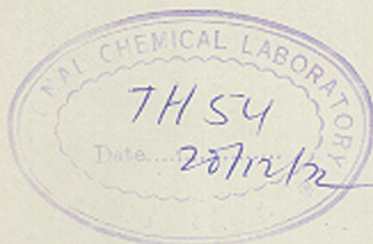


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ADIABATIC COMPRESSIBILITY OF POLYELECTROLYTES

AND OTHER ALLIED MACROMOLECULES

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1.1 A THESIS

1.1.1 SUBMITTED TO

THE MARATHWADA UNIVERSITY, AURANGABAD

FOR THE DEGREE OF

DOCTOR OF PHILOSOPHY IN CHEMISTRY

1.4 Relation between partial and
apparent molar

541.64:536.711(043)

KAL

1.7 Some general aspects of
ultrasonic

1.8 Experimental methods of ultrasonic
velocity measurement

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1.8.1 Mechanical method

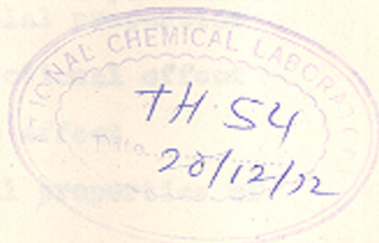
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(b) Pulse method

1.9 Pressure

MARCH, 1972



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NOMENCLATURE

AA	:	Acrylic acid
AAm	:	Acryl amide
AA-ViBuPyBr	:	Acrylic acid-4-vinyl N-n butylpyridinium bromide copolymer
AA-ViPy	:	Acrylic acid-4-vinyl pyridine copolymer
α	:	Degree of neutralization
β	:	Compressibility of the solution
β_1	:	Compressibility of the solvent
β_s	:	Adiabatic compressibility
b_s	:	Length for a statistical chain element
c	:	Polymer concentration (gm/dl)
d	:	density of the solution
d_1	:	Density of the solvent
D	:	Dielectric constant
D_e	:	Effective dielectric constant
ϵ	:	Extinction coefficient
η_{sp}	:	Specific viscosity
η_{sp}/c	:	Reduced specific viscosity
$[\eta]$:	Intrinsic viscosity (dl/gm)
F_e	:	Electrostatic free energy as a function of charge e.
F_γ	:	Electrostatic free energy as a function of angle γ .
γ	:	The angle subtended by two adjoining chain elements.
\tilde{r}_n	:	End-to-end distance in molecular coil (viscosity measurements).

\bar{r}_z	:	End-to-end distance in molecular coil (light scattering measurements).
h	:	End-to-end distance of the charged molecule.
h_0	:	The corresponding end-to-end distance in an uncharged state.
ΔH_M	:	Heat of mixing
k	:	Reciprocal of the equivalent thickness of ion atmosphere.
λ	:	Wavelength.
M_2	:	Molecular weight of the monomer or polymer repeat unit.
\bar{M}_n	:	Number average molecular weight.
\bar{M}_w	:	Weight average molecular weight.
MAA-ViBuPyBr	:	Methacrylic acid-4-vinyl N-n butylpyridinium bromide copolymer
MAA-ViPy	:	Methacrylic acid-4-vinyl pyridine copolymer
ν	:	Number of charged groups per molecule.
n	:	Frequency
n_1	:	Moles of the solvent
n_2	:	Moles of the solute
P	:	Pressure
PAA	:	Polyacrylic acid
PAAM	:	Polyacrylamide
PoA-ViBuPyBr	:	Potassium acrylate-4-vinyl N-n butylpyridinium bromide copolymer
PoMA-ViBuPyBr	:	Potassium methacrylate-4-vinyl N-n butylpyridinium bromide copolymer
PSA	:	Polysodium acrylate

q_i	:	Charge on the i^{th} polymer chain segment.
$(\bar{r}^2)^{1/2}$:	Root mean square end-to-end distance.
r	:	Distance from fixed charge.
R_θ	:	Rayleigh's scattering at an angle θ .
S	:	Entropy
ΔS_M	:	Entropy of mixing.
SY-MA	:	Styrene-maleic acid copolymer.
SY-SMA	:	Styrene-sodium maleiate copolymer.
ϕK_2	:	Apparent molal compressibility of solute.
ϕK_2^0	:	Apparent molal compressibility of solute at infinite dilution.
u	:	Ultrasonic velocity in the medium.
V	:	Volume of the solution.
V_1^0	:	Molal volume of pure solvent.
\bar{V}	:	Partial molal volume.
V_{int}	:	Intrinsic volume occupied by the solute in solution.
ϕV_2	:	Apparent molal volume of solute.
ϕV_2^0	:	Apparent molal volume of the solute at infinite dilution.

