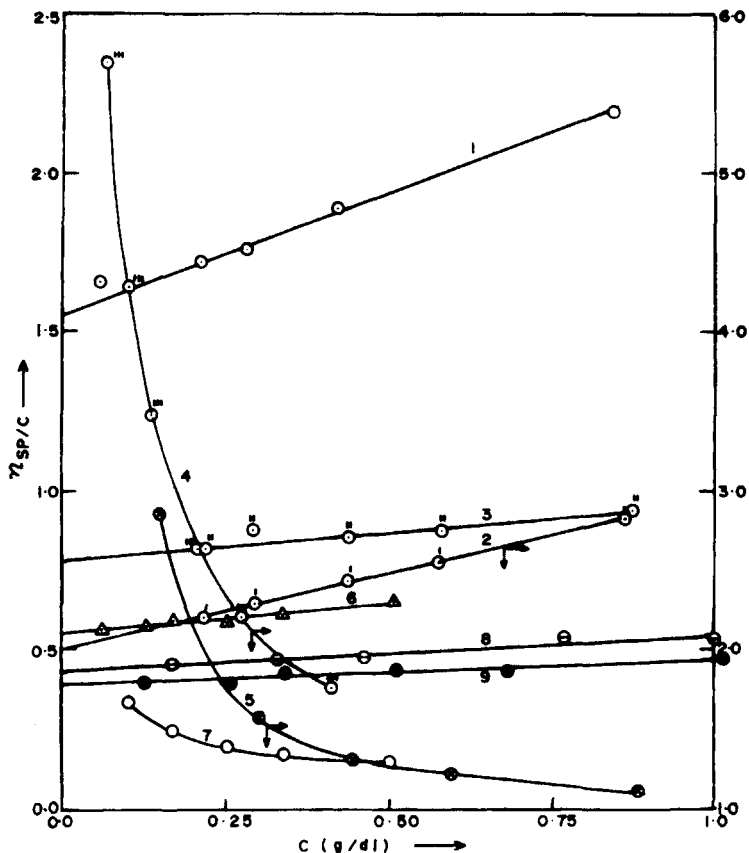
Fig. 1. Plots of reduced viscosity as function of concentration: (1) PVP in water; (2) PVP in methanol; (3) PVP in dioxane; (4) PAA in water; (5) PAA in methanol; (6) PAA in dioxane; (7) PDAM in water; (8) PDAM in methanol; (9) PDAM in dioxane. Curves (4) and (7) have been taken from Ph.D thesis, K. M. Kale, Marathwada University, 1972, and ref. 9, respectively, for comparison.

ization degree is only of a few percent, and even though it increases as the concentration is decreased (thereby resulting in an increase of viscosity), it remains very small and has a very small effect on ϕK_2 and ϕV_2. The limiting values, ϕK_2^0 and ϕV_2^0, are shown in Table XVI. The limiting values in aqueous solution for AA, PAA, DAM, and PDAM are listed in the same table for comparison. The earlier data on ϕK_2^0 and ϕV_2^0 of DAM in water[9] have been redetermined as they were found to be too low. Only the corrected values have been recorded on the table. It should be mentioned that in the case of PVP in aqueous solution Scholtan[21] had obtained a value of 86.9 cm^3/mol for ϕV_2^0, which is in excellent agreement with that obtained in this work.

