

# Adiabatic Compressibility of Polyelectrolytes: Effect of Solvents on Copolymers of Vinyl Pyrrolidone with Acrylic Acid and *N*-dimethylaminoethyl Methacrylate\*

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## Synopsis

The results of adiabatic compressibility measurements for two copolymers, acrylic acid-vinyl pyrrolidone (AA-VP) and *N*-dimethylaminoethyl methacrylate-vinyl pyrrolidone (DAM-VP), in three different solvents, namely, water, methanol, and dioxane, have been described. The molecular weight of copolymers was determined by the light scattering method and the IR and NMR spectra of the polymers and copolymers were examined to establish that the alternating acrylic acid-vinyl pyrrolidone and *N*-dimethylaminoethyl methacrylate-vinyl pyrrolidone structure exists in the copolymers. The AA-VP copolymer behaves as a slightly weaker acid than the homopolymer of acrylic acid, while DAM-VP copolymer is very feebly basic and has the same strength as that of the homopolymer of *N*-dimethylaminoethyl methacrylate. The reduced viscosity for the two copolymers in aqueous solution is very low ( $\sim 0.08$  dL/g for AA-VP copolymer). In methanol solution AA-VP and DAM-VP copolymers show a decrease of  $\phi K_2^0$  and  $\phi V_2^0$  by  $61.6 \times 10^{-4}$  cc/bar/mol and 8.0 cc/mol, and  $191.0 \times 10^{-4}$  cc/bar/mol and 20.0 cc/mol, respectively, over that of the values of aqueous solution. The void space around the solute is smaller in methanol than in water, and accordingly this decrease has been attributed to geometric effect. Only one copolymer, DAM-VP is soluble in dioxane, and the values are seen to have increased in this solution by  $71.0 \times 10^{-4}$  cc/bar/mol and 18.7 cc/mol, respectively, compared to the values obtained from aqueous solution. The experimentally determined  $\phi K_2^0$  and  $\phi V_2^0$  for AA-VP and DAM-VP copolymer are  $0.6 \times 10^{-4}$  cc/bar/mol, and 102.4 cc/mol and  $-61.0 \times 10^{-4}$  cc/bar/mol, 94.4 cc/mol, respectively, in aqueous solution, and  $-12.0 \times 10^{-4}$  cc/bar/mol, 211.0 cc/mol and  $-203.0 \times 10^{-4}$  cc/bar/mol, 191.0 cc/mol, respectively, in methanol solution. In dioxane solution the values for DAM-VP copolymer are  $59.0 \times 10^{-4}$  cc/bar/mol and 229.7 cc/mol, respectively. These experimentally determined values for AA-VP copolymer show an increase by  $0.04 \times 10^{-4}$  cc/bar/mol, 4.4 cc/mol and  $28.3 \times 10^{-4}$  cc/bar/mol, 8.0 cc/mol in aqueous and methanol solution, respectively, compared to calculated values determined on the basis of no interaction between acid and the pyrrolidone group. In contrast, the DAM-VP copolymer shows a decrease of  $27.6 \times 10^{-4}$  cc/bar/mol and 10.3 cc/mol,  $149.3 \times 10^{-4}$  cc/bar/mol and 20.2 cc/mol, and  $23.0 \times 10^{-4}$  cc/bar/mol and 4.1 cc/mol in aqueous, methanol, and dioxane solutions, respectively. In aqueous solution these differences between calculated and observed values have been attributed to a change of water structure around the copolymer chain. A similar effect is responsible for the difference of the values in the methanol solution also. In the dioxane solution the difference is rather small, and the solvent structure has probably not altered much due to the presence of the DAM unit in the chain.

\* Communication No. 2706 from National Chemical Laboratory, Poona, India.

## INTRODUCTION

In an earlier communication<sup>1</sup> the results of the adiabatic compressibility measurements on some ionic and nonionic polymers, namely, poly(acrylic acid) (PAA), poly(*N*-dimethylaminoethyl methacrylate) (PDAM) and poly(vinyl pyrrolidone) (PVP) in three different solvents, water, methanol, and dioxane, have been reported. It has been shown that the change of solvent nature has a remarkable influence on the compressibility and volume of the polymers. For instance, in dioxane solution, the electrostrictional effect as well as the structural hydration effect are found to be minimized; as a result the volume of the solute has increased over that of the value of the aqueous solution. On the other hand, in methanol solution the volume of the solute has decreased compared to the value obtained from aqueous solution, which has been ascribed to geometric effect. The present paper is an extension of a similar study in different solvents with copolymers prepared in combination with the same ionic and nonionic polymers so as to produce additional data of solvent effect on polymers and to substantiate our considerations. Our choice of these copolymers was governed by the fact that the polymers and copolymers soluble both in aqueous and non-aqueous media are very limited and since our earlier-studied ionic and nonionic polymers were soluble both in aqueous and nonaqueous solvents, the combination of them may yield copolymers which are soluble in both the media. Further, since the homopolymers have already been studied in different solvents, a similar study of the corresponding copolymers where the two units (acid and pyrrolidone, base and pyrrolidone, or acid and base—three combinations are possible) are put together randomly in the same chain on copolymerization may give an insight about the nature of interactions between the groups present in them as well as the role of the solvents in effecting the interactions if any. The two copolymers, acrylic acid–vinyl pyrrolidone (AA–VP) and *N*-dimethylaminoethyl methacrylate–vinyl pyrrolidone (DAM–VP), studied in this work were soluble both in aqueous and methanol solution, but in dioxane only *N*-dimethylaminoethyl methacrylate–vinyl pyrrolidone copolymer was soluble. In this connection it may be stated that the copolymers prepared with acrylic acid and *N*-dimethylaminoethyl methacrylate (AA–DAM) (polyampholytes) were studied earlier in this laboratory where acid–base type interaction was observed.<sup>2</sup> Unfortunately, these polyampholytes can not be studied in nonaqueous media as they are found insoluble. In the present study vinyl pyrrolidone (VP) is a common constituent for both the copolymers, and, since this unit is inert in character, the near-neighbor interaction between charged groups, due to its presence, in the chain would be greatly reduced. However, the conformation of PVP has changed considerably by the incorporation of acrylic acid (AA) or *N*-dimethylaminoethyl methacrylate (DAM) unit in the chain. This effect is evident in the viscometric results of the copolymers which are much lower than that of PVP. Worley and Koltz<sup>3</sup> in the study of PVP for its effect on the near-infrared spectra of water observed that PVP exhibits a structure-making character. Further, it was observed that any solute which modified the structure of aqueous solution affected the conformation of a dissolved macromolecule. It has been observed from the compressibility data in this study that the presence of AA or DAM unit in the copolymer has also influenced to a great extent the water-structure (breaking or making) around the solute.