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CHAPTER - I

CHAPTER - IINTRODUCTION

The linear polymers with ionizable groups have attracted much attention in recent years. The peculiar characteristics that a linear polyelectrolyte shows in aqueous solution are due to the fact that these solutions possess both electrolytic as well as chain molecular properties¹⁻⁴. By "polyelectrolytes" we refer to macromolecular substances containing a large number of rather easily ionizable groups forming polyions, surrounded with small counter ions which render the system electroneutral⁵. Whenever an uncharged polymer chain is converted by titration or by chemical modification to a chain carrying a large number of ionized groups, the mutual electrostatic repulsion of fixed charges may lead to chain expansion which are far beyond the range attainable by a change of the medium from poor to good solvents. The ionic charges attached to the polymer chain affect not only the conformation of the macromolecule but also create a high local charge density. This must affect strongly the distribution of simple ions present in the solution. Thus the study of polyelectrolytes with flexible chain is concerned with two kinds of phenomena. On the one hand the problem is confined to evaluating the extent over which a polymer chain is expanded as a result of the mutual repulsion of the fixed charges and how this expansion affects the properties of a polyelectrolyte solution. On the other hand, the problem is

connected with electrochemical properties of the polyelectrolyte solution such as the effect of the polyion on ionic activity coefficients, ion-pair formation and electrophoretic phenomenon. However, the two problems cannot be strictly separated. The interaction of the polyion with simple ions will lead to a redistribution of the ions which modifies the repulsion factor of the fixed charges and the polyion expansion. Conversely not only the charge but also the shape of the polyion will determine its extent of interaction with the small ions. It is this interdependence which is responsible for the complexities and at the same time an attractive feature for systematic studies in this field.

In Table 1.1 are listed some flexible chain molecules with ionizable groups. In polyacrylic acid, poly(methacrylic acid) etc., these ionizable groups are weakly acidic in nature so that the charge density along the molecular chain can be varied at will by varying the degree of neutralization. Polyvinyl sulphonic acid and polystyrene sulphonic acid are strongly ionizing polymers. A very interesting class of materials is available in the form of hydrolysed copolymers of maleic anhydride. Hydrolysis of copolymers, say styrene and maleic anhydride leads to macromolecules containing closely spaced pairs of carbonyls separated from other such pairs by at least one comonomer unit. Such materials are called 'polydibasic acid'.

Weakly basic polymer is available as poly(4-vinyl pyridine) which may be converted into a stronger base by quaternization.

Table 1.1

A list of typical flexible ionizable chain molecules

Polymers	Chemical formula
Poly(acrylic acid)	$\left[\begin{array}{c} -\text{CH}_2 - \text{CH} - \\ \\ \text{COOH} \end{array} \right]_n$
Poly(methacrylic acid)	$\left[\begin{array}{c} -\text{CH}_2 - \text{C}(\text{CH}_3) - \\ \\ \text{COOH} \end{array} \right]_n$
Poly(vinyl sulphonic acid)	$\left[\begin{array}{c} -\text{CH}_2 - \text{CH} - \\ \\ \text{SO}_3\text{H} \end{array} \right]_n$
Poly(styrene sulphonic acid)	$\left[\begin{array}{c} -\text{CH}_2 - \text{CH} - \\ \\ \text{C}_6\text{H}_4 \\ \\ \text{SO}_3\text{H} \end{array} \right]_n$
Styrene-maleic acid copolymer	$\left[\begin{array}{c} -\text{CH}_2 - \text{CH} - \text{CH} - \text{CH} - \\ \quad \quad \\ \text{C}_6\text{H}_5 \quad \text{COOH} \quad \text{COOH} \end{array} \right]_n$
Vinyl methyl ether-maleic acid copolymer	$\left[\begin{array}{c} -\text{CH}_2 - \text{CH} - \text{CH} - \text{CH} - \\ \quad \quad \\ \text{OCH}_3 \quad \text{COOH} \quad \text{COOH} \end{array} \right]_n$
Acrylic acid-maleic acid copolymer	$\left[\begin{array}{c} -\text{CH}_2 - \text{CH} - \text{CH} - \text{CH} - \\ \quad \quad \\ \text{COOH} \quad \text{COOH} \quad \text{COOH} \end{array} \right]_n$
Poly(vinyl pyridine)	$\left[\begin{array}{c} -\text{CH}_2 - \text{CH} - \\ \\ \text{N} \end{array} \right]_n$