Table XVI indicates that there is a marked difference in the ϕK_2^0 and ϕV_2^0 values between the monomer and polymer in all three solvents. In aqueous solution the difference in ϕV_2^0 between monomer and polymer is, on an average, 16.1 cm^3/mol. On the other hand, in nonaqueous solution the difference is even greater; it is, on an average, 24.0 cm^3/mol and 20.5 cm^3/mol in methanol and dioxane solution, respectively. A few more monomer–polymer systems, namely, methacrylic acid (MAA) and poly(methacrylic acid) (PMAA), methacrylamide
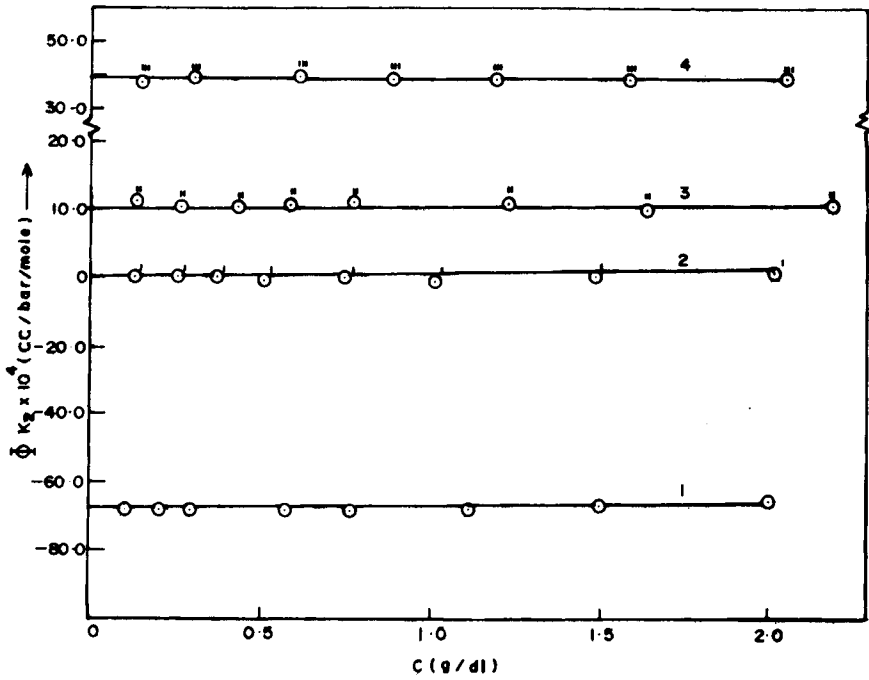
Fig. 2. Plots of apparent molal compressibility as function of concentration: (1) PAA in methanol; (2) PAA in dioxane; (3) AA in methanol; (4) AA in dioxane.
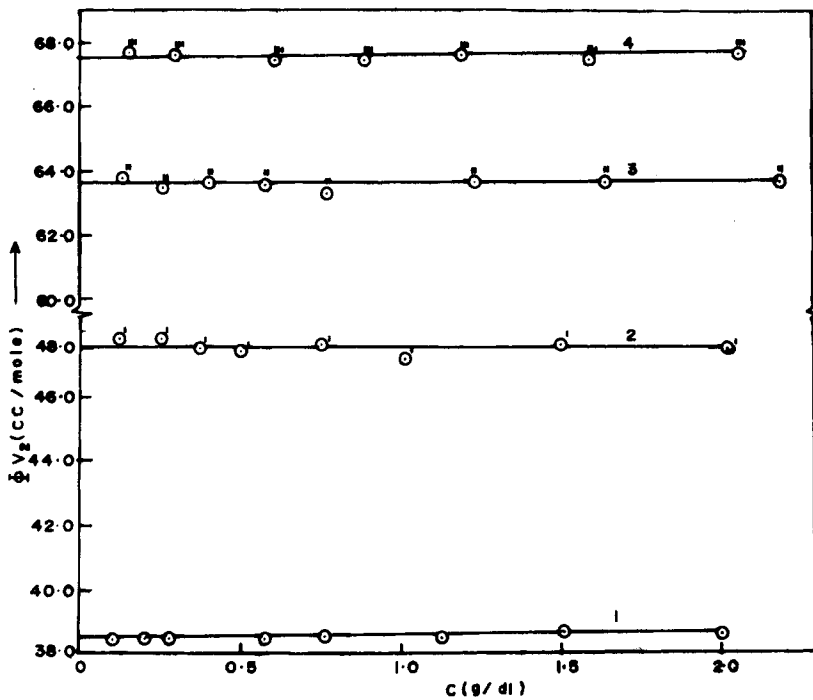