## EXPERIMENTAL

## Synthesis and Purification of Copolymers

Acrylic acid–vinyl pyrrolidone (AA–VP) copolymer: This copolymer was prepared by polymerization of a mixture of freshly distilled acrylic acid (50 mol % in monomer) and *N*-vinyl 2-pyrrolidone in a 2*M* dioxane solution with 0.25% benzoyl peroxide at 70°C with constant stirring and bubbling with nitrogen for 2 h. The polymer came out as a white precipitate which was washed several times with dioxane until it was free from monomers and dried *in vacuo* to constant weight. The product was further dried in an oven over night at 110°C. The conversion into polymer was about 72%.

*N*-dimethylaminoethyl methacrylate–vinyl pyrrolidone (DAM–VP) copolymer: This was prepared in a similar way by polymerization of a mixture of monomers of *N*-dimethylaminoethyl methacrylate (50 mol % in the monomer) and *N*-vinyl 2-pyrrolidone in a 2*M* dioxane solution with 0.25% benzoyl peroxide at 90°C with a constant stirring and bubbling with nitrogen for 6 h. The product was diluted with dioxane, precipitated with petroleum ether, and dried in a vacuum to constant weight. It was further dried in an oven over night at 110°C. The conversion into polymer was 64%.

## Characterization of Copolymers

The weight average molecular weight  $\bar{M}_w$  for DAM–VP and AA–VP copolymers was estimated using a Brice-Phoenix light scattering photometer with methanol and 0.067*M* HCl acid in methanol as solvents, respectively. Dilute HCl acid was used to suppress the dissociation of carboxyl group in AA–VP copolymer. The molecular weight of the two copolymers, DAM–VP and AA–VP, was obtained as  $2.12 \times 10^5$  and  $7.68 \times 10^4$ , respectively.

The IR spectra were recorded on a Perkin-Elmer 221 spectrometer using thin film and NMR spectra with Varian T-60 type spectrometer.

*Structure of AA–VP and DAM–VP copolymers:* The IR spectra of the polymers and the copolymers studied in the region 700–3700  $\text{cm}^{-1}$  are compared in Figure 1. The spectra of copolymers are virtually identical to those of the corresponding polymers and show characteristic absorptions of  $\nu_{\text{C=O}}$  at 1680–1720  $\text{cm}^{-1}$  and  $\nu_{\text{C-O}}$  at 1420  $\text{cm}^{-1}$  for PAA,  $\nu_{\text{C=O}}$  at 1640  $\text{cm}^{-1}$  and  $\nu_{\text{C-N}}$  at 1410  $\text{cm}^{-1}$  for PVP, and  $\nu_{\text{C-H}[\text{N}(\text{CH}_3)_2]}$  at 2780–2790  $\text{cm}^{-1}$ ,  $\nu_{\text{C=O}}$  at 1715  $\text{cm}^{-1}$ , and  $\nu_{\text{C-N}}$  at 1120–1170  $\text{cm}^{-1}$  for PDAM. Since it is very difficult to remove water completely from PAA and PVP, characteristic absorption due to the same is found for those polymers at 2850–3400  $\text{cm}^{-1}$  and 3200–3600  $\text{cm}^{-1}$ , respectively.

The NMR spectra of the homopolymers are shown in Figure 2, and the corresponding copolymers are shown in Figure 3. The spectra exhibit poor resolution, and the peaks are broad in most cases. All the polymer and copolymer spectra have been split into mainly two areas which are designated as X and Y. It may be noted that additional splitting is found in each of these areas particularly in case of two copolymers. Peaks at areas X and Y are ascribed to protons of groups marked on the structural formula a and b, respectively (Figs. 2 and 3). From the integration peaks X and Y for the copolymers (so also for the homopolymers) it was observed that the total step heights corresponding to each of