continued

Table 1.1 continued

Polymers	Chemical formula
Poly(4-vinyl N-n butyl-pyridinium bromide)	$\left[\begin{array}{c} -\text{CH}_2 - \text{CH} - \\ \\ \text{C}_5\text{H}_4\text{N}^+ \text{Br}^- \\ \\ \text{C}_4\text{H}_9 \end{array} \right]_n$
Acrylic acid-4-vinyl N-n butyl pyridinium bromide copolymer	$\left[\begin{array}{c} -\text{CH}_2 - \text{CH} - \text{CH}_2 - \text{CH} - \\ \qquad \qquad \\ \text{COOH} \qquad \qquad \text{C}_5\text{H}_4\text{N}^+ \text{Br}^- \\ \qquad \qquad \qquad \\ \qquad \qquad \qquad \text{C}_4\text{H}_9 \end{array} \right]_n$

If quaternization is carried out with a long chain alkyl halide, the hydrophobic bond between the paraffin residues will result in a stabilization of compact conformation analogues to the formation of soap micelles. Such materials have therefore been described as 'polysoaps'.

Amphoteric polyelectrolytes may be obtained by copolymerization of suitable acidic and basic monomers, for instance, acrylic acid and 4-vinyl pyridine. The 4-vinyl pyridine in the copolymer may be quaternized to give strongly basic property.

Polymers which are weak Lewis bases may acquire polyelectrolytic character in strongly acidic media, although the polymer chains would not be charged by other solvents. Thus polyamides have been observed to behave like polyelectrolytes in formic acid solutions⁶⁻⁸.

In addition to polyelectrolytes with flexible chain polyions which may assume a wide range of conformations, there are some charged macromolecules that exist in a specific configuration. Proteins carry a variety of ionizable groups in the side chains of the amino acid residues i.e., the amino groups of lysine, the phenolic groups of tyrosene, the thiols of cysteine and the guanidino residues of arginine. They may therefore carry a net positive or negative charge depending on their state of overall ionization and stabilized in a particular shape. The tertiary nature of globular proteins is usually sufficiently stable in shape to allow the build up of a considerable net charge density before denaturation sets in. Another polyelectrolyte with specific conformation is the native form of deoxyribose nucleic acid (DNA). In solution it exists in the form of a double helix which behaves more or less like a rigid rod-shaped particle. However, much of the stimulation for the study of these systems has arisen from the fact that proteins and nucleic acids which play such an important factor in our biological processes, fall into the category of polyelectrolytes. With our present knowledge of the rather stable molecular architecture of globular proteins and DNA, the apparent analogy between these materials and synthetic polyelectrolytes is more limited than it might have once appeared. Let us next consider briefly the various theories for the polyion expansion.

1.1 THEORIES FOR POLYION EXPANSION

In the past two decades there have been several attempts to evaluate the thermodynamic properties of polyelectrolyte solutions based on some molecular model of the polyion in the solution state. In the earliest theories, the polyion was considered as a spherical distribution of charge, and the distribution of small ions in the system was assumed to be described by the Poisson-Boltzmann equation. Hermans and Overbeek⁹ proceeded from this point by solving the Poisson-Boltzmann equation with the linearization approximation of Debye-Huckel¹⁰ and calculating the electrostatic potential and free energy of the polyion as a function of its size and charge. Kimball, Cutler and Samelson¹¹ on the other hand suggested that the effect of the electrostatic potential is not adequately approximated by the Debye-Huckel approximation. They in turn assumed that the distribution of small ions could be calculated using Donnan condition and neglecting the term of the Boltzmann equation involving derivatives of the potential. Solution for the potential and polyion size could then be made, treating the polymer as a collection of charges bound by a central force. However, the maximum expansion which is permitted by this theory is given by a factor $(2)^{1/2}$ only, which is far less than the experimental values. Flory¹² made a somewhat different approach and ignored the potential altogether, considering the system to be determined by the osmotic effects of the small mobile ions in the presence of bound charges of the polyelectrolytes. The equilibrium value of the expansion is then found by

minimizing the free energy of the system.