Fig. 3. Plots of apparent molal volume as function of concentration: (1) PAA in methanol; (2) PAA in dioxane; (3) AA in methanol; (4) AA in dioxane.
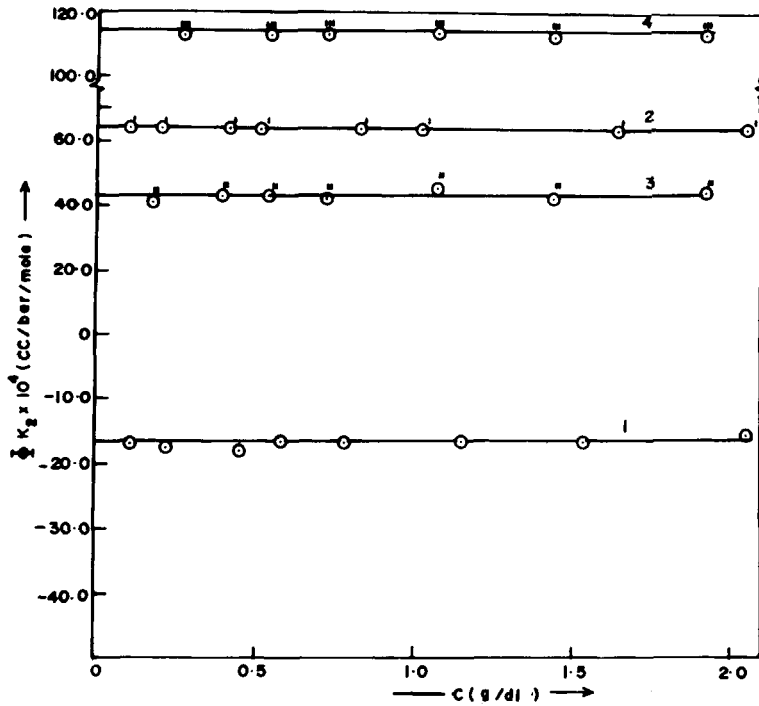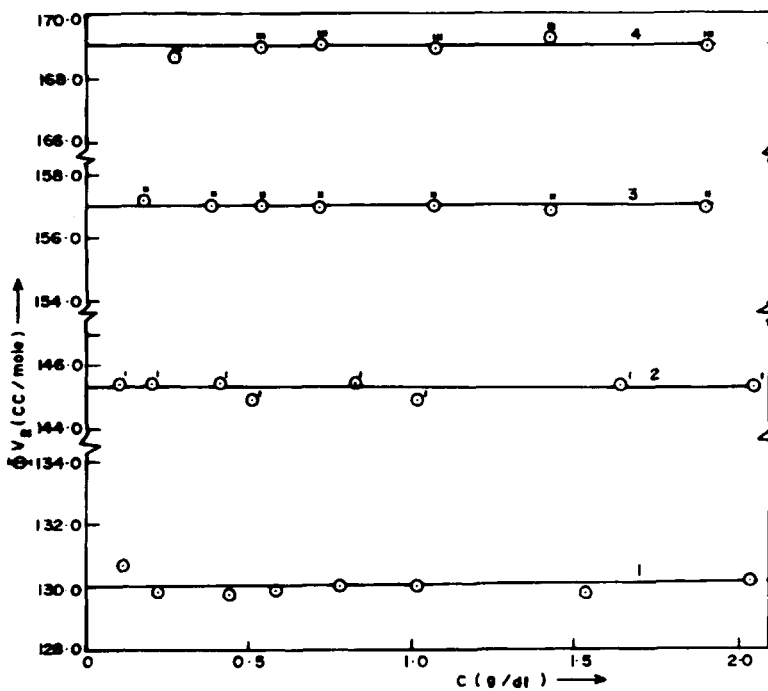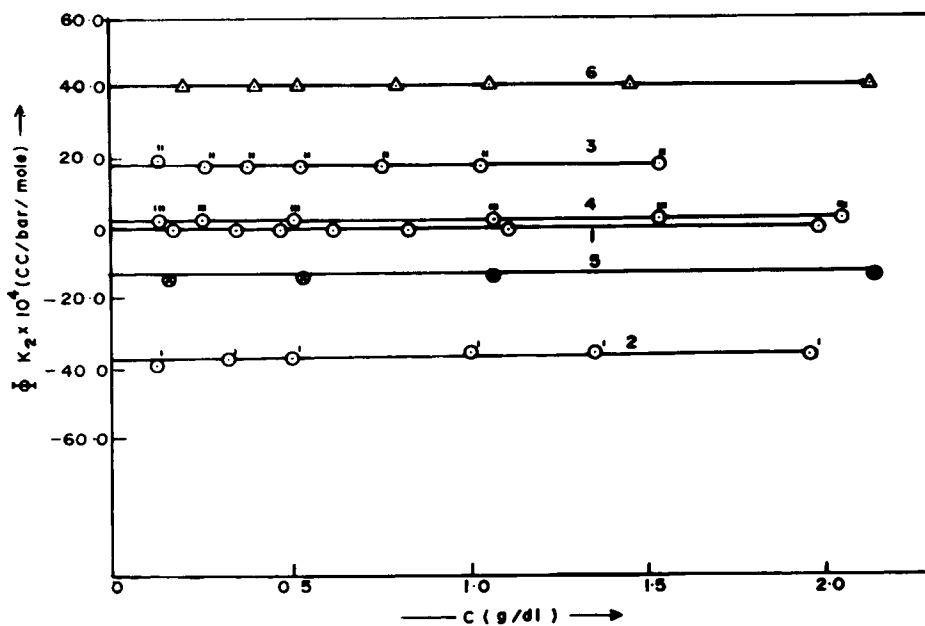
Fig. 4. Plots of apparent molal compressibility as function of concentration: (1) PDAM in methanol; (2) PDAM in dioxane; (3) DAM in methanol; (4) DAM in dioxane.