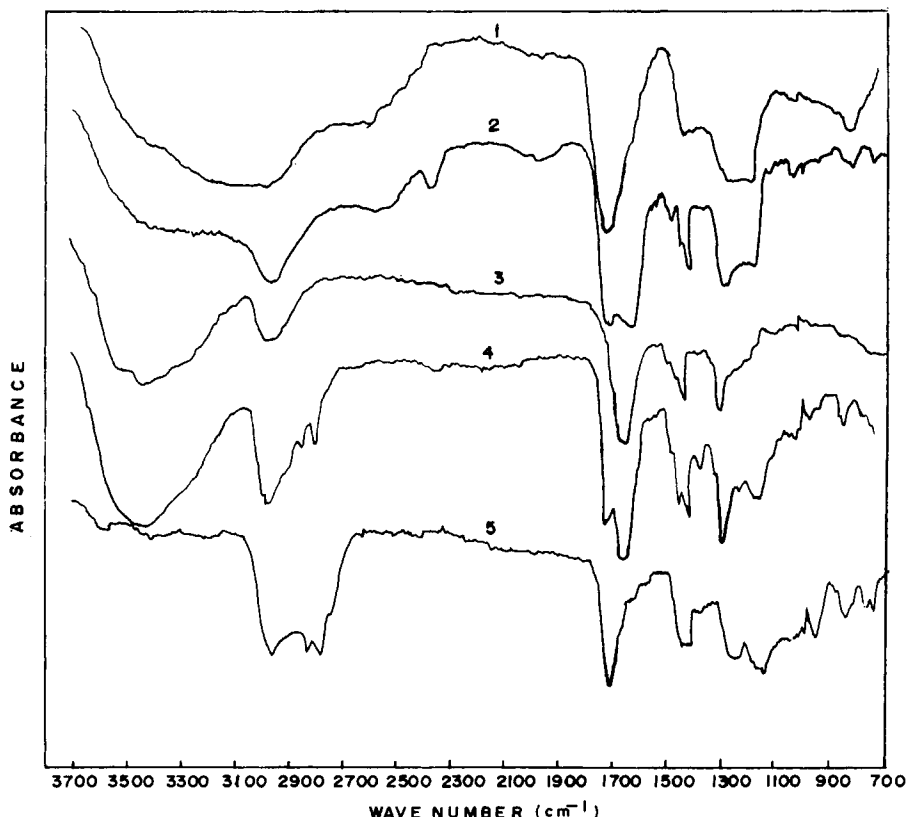


Fig. 1. IR spectra of polymer and copolymer films: (1) PAA, (2) AA—VP, (3) PVP, (4) DAM—VP, (5) PDAM.

these areas (X and Y) are equal in ratio to the ratio of protons of a and b. All these suggest that the alternating acrylic acid–vinyl pyrrolidone and *N*-dimethylaminoethyl methacrylate–vinyl pyrrolidone structure exists in the copolymers.

*Determination of composition of the copolymers:* The acid and amine groups were estimated pH-metrically with 0.5 N NaOH and 0.51 N HCl, respectively. The nitrogen content of the copolymers were determined by the Kjeldahl method, and on this basis the equivalent weight was calculated. In the case of DAM—VP copolymer, the nitrogen content due to VP was estimated by subtracting from the total quantity the amount due to DAM obtained from pH-metric titration. The equivalent weight as obtained from pH-metric titration and nitrogen estimation are given in Table I. The two sets of data are in close agreement. It was found that in the two copolymers, AA—VP and DAM—VP, the ratio of the acid to vinyl pyrrolidone and base to vinyl pyrrolidone were 1:0.59 and 1:1, respectively.