The first attempt to deduce the properties of polyelectrolyte solutions from a chain model for the polymer was due to Kuhn, Kunzle and Katchalsky¹³. These authors assumed that the probability of the various possible configurations of the chain depend only upon its end-to-end distance and calculated the electrostatic interaction between the different charges of the chain as a function of end-to-end distance. The two most unrealistic approximations of this random chain model are, first, the inclusion with undiminished statistical weight of all configurations of the polyion with the same end-to-end distance and second, the assumption that it is the total electrostatic interaction energy which is capable of causing the polyion to expand. Since each of these approximations materially overestimates the free energy available for producing expansion, the calculated values were far more greater than those actually obtained by experiments. However, Katchalsky and Lifson¹⁴ assumed that each fixed charge will build up in its vicinity an ion atmosphere similar to one which would exist in a simple salt solution with an ionic strength corresponding to the concentrations of the mobile ions in the polyelectrolyte solution. The potential at a distance r from a fixed charge was assumed to be given by the Debye-Huckel limiting law as $q \exp(-k r)/D r$, where k is the reciprocal of the equivalent thickness of the ion atmosphere. The electrostatic contribution per molecule to the free energy of the

solution was found as

$$F_0 = (\gamma)^2 \epsilon^2 / Dh \ln [1 + (\epsilon h / k h_0^2)]$$

where γ is the number of charged groups per molecule, ϵ is the unit of charge, D the dielectric constant, h the end-to-end distance of the charged molecule and h_0 the corresponding end-to-end distance in an uncharged reference state. The Katchalsky-Lifson treatment tends to overestimate the electrostatic contribution per macromolecule to the free energy of the solution, F_0 and this error should be largest for the smallest value of h so that the calculated driving force toward chain expansion is too high.

Harris and Rice¹⁵ and Rice and Harris¹⁶ had used a different model for the estimation of polyeion expansions. They considered an equivalent chain with the ionic charges carried by the monomer units concentrated at the mid points of each statistical chain element. The extension of the chain depended then on the probability distribution of the angles γ subtended by two adjoining chain elements. The electrostatic contribution to the free energy is then obtained as

$$F_\gamma = q^2 \exp \left[-k b_s \sin(\gamma/2) / D_0 b_s \sin \gamma/2 \right]$$

where b_s is the length for a statistical element and so the separation of two neighbouring charges is $b_s \sin(\gamma/2)$, D_0 is the effective dielectric constant, q is the unit of charge. It may be noted that Rice and Harris did not use here the

actual dielectric constant of water (~ 80) but an effective value D_e (~ 5.5) was considered. It was pointed out that the charges carried by polyions were in a region containing a high concentration of nonpolar organic material and that the high local concentration of ionic charges tended to disrupt the water structure. They also took into consideration the formation of ion pairs by some of the counter ions with the fixed charges of the polyion so that the charge of the polymeric chain substantially reduced at high charge densities. The calculated results followed closely to the physical behaviour of polyelectrolytes.

In all the theories discussed so far, (except Rice and Harris) the calculated values of the polyion volume were found much larger than those obtained experimentally. Nagasawa¹⁷ pointed out that the main reason for this discrepancy is the neglect of the electrostatic effect of the polyion on the counter ions i.e., the neglect of the activity coefficient of the counter ions. If the activity coefficient of the counter ions, determined experimentally, is introduced into the theories, the calculated expansions are found to correspond closely to the experimentally determined ones. The introduction of the counter ion activity coefficient is equivalent to the use of an effective charge density and hence to the introduction of the site binding model.