Fig. 5. Plots of apparent molal volume as function of concentration: (1) PDAM in methanol; (2) PDAM in dioxane; (3) DAM in methanol; (4) DAM in dioxane.

Fig. 6. Plots of apparent molal compressibility as function of concentration: (1) PVP in water; (2) PVP in methanol; (3) PVP in dioxane; (4) VP in water; (5) VP in methanol; (6) VP in dioxane.

TABLE XVI

Limiting Values of Apparent Molal Compressibility, ϕK_2^0 and Apparent Molal Volume, ϕV_2^0 of Solutes in Different Solvents

Materials	M_2	Molar volume, cm^3/mol	ϕV_2^0, cm^3/mol			$\phi K_2^0 \times 10^4$, cm^3/bar/mol		
			water	methanol	dioxane	water	methanol	dioxane
AA	72.06	68.56[a]	61.7[a]	63.6	67.5	6.0[a]	11.0	39.0
PAA			46.7[a]	38.5	47.5	0.85[a]	−68.0	0.3
DAM	157.2	169.7[b]	152.8[c]	157.0	169.0	−8.9[c]	43.0	114.0
PDAM			134.3[b]	130.0	145.3	16.0[b]	−16.7	64.3
VP	111.14	106.86[d]	101.9	101.0	106.5	2.2	−14.0	40.8
PVP			87.0	81.2	88.5	−0.35	−37.0	18.0

[a] Data from Roy-Chowdhury and Kale.[6]
[b] Data from Roy-Chowdhury and Dewhare.[9]
[c] Values of ref. 9 redetermined.
[d] Density of monomer was taken as 1.04 g/ml at 25°C.[20]