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

Experimental procedures, purification of solvents, and preparation of solutions

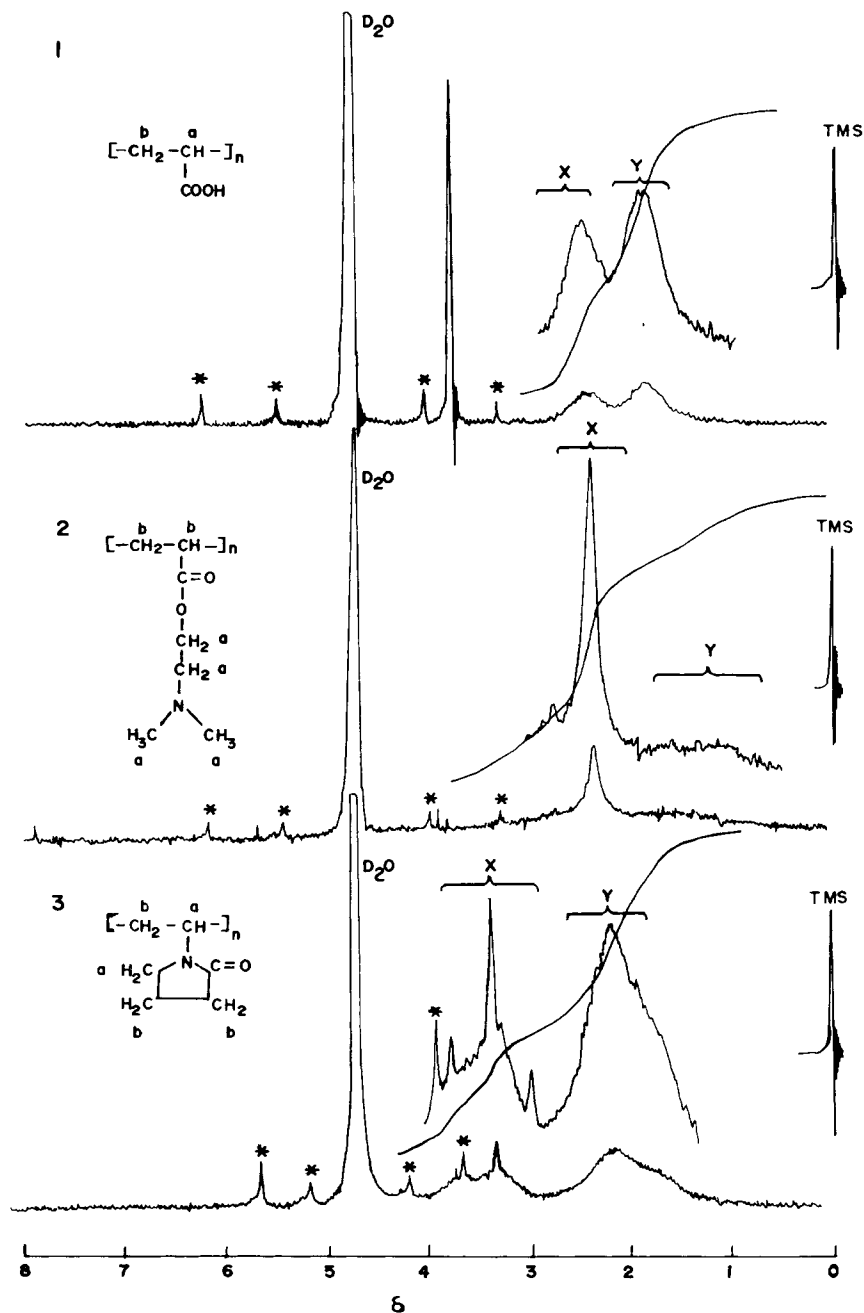


Fig. 2.  $^1\text{H}$  NMR spectra (60 MHz) of polymers in  $\text{D}_2\text{O}$ : (1) PAA, (2) PDAM, and (3) PVP. Spinning side bands which are symmetrically placed on either side of  $\text{D}_2\text{O}$  resonance are marked with an asterisk.

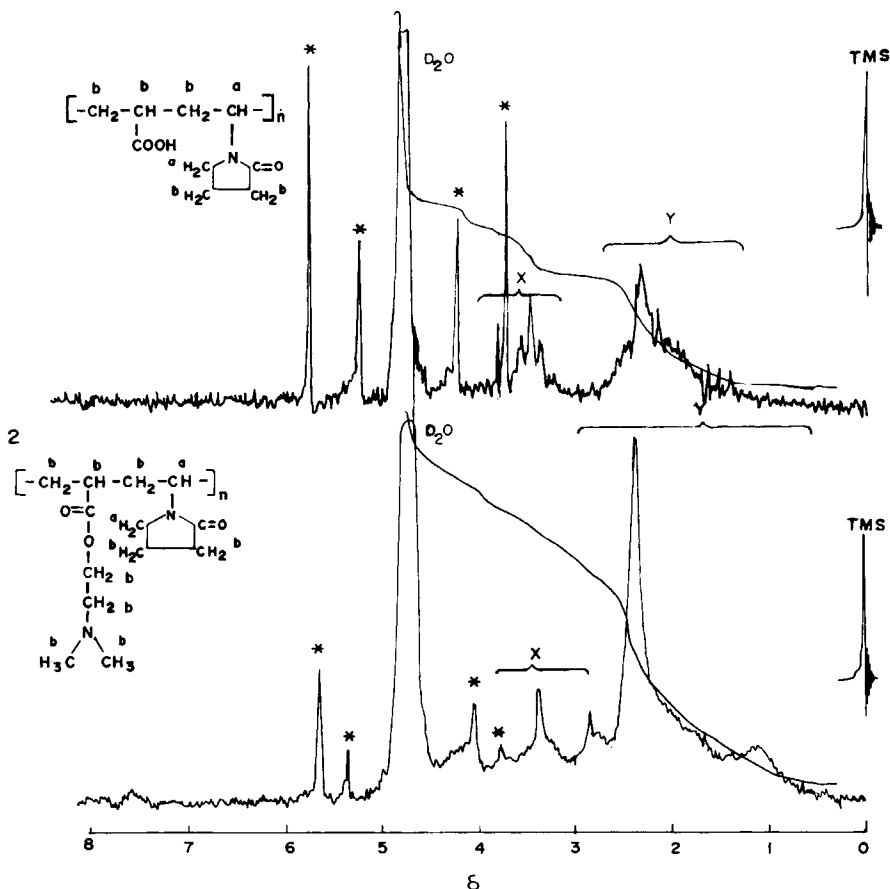


Fig. 3.  $^1\text{H}$  NMR spectra (60 MHz) of copolymers in  $\text{D}_2\text{O}$ : (1) AA—VP, (2) DAM—VP. Spinning side bands which are symmetrically placed on either side of  $\text{D}_2\text{O}$  resonance are marked with an asterisk.

were given in the preceding paper.<sup>1</sup> All precautions were taken that the methanol and dioxane solutions were not exposed to moist air. The adiabatic compressibility  $\beta_s$ , the apparent molal compressibility  $\phi K_2$ , and the apparent molal volume  $\phi V_2$  of the solute have been determined from the velocity and density data in the usual way. The limiting values of the apparent molal compressibility  $\phi K_2^0$  and apparent molal volume  $\phi V_2^0$  of the solute at different solvents at  $25^\circ\text{C}$

TABLE I  
Composition of Copolymers: Equivalent Weight or Average Molecular Weight of Repeat Unit of Copolymers

Copolymer	Vinyl pyrrolidone in monomer mixture (mol %)	Equiv on basis of nitrogen analysis, VP	Equiv wt on basis of pH-metric titration acid/base	Ratio of acid- or base-to-VP group in copolymer	Group in copolymer (mol %)	
					Acid or base	VP
AA—VP	50	233	137	1:0.59	63	37
DAM—VP	50	268	268	1:1	50	50

were obtained by extrapolation of  $\phi K_2$  and  $\phi V_2$  vs. concentration curves to infinite dilution. The values are given in parenthesis in Tables II–VI.

The viscosity measurements were carried out with Ubbelohde viscometer thermostated at  $25 \pm 0.02^\circ\text{C}$ .