1.1.1 EXPERIMENTAL VERIFICATION FOR POLYION EXPANSION

The theoretically predicted chain expansion of polyions may be compared in principle, with estimates calculated from the frictional properties of polyelectrolyte solutions, particularly their viscosity or from the angular dependence of light scattering. In either case, the interpretation of the experimental data involves uncertainty unless simple salts are added to shield the charges of polyions. However, the expansion of polyelectrolyte molecules on ionization and their tighter coiling with increased electrolyte concentration has been confirmed from the light scattering and viscosity data obtained by Oth and Doty¹⁸. The intrinsic viscosity for poly(methacrylic acid) at different degrees of neutralization in the absence of neutral salt were determined from an extrapolation of the Fuoss's equation¹⁹. The root mean square end-to-end distance, $(r^2)^{1/2}$ was estimated by means of the Flory-Fox equation²⁰,

$$(r^2)^{3/2} = M[\eta]/\phi.$$

They were consistent with the values measured by the light scattering method. On the other hand, 60% neutralized poly(acrylic acid)²¹ measured in presence of 1.0 M and 0.1 M NaCl solution was found to give consistent values for (r_z) and (r_η) . The good agreement between values of (r_z) from light scattering measurements and values of (r_η) from viscosity measurements means that Flory-Fox equation which was originally derived for

neutral polymers can be used to treat polyelectrolytes provided the molecules are not highly expanded.

1.2 MOLECULAR WEIGHT OF POLYELECTROLYTES

Various types of complications due to ionizations are generally encountered for determination of the molecular weights of the polyelectrolytes. For this reason sometimes a polyelectrolyte is converted to a nonionized derivative and the molecular weight is estimated from the viscosity-molecular weight relationship for the derivative²².

Molecular weights of polyelectrolytes, however, can be measured by osmotic pressure in salt solution, provided the salt solutions are sufficiently concentrated to "swamp out" polyelectrolyte effects. The second virial coefficient A_2 in the semiempirical equation for the reduced osmotic pressure $\bar{\pi}/c = RT [1/\bar{M}_n + A_2c + A_3c^2 + \dots]$ where c is the polymer concentration and \bar{M}_n is the molecular weight or in the equation for the excess scattering intensity

$$Kc/R_\theta = 1/\bar{M}_w + 2A_2c + 3A_3c^2 + \dots,$$

where K is the optical constant and R_θ is the Rayleigh's ratio at zero angle, bears an intimate relationship to the sizes of the dissolved polymer molecule. Accordingly the slope of the plot of $\bar{\pi}/c$ versus c or Kc/R_θ versus c is independent of molecular weight (provided the molecular weight is high) and varies linearly and inversely with the concentration of the added salt. The osmotic behaviour observed by Pals and Hermans²³

and the light scattering behaviour observed by Trap and Hermans²⁴, and Orofino and Flory²⁵ for polyelectrolytes in various concentrations of added salt confirmed the same.

The theory of light scattering is based on the assumption that polymer molecules are largely independent of one another, but this no longer obtains when the polymer chain carry ionized groups, because of the electrostatic repulsions between like charges. Accordingly the distance of closest approach of two ionized molecules in solution is much greater than that of two molecules in the nonpolar solvents. This restriction imposes some degree of order on the distribution in space of charged molecules and therefore there is a decrease in the extent of concentration fluctuations. This in turn, increases the interference between the scattered radiation so that the scattering of systems of highly interacting molecules is always less than the theoretical value. The first observation of this effect were those of Guinand et al²⁶ who found that the intensity of the 90° scattering of polyacrylic acid fell on ionization to one-fiftieth of that of the unionized acid. This effect was also observed by Doty and Steiner²⁷ on solution of serum albumin hydrochloride, which exhibited a strong dissymmetry of light scattering although the dimension of this globular protein are only of the order of 40 \AA . In this case the phenomena reflects the interference of light scattered by different molecules and conclusions about the extension of the individual particle could be obtained only at dilutions which are too high for significant measurements. The situation is

much more favourable when the polyelectrolyte solution contains simple salts. Orofino and Flory²⁵ have shown that Zimm's double extrapolation procedure can then be used to estimate the radius of gyration of the polyion. However, when there is no added salt, or when the concentration of salt is low, Zimm plots for polyelectrolyte are not simple^{24,28}.

Polyelectrolyte solutions containing added salt are three component systems (polymer, solvent and salt) and as such contain nonhomogeneities that are not present in two component systems (polymer and solvent). These nonhomogeneities occur because the region of the solution immediately surrounding a polymer is richer in counter ions, and poorer in coions, than other parts of the solution. The concentration of the polyions fluctuates and the density of ions in the ionic atmosphere surrounding the polymers also fluctuates. These fluctuations of the ionic atmosphere are not taken into account in the classical theory of light scattering. However, when the salt concentrations are greater than 10^{-4} molar, the thickness of the ionic atmosphere is less than the wavelength of light and the classical theory of fluctuations is applicable to solutions of polyelectrolytes at such salt concentration. Light scattering measurements on solutions of polyelectrolytes diluted with salt solution in which the salt has the same chemical potential as it has in the polymer solution give correct values for molecular weights, but light scattering measurements on polyelectrolyte solutions diluted with salt solutions containing

the same concentration of salt as the polymer solutions give erroneous molecular weights²⁹.