(MAAm) and polymethacrylamide (PMAAm),[22] and acrylamide (AAm) and polyacrylamide (PAAm),[6] in aqueous solution also showed a similar decrease in ϕK_2^0 and ϕV_2^0. This decrease in the case of polymers indicates that water cluster becomes stronger and better formed as the molecules grow larger on polymerization. When hydrophobic solutes and water are mixed, an overall increase in ice-likeness of the solution occurs. Since most forms of ice have a lower density than water, a positive volume of mixing is expected. On the contrary, a negative volume of mixing is observed in all cases. According to Nemethy
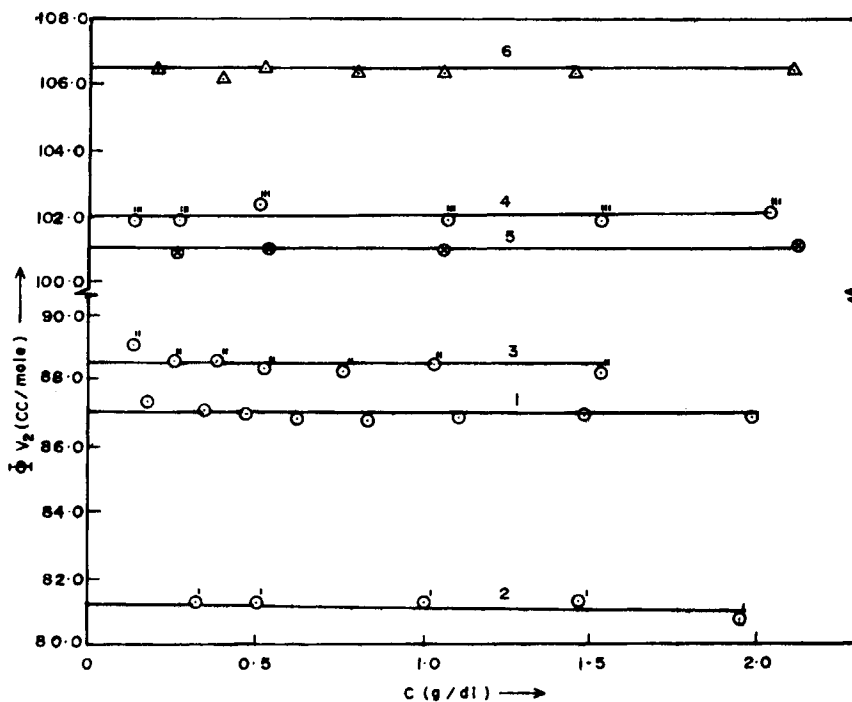
Fig. 7. Plots of apparent molal volume as function of concentration: (1) PVP in water; (2) PVP in methanol; (3) PVP in dioxane; (4) VP in water; (5) VP in methanol; (6) VP in dioxane.

and Scheraga,[23] the solute molecules are filling up the space that would normally be empty to a large extent with pure liquid leading to a decrease in volume. It must be mentioned here that similar lowering of ϕV_2^0 was observed by Wen and Saito[24] in the study of five tetraalkylammonium salts (methyl to pentyl) at 25°C; ϕV_2^0 per methyl group is found on an average of 15.7 cm^3/mol compared to the average 23.75 cm^3/mol obtained by Masterton[25] for comparatively smaller molecules, methane, ethane, and propane at 23°C. In this connection, it may be added that in the case of ionic polymers in aqueous solution, besides the enhanced hydrophobic hydration, the electrostriction per monomer group (repeat unit) within the polymer chain is larger than that in the monomer state as the proximity of the charge sites on the polymer chain results in an increased electrostriction per monomer unit. However, in PAA and PDAM, as has been stated earlier, the dissociation is very small, and hence, the electrostrictive concentration due to this effect is negligible.

The molar volumes of the three monomers, AA, DAM, and VP are 68.56, 169.7, and 106.86 cm^3, respectively. When these monomers are dissolved in aqueous solution to form an infinitely dilute solution, there is a decrease in volume of 6.86, 16.9, and 4.96 cm^3, respectively. The apparent molal volume in water for the nonionic monomer, vinyl pyrrolidone, has been calculated by the method of Traube,[26–28] taking into consideration the effect of ring and double bond (C=C) on the volume of the molecule. The calculation of some other monomers with atomic volume and structural corrections tabulated by Partington[29] lead to the values of ϕV_2^0 as recorded in Table XVII. The experimentally observed values are 2–3 cm^3 higher than those calculated, with the exception of DAM, which is

TABLE XVII
Apparent Molal Volume, ϕV_2^0 Calculated by the Method of Traube[26]

Monomers	ϕV_2^0, cm³/mole		Difference, cm³/mol
	calculated	experimental	
AA	59.3	61.7[c]	+2.4
DAM[a]	144.4	152.8[a]	+8.4
VP[b]	98.8	101.9[d]	+3.1
AAm	63.5	65.5[c]	+2.0
MAAm	78.8	82.0[e]	+3.2
MAA	75.3	78.6[e]	+3.3

[a] Values redetermined with pure monomer (E. Mark product, Ger.). Monomer in aqueous solution polymerizes very rapidly and solution cannot be stored in refrigerator more than 4–5 hr without appreciable polymerization.

[b] Structural correction taking 6.8 cm³/mol for five-carbon ring of pyrrolidone. For six-carbon ring benzene, naphthalene, anthracene, etc., reduction of volume by 8.1 cm³/mol was proposed by Traube.