## RESULTS AND DISCUSSION

The pH-metric titration curves for two copolymers, AA—VP and DAM—VP, are shown in Figure 4. About 0.15 g of each copolymer in 50 cc water was titrated with 0.5 N NaOH and 0.51 N HCl acid, respectively. For comparison, the plots of poly(acrylic acid)<sup>4</sup> and poly(*N*-dimethylaminoethyl methacrylate)<sup>5</sup> are shown on the same graph. It is interesting to note that the acid copolymer containing excess of carboxylic group (63%) and base copolymer containing 50% amino groups behave more or less similar to the neutralization curves of poly(acrylic acid) and poly(*N*-dimethylaminoethyl methacrylate), respectively. However, the AA—VP copolymer containing 63% carboxyl group in the chain behaves in the initial stage as a slightly weaker acid than the homopolymer of acrylic acid. After half-neutralization, the acid strength of the copolymer is found to be increased than that of the poly(acrylic acid). On the other hand, the DAM—VP copolymer containing 50% amino groups in the chain, though initially having the same strength as that of the homopolymer of *N*-dimethylaminoethyl methacrylate, behaves as a stronger base (even up to the complete neutralization stage) than that of PDAM when they are titrated with HCl acid. Both the copolymer, DAM—VP, and the homopolymer, PDAM, are very weak bases and the contribution for the amino groups to the pH of the solution in both the cases

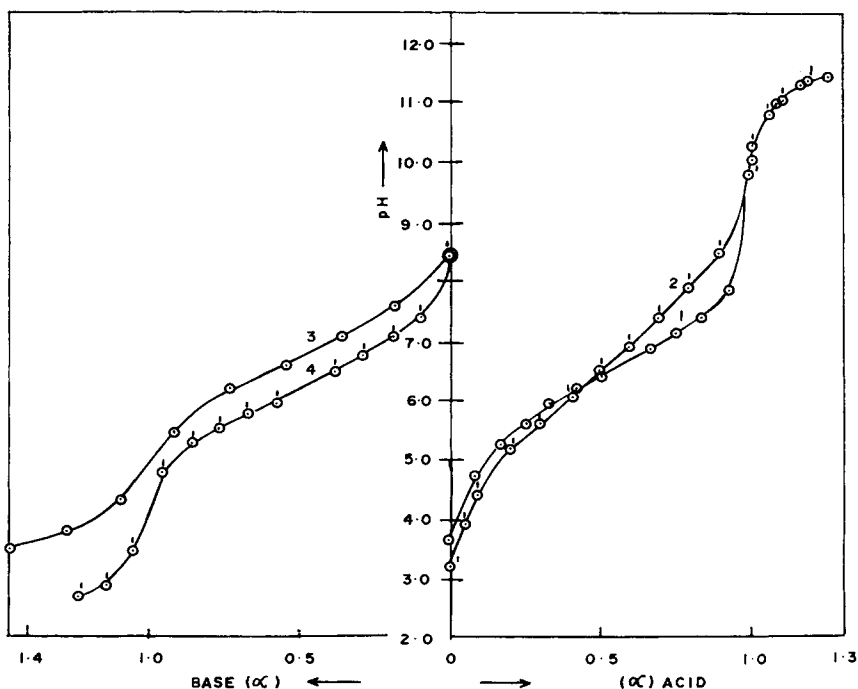


Fig. 4. pH-metric titration curves for the copolymers: (1) AA—VP copolymer, (2) PAA, (3) DAM—VP copolymer, (4) PDAM.

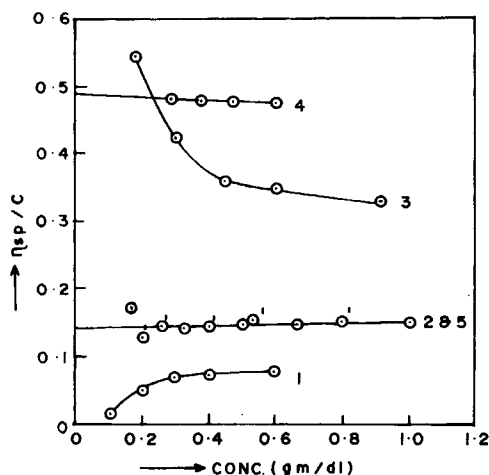


Fig. 5. Plots of reduced viscosity as a function of concentration: (1) AA—VP in water; (2) AA—VP in methanol; (3) DAM—VP in water; (4) DAM—VP in methanol; (5) DAM—VP in dioxane,  $\circ$ '.

is the same; as soon as the titration starts, the amino groups acquire the charges, and the base strength of the DAM—VP copolymer is increased more than that of PDAM because of the fact that the near neighbour interaction between charged groups ( $-\text{N}^+(\text{CH}_3)_2$ ) is greatly reduced due to the presence of inert vinyl pyrrolidone units in the copolymer.

The viscosity data for the copolymers in different solvents are given in Figure 5. It may be pointed out that the reduced viscosity for the two copolymers in aqueous solution is very low ( $\sim 0.08$  dL/g in case of AA—VP copolymer). Such low viscosity (0.03–0.06 dL/g) is observed in proteins such as glycogen or albumin. In case of DAM—VP copolymer, the reduced viscosity has shown an increase on dilution in aqueous solution due to polyelectrolytic expansion. In contrast, in the case of AA—VP copolymer, the reduced viscosity is progressively reduced as the solution is diluted more and more. The probable explanation may be that the  $\text{H}^+$  ions as formed on dilution in this case get entrapped into the copolymer network containing the bulky pyrrolidone groups, causing a progressive decrease of reduced viscosity of the solution. On the other hand, the amino groups in DAM—VP copolymer acquire more protons ( $\text{H}^+$  ions) on dilution, which is available as a result of the slight ionization of  $\text{H}_2\text{O}$  and the chain is expanded

TABLE II  
Summary of Results of Acrylic Acid-Vinyl Pyrrolidone (AA-VP) Copolymer in Aqueous Solution at  $25^\circ\text{C}$  ( $M_2 = 137$ )