Measurement of the molecular weight of polyelectrolytes by ultracentrifugation encounters difficulties similar to the difficulties encountered in the light scattering measurements. The attachment of ionic charges to a macromolecular particle results in a reduction of its sedimentation coefficient. This reduction may be minimized by the addition of simple salts to the polyelectrolyte solutions. When a polyelectrolyte solution is subjected to gravitational field of the ultracentrifuge, the small ions would tend to sediment much more slowly than the polyion. However, such a macroscopic separation of the polyion from its counter ions is not possible, the sedimenting polyion will necessarily have to pull its counter ions with it. If the polyion is a hydrodynamically impermeable coil, all ions which are located within the coil will be carried with it without any additional dissipation of energy by viscous friction. On the other hand counter ions which are outside the coil will add a relatively large term to the frictional coefficient of the polyelectrolyte and will thus lead to an appreciable decrease of the sedimentation rate. We may note that this effect should decrease with increasing salt concentration, since a polymer coil with the ions located in its interior becomes more nearly a Donnan system with vanishing net charge.

The theory of this phenomena was first formulated by Pedersen³⁰ who considered the sedimentation rate of the polyion

as the sum of two virtual motions, the first due to the gravitational field without consideration of electrostatic interactions and the second an electrophoretic flow caused by the electric field which is produced by the unequal sedimentation rate of the polyions and the small ions. In practice Pedersen has noted that the sedimentation constant when concentration approached to zero, for proteins bearing a net charge is always significantly smaller than it is at the isoelectric point. He ascribed this discrepancy to a swelling of the globular proteins but such swelling would have to be improbably large to explain this data.

In sedimentation, the driving force on the light counter ions is small and they retard the polyion, while in diffusion, the driving force is independent of particle size, so that the counter ions increase the driving force by a large factor than the frictional resistance to translation. Since the expansion of the polyions in salt free solutions of flexible chain polyelectrolytes increases sharply with the diffusion of the system, the frictional coefficient of these polyions is correspondingly increased. This effect and the increased electrophoretic effect cooperate in producing a diffusion coefficient which drops sharply as the polyelectrolyte concentration is reduced, instead of increasing slowly as with the uncharged polymers. A polyelectrolyte solution diffusing into a pure solvent tends, therefore to produce a front with an extremely high concentration gradient, frequently giving the appearance of the swelling of a crosslinked gel. A detailed investigation of this phenomenon has been reported by Nagasawa and Fujita³¹.

1.3 APPARENT MOLAL COMPRESSIBILITY AND APPARENT MOLAL VOLUME OF ELECTROLYTES

The study of a solution is frequently simplified by comparison with an idealized one. Generally thermodynamic properties such as molar volume, enthalpy or free energy of pure substances are considered functions of temperature and pressure, corresponding properties of components of solutions also depend on concentration. The total volume of n moles of pure substance of molar volume V is simply nV at fixed temperature and pressure, while that of a solution containing n_1 moles of first component, n_2 of the second, and so on, in general is not $n_1V_1 + n_2V_2 + \dots$. Two functions are useful in describing the behaviour of such a solution: the apparent molal property of the solute and the partial molal properties of solute and solvent. Apparent molal properties have the great advantage of being determined from a single measurement of a property of a solution and the same measurement of the pure solvent, and do not depend upon extrapolation from a series of experiments. One of the first of these functions to be defined and used was the apparent molal volume of the solute \bar{V}_2 given by the equation

$$\bar{V}_2 = (V - n_1V_1^0)/n_2 \quad \dots \quad (1)$$

Here V is the volume of solution containing n_1 moles of solvent and n_2 moles of solute, V_1^0 is the molal volume of the pure solvent. The apparent molal volume of the solute is obtained by subtracting the volume of the solvent from that of an amount

of solution containing one mole of solute. If the solution is ideal, the apparent molal volume of solute is the same as that of the pure substance. Any difference between these two quantities measures the deviation from the ideality arising from the interaction in the solution.