[c] Data from Roy-Chowdhury and Kale.[6]

[d] Data from present investigation.

[e] Data from Roy-Chowdhury.[22]

8.4 cm³ higher. Considering the approximations involved in these calculations, the agreement between the calculated and observed values is fairly good. In DAM, the observed higher value may be due to blocking of the N center with two methyl groups; as a result the close packing between solvent and solute is prevented causing an increase in ϕV_2^0. Similar to our observation, Laliberte and Conway[30] noted that in dialkyl ammonium salts (R_2NH_2Cl) and in trialkyl ammonium ions (Et_3NH^+ and (n-$Pr)_3NH^+$), the electrostriction was diminished as the N-charge center was effectively blocked by two or three alkyl groups.

It has been observed that the monomers, AA, DAM, and VP show an increase in volume and compressibility in methanol and dioxane solutions over that of the values of aqueous solution (Table XVI). This increase is found to be 5.8, 16.2, and 4.6 cm³/mol, respectively, in going from water to dioxane. Since the ϕV_2^0 values for all the monomers in dioxane solution very closely approach the molar volume of the monomers, solvent–solute interaction seems to be absent in these cases and they form ideal solutions. It must be pointed out that similar to our observations, Masterton[25] obtained the ϕV_2^0 for methane, ethane, and propane smaller in water than in nonpolar liquids by about 20 ml/mol. The high internal pressure of water and the change occurring in structure have been suggested as the cause of this behavior.

The ϕV_2^0 for PAA, PDAM, and PVP were found to have increased by 0.8, 11.0, and 1.5 cm³/mol, respectively, in dioxane solution over that of the value of aqueous solution. The dissociation of PAA in aqueous solution is very low and the electrostriction contributes only a very small amount in ϕV_2^0 (~0.8 cm³/mol, obtained as the difference between the volumes in water and dioxane). This can be demonstrated in another way. According to Jolicoeur and Lacroin,[31] and Perron and Desnoyers,[19] the ϕV_2^0 for the repeat unit of PAA, when calculated to a good approximation according to ϕV_2^0 (PAA) = ϕV_2^0(Propoinic acid) $- 2\phi V_2^0$ (H), where ϕV_2^0(Propoinic acid) refers to un-ionized propoinic acid (67.9 cm³/mol) and ϕV_2^0 (H) is the volume increment of a terminal H-atom (10.7 cm³/mol), gives a value of 46.5 cm³/mol, which is in excellent agreement with the observed value.

The most interesting point is that in methanol solution, PAA, PDAM, and PVP show a decrease in adiabatic compressibility and volume by 68.8 cm^3/bar/mol and 8.2 cm^3/mol, 32.7 cm^3/bar/mol, and 4.3 cm^3/mol, and 36.6 cm^3/bar/mol, and 5.8 cm^3/mol, respectively, compared to the values obtained from aqueous solution. It may be pointed out that the largest contribution to ϕV_2 of a solute is the geometric one. This includes the intrinsic volume of the solute plus the void space in the solvent molecule packing around the solute. This last contribution depends very much on the solvent, and, its changes from solvent to solvent for a given solute may very well be responsible for the changes of ϕV_2^0 and ϕK_2^0. The studies of some ions in methanol by Kawaizumi and Zana[32] has clearly established that the geometric contribution in this solvent is smaller than in water; further, the electrostrictive effect is also greater in methanol than in water. Since the electrostrictive effect in the case of PAA and PDAM is very small, this decrease in ϕV_2^0 and ϕK_2^0 for all three polymers is mainly due to geometric effect. All the results show that changes in the solvent nature has a remarkable influence on the compressibility of the polymers.

From the viscosity data, shown in Table XV, it is observed that Huggins constant K', a measure for solvent–solute interaction, is the same for PVP in water and dioxane solutions but the intrinsic viscosity, $[\eta]$ (related to hydrodynamic volume) of PVP in water is twice as large as in dioxane. In strongly associating solvent-like methanol, $[\eta]$ is still larger (2.0 dl/g) and the Huggins constant, K', has decreased further. It may be pointed out that Huggins constant usually, but not always, decreases with increase of solvent power.[33] In methanol, the ϕV_2^0 is found to have decreased more compared to water and dioxane.

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