$c$ (g/dL)	$d$ (g/cc)	$\phi V_2$ , (cc/mol)	$u$ (m/s)	$\beta \times 10^6$ (bar $^{-1}$ )	$\phi K_2 \times 10^4$ (cc/bar/mol)
0.0000	0.99705	(102.4)	1496.29	44.797	(0.6)
0.1101	0.99733	102.5	1496.68	44.761	0.8
0.2202	0.99761	102.5	1497.09	44.724	0.5
0.2936	0.99780	102.3	1497.35	44.700	0.5
0.3915	0.99805	102.3	1497.70	44.668	0.7
0.5220	0.99838	102.4	1498.17	44.625	0.8
0.6525	0.99872	102.2	1498.64	44.582	0.7
0.9325	0.99942	102.2	1499.67	44.489	0.5



TABLE III  
Summary of Results for Acrylic Acid-Vinyl Pyrrolidone (AA-VP) Copolymer in Methanol Solution at 25°C ( $M_2 = 137$ )

$c$ (g/dL)	$d$ (g/cc)	$\phi V_2$ (cc/mol)	$u$ , (m/s)	$\beta \times 10^6$ (bar <sup>-1</sup> )	$\phi K_2 \times 10^4$ (cc/bar/mol)
0.0000	0.78664	(94.4)	1102.49	104.587	(-61.0)
0.2138	0.78762	94.3	1103.13	104.335	-61.7
0.2769	0.78791	94.3	1103.32	104.261	-62.1
0.5538	0.78916	94.9	1104.08	103.952	-57.4
0.7743	0.79017	94.8	1104.82	103.680	-61.0
1.1352	0.79183	94.5	1105.89	103.263	-60.7
1.5135	0.79357	94.4	1107.03	102.824	-60.8
2.0182	0.79589	94.3	1108.24	102.301	-60.5

accordingly. However, both the copolymers, AA-VP and DAM-VP, when neutralized with NaOH and HCl acid, respectively, show the usual polyelectrolytic expansion and contraction on dilution (plots are not shown). In methanol and dioxane solutions, since dissociation for the ions is minimized, normal dependence of reduced viscosity with concentration is observed.

The results of adiabatic compressibility measurements in different solvents are summarized in Tables II-VI. The plots of  $\phi K_2$  and  $\phi V_2$  vs. concentration are shown in Figures 6 and 7, respectively. Similar to PAA, PDAM, and PVP, the  $\phi K_2$  and  $\phi V_2$  values for these copolymers are found to be concentration independent in all the three solvents. The limiting values,  $\phi K_2^0$  and  $\phi V_2^0$ , are shown in Table VII. The results confirmed in many respects to those observed earlier<sup>1</sup>

TABLE IV  
Summary of Results for *N*-Dimethylaminoethyl Methacrylate-Vinyl Pyrrolidone (DAM-VP) Copolymer in Aqueous Solution at 25°C ( $M_2 = 268$ )

$c$ (g/dL)	$d$ (g/cc)	$\phi V_2$ (cc/mol)	$u$ (m/s)	$\beta \times 10^6$ (bar <sup>-1</sup> )	$\phi K_2 \times 10^4$ (cc/bar/mol)
0.0000	0.99705	(211.0)	1496.29	44.797	(-12.0)
0.1074	0.99728	211.2	1496.83	44.754	-12.6
0.2149	0.99751	211.3	1497.36	44.713	-10.9
0.4299	0.99798	210.6	1498.45	44.626	-12.2
0.5733	0.99829	210.6	1499.19	44.568	-12.6
0.7643	0.99870	210.8	1500.11	44.495	-11.5
1.1525	0.99952	211.2	1502.05	44.344	-10.7
1.6465	1.00057	211.3	1504.52	44.152	-10.3

TABLE V  
Summary of Results for *N*-Dimethylaminoethyl Methacrylate-Vinyl Pyrrolidone (DAM-VP) Copolymer in Methanol Solution at 25°C ( $M_2 = 268$ )

$c$ (g/dL)	$d$ (g/cc)	$\phi V_2$ (cc/mol)	$u$ (m/s)	$\beta \times 10^6$ (bar <sup>-1</sup> )	$\phi K_2 \times 10^4$ (cc/bar/mol)
0.0000	0.78664	(191.0)	1102.49	104.587	(-203.0)
0.1786	0.78742	191.9	1103.36	104.318	-200.8
0.3573	0.78821	191.0	1104.24	104.047	-204.6
0.4764	0.78873	191.2	1104.82	103.869	-203.8
0.6351	0.78943	191.0	1105.60	103.631	-203.3
0.8467	0.79036	191.0	1106.64	103.315	-202.5

TABLE VI  
Summary of Results for *N*-Dimethylaminoethyl Methacrylate-Vinyl Pyrrolidone (DAM-VP)  
Copolymer in Dioxane Solution at 25°C ( $M_2 = 268$ )