The apparent molal compressibility of the solute is defined by the equation

$$\beta \kappa_2 = (\beta V - n_1 \beta_1 V_1^0) / n_2 \quad \dots \quad (2)$$

where β and β_1 are, respectively, the compressibility of the solution and that of the pure solvent. Here $\beta V / n_2$ is the compression per unit of pressure, of an amount of solution containing one mole of solute, and $n_1 \beta_1 V_1^0 / n_2$ is the corresponding compression of the solvent, hence the physical significance of the apparent molal compressibility is like that of apparent molal volume.

In general, any apparent molal property of the solute may be defined by the equation

$$\beta G_2 = (G - n_1 G_1^0) / n_2 \quad \dots \quad (3)$$

where G is the extensive property of the solution and G_1^0 is the corresponding molal property of the solvent.

1.4 RELATION BETWEEN PARTIAL AND APPARENT MOLAL PROPERTIES

The partial molal properties of solute and solvent are given respectively by the equation,

541.64; 536.711 (043)
KAL

TH.54

$$\bar{G}_2 = \left(\frac{\partial G}{\partial n_2} \right)_{T, P, n_1} \quad \text{and} \quad \bar{G}_1 = \left(\frac{\partial G}{\partial n_1} \right)_{T, P, n_2} \quad \dots \quad (4)$$

The relationship between apparent and partial molal solute properties in a binary solution is obtained by changing the equation (3) defining ϕG_2 to the form

$$G = n_1 G_1^0 + n_2 \phi G_2 \quad \dots \quad (5)$$

Differentiating with respect to n_2 at constant T , P and n_1 yields,

$$\begin{aligned} \bar{G}_2 &= \left(\frac{\partial G}{\partial n_2} \right)_{T, P, n_1} = \phi G_2 + n_2 \left(\frac{\partial \phi G_2}{\partial n_2} \right)_{T, P, n_1} \\ &= \phi G_2 + n_2 \left(\frac{\partial \phi G_2}{\partial \ln m} \right) \quad \dots \quad (6) \end{aligned}$$

where m is the molality. Partial molal properties are easily obtained from the corresponding apparent molal ones when they are known as functions of the molarity. If they are expressed in terms of molarity, c , (moles of solute per litre of solution), the calculations are straightforward. In very dilute solutions, the relationship becomes

$$\bar{G}_2 = \phi G_2 + \left(\frac{\partial \phi G_2}{\partial \ln c} \right) \quad \dots \quad (7)$$

At infinite dilution \bar{G}_2 and ϕG_2 are equal.

The activity coefficients of many electrolytes have been determined in aqueous solutions, and are found to obey the limiting laws of the Debye-Huckel theory. Other properties of solutions related thermodynamically to the activity coefficient are the partial and apparent molal volume, compressibility and others. Considerable information is available for the said apparent molal properties of simple electrolytes³²⁻³⁷, but corresponding measurements for polyelectrolytes have not been made so far. In this thesis we report the studies of such properties of some polyelectrolytes.

The studies of polyelectrolytes seem to indicate that in aqueous solution, there are two types of solute-solvent interactions, namely the electrostrictional hydration by electric charges of gegeion or macroion i.e., charge effect and the hydrophobic structural enhancement or ice berg formation by the hydrophobic parts of the electrolytes i.e., the hydrophobic effect. Both electrostrictional effect and the hydrophobic effect have a large influence on the solution density and so also on the compressibility.

1.5 ELECTROSTRICTIONAL EFFECT

Electrostriction is usually defined in terms of the apparent decrease in the volume of ions when dissolved, an effect which originates from strong ion-solvent interaction. This decrease is largely the result of the polarization and attraction of surrounding solvent molecules by the ions. Mathematically it may be expressed as

$$\Delta V = V_{int} - \bar{V}$$

where V_{int} is the intrinsic or actual volume occupied by the salt in solution and \bar{V} is the partial molal volume. The quantity ΔV can be obtained from interpretations of experimental density measurements and more directly from compressibility and mobility measurements, but its theoretical prediction is much more difficult. The usual method of calculating the electrostriction is based on use of Born equation which gives the free energy of charging of ions in aqueous solution, by differentiation with respect to pressure, the change in volume associated with the presence of the ion is obtained