$c$ (g/dL)	$d$ (g/cc)	$\phi V_2$ (cc/mol)	$u$ (m/s)	$\beta \times 10^6$ (bar <sup>-1</sup> )	$\phi K_2 \times 10^4$ (cc/bar/mol)
0.0000	1.02801	(229.7)	1345.09	53.765	(59.0)
0.1223	1.02815	230.8	1345.36	53.736	60.5
0.2446	1.02830	229.8	1345.63	53.706	58.9
0.4476	1.02854	229.8	1346.13	53.654	57.1
0.5967	1.02873	229.2	1346.41	53.622	59.0
0.7955	1.02897	229.2	1346.85	53.574	58.9

that the decrease of compressibility and volume are more pronounced in methanol than in aqueous solution, while, in dioxane solution, an increase of the values over that of water is observed. In methanol solution, AA-VP and DAM-VP copolymers show a decrease of  $61.6 \times 10^{-4}$  cc/bar/mol, 8.0 cc/mol and  $191.0 \times 10^{-4}$  cc/bar/mol, and 20.0 cc/mol, respectively, over that of the values of aqueous solution. It may be pointed out that  $\phi V_2^0$  is determined by the following four factors<sup>6</sup>:

$$\phi V_2^0 = V_i + V_s + V_e + V_c$$

where  $V_i$  is the intrinsic volume of the solute including the dead space between solute and solvent molecules,  $V_s + V_c$  are the structural volume terms (structure promotion and cavity effect) (the contribution due to these factors depend very much on the solvent, and the change of solvent for a given solute is very much responsible for the change of these quantities), and  $V_e$  is the negative volume change due to electrostriction. In the study of the partial molal volumes of monovalent ions in methanol Kawaizumi and Zana<sup>7</sup> have observed that the void space around the ions is smaller in methanol than in water (geometric effect) and also that the effect of electrostriction is larger in methanol than in water; as a result the partial molal volumes obtained in methanol are smaller than those obtained in water. Since dissociation of the acid or amine groups in the two copolymers is negligible, this decrease on  $\phi K_2^0$  and  $\phi V_2^0$  values in methanol appears solely due to geometric effect. Only one copolymer, DAM-VP, is soluble in dioxane and the  $\phi K_2^0$  and  $\phi V_2^0$  values in this solution are found to have increased by  $71.0 \times 10^{-4}$  cc/bar/mol and 18.7 cc/mol, respectively, compared to the values obtained from aqueous solution. It may be pointed out that under normal condition a molecular of dioxane exists in a chair form in which the C—O—C dipoles oppose each other and the bulk dielectric constant of this solvent becomes very low (2.2). The polar boat form is apparently favored in the vicinity of ions only with the consequent increase of effective dielectric constant. Since the charge in DAM-VP copolymer is negligible, solvent-solute interaction seems to be minimized, and accordingly  $\phi K_2^0$  and  $\phi V_2^0$  approach values to that of ideal solution.

From Table VII it is observed that the equivalent weight of the repeat unit of AA-VP and DAM-VP copolymers have increased over that of PAA and PDAM by 65 and 111, respectively. If we consider that there is no interaction between acid or the amino group and the pyrrolidone group, the  $\phi K_2^0$  and  $\phi V_2^0$  values for the copolymers would have been  $0.64 \times 10^{-4}$  cc/bar/mol, 98.0 cc/mol

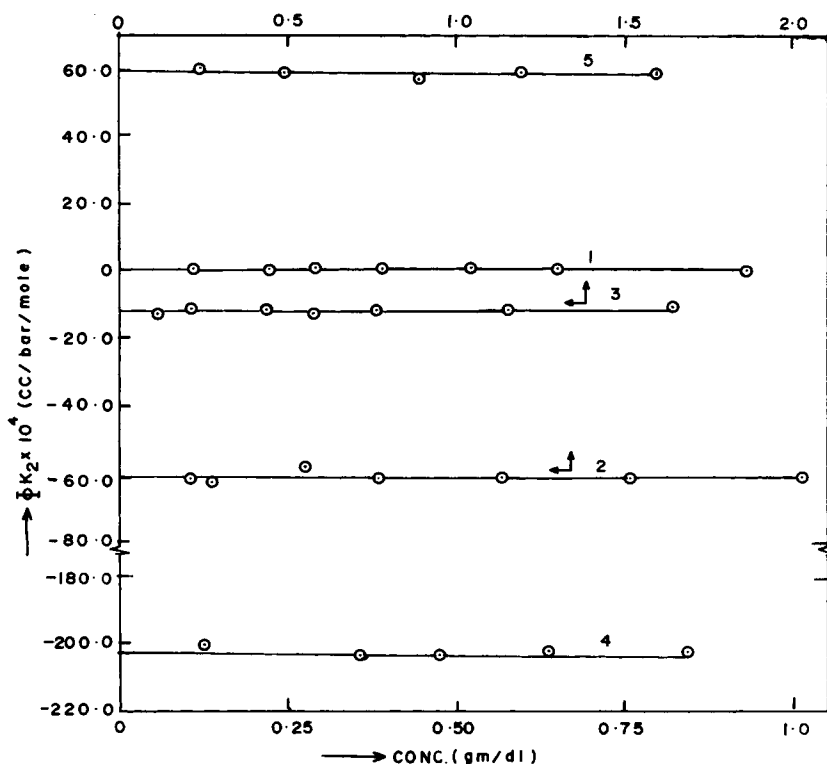


Fig. 6. Plots of apparent molal compressibility as a function of concentration: (1) AA—VP in water, (2) AA—VP in methanol, (3) DAM—VP in water, (4) DAM—VP in methanol, (5) DAM—VP in dioxane.

and  $15.65 \times 10^{-4}$  cc/bar/mol, 221.3 cc/mol, respectively, in aqueous solution,  $-89.8 \times 10^{-4}$  cc/bar/mol, 86.4 cc/mol and  $-53.7 \times 10^{-4}$  cc/bar/mol, 211.2 cc/mol, respectively, in methanol solution, and, in dioxane solution for DAM—VP copolymer,  $82.3 \times 10^{-4}$  cc/bar/mol, 233.8 cc/mol, respectively. Comparing the experimentally observed values with the calculated ones, we obtain for AA—VP copolymer an increase in  $\phi K_2^0$  and  $\phi V_2^0$  values by  $0.04 \times 10^{-4}$  cc/bar/mol, 4.4 cc/mol and  $28.3 \times 10^{-4}$  cc/bar/mol, 8.0 cc/mol in aqueous and methanol solution,

TABLE VII  
Limiting Values of Apparent Molal Compressibility,  $\phi K_2^0$  and apparent molal volume,  $\phi V_2^0$ , in different solvents at 25°C

Copoly- mers	$M_2$	$\phi V_2^0$ (cc/mol)			$\phi K_2^0 \times 10^4$ (cc/bar/mol)		
		water	methanol	dioxane	water	methanol	dioxane
AA—VP	137	102.4	94.4	—	0.6	-61.0	—
DAM—VP	268	211.0	191.0	229.7	-12.0	-203.0	59.0
PAA <sup>a</sup>	72.06	46.7	38.5	47.5	0.85	-68.0	0.3
PDAM <sup>a</sup>	157.2	134.3	130.0	145.3	16.0	-16.7	64.3
PVP <sup>a</sup>	111.14	87.0	81.2	88.5	-0.35	-37.0	18.0

<sup>a</sup> Data obtained from Ref. 1. The data for PAA, PDAM, and PVP have been listed in the table for comparison.

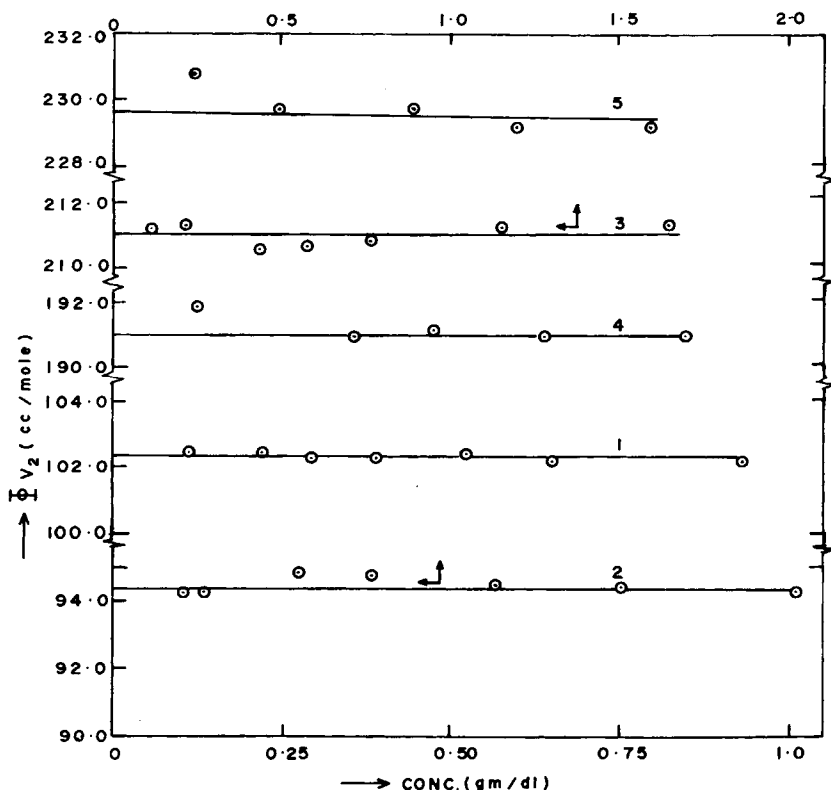


Fig. 7. Plots of apparent molal volume as a function of concentration: (1) AA—VP in water, (2) AA—VP in methanol, (3) DAM—VP in water, (4) DAM—VP in methanol, (5) DAM—VP in dioxane.

respectively. On the other hand, for DAM—VP copolymer, a decrease in  $\phi K_2^0$  and  $\phi V_2^0$  values by  $27.6 \times 10^{-4}$  cc/bar/mol and  $10.3$  cc/mol,  $149.3 \times 10^{-4}$  cc/bar/mol and  $20.2$  cc/mol, and  $23.0 \times 10^{-4}$  cc/bar/mol and  $4.1$  cc/mol in aqueous, methanol, and dioxane solution, respectively, has been observed.

It is presumed that these differences between the calculated and observed values are neither due to dissociation of acid and base groups present in the copolymers nor due to acid–base type interaction as the vinyl pyrrolidone unit present in the chain is inert in character. The most probable explanation for the difference is due to the fact that a change of water structure around the copolymer chain has occurred. The presence of DAM unit in the chain enhances the hydrophobic interaction and water structure surrounding the solute is reinforced causing the decrease of  $\phi V_2^0$  and  $\phi K_2^0$  values, whereas a structurally perturbed state of water molecules (structure breaking) arises due to the presence of AA in the copolymer chain containing the vinyl pyrrolidone unit. Probably a similar effect is responsible for the difference of the values in methanol solution also. In this connection it may be mentioned that in the study of hexamethylenetetramine (HMT), a feebly basic amine, for its effect on the binding of methyl orange homologues by polyvinyl pyrrolidone, Takagishi and Kuroki,<sup>8</sup> has observed the enhancement of hydrophobic interaction in the binding in presence

of HMT. The study of PVP for its effect on the near-infrared spectra of water revealed that PVP exhibit a structure-making character.<sup>3</sup> The presence of HMT noticeably influences water-structure organization and behaves in a way typical of a structure-making solute in aqueous solution. In dioxane solution, the difference of the values is comparatively small, and the solvent structure has probably not altered much due to the presence of the DAM unit in the copolymer chain.

The authors' thanks are due to Dr. C. I. Jose and Dr. C. R. Narayanan for very helpful discussions on infrared and NMR spectra, respectively.

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Received November 24, 1980

Accepted November 19, 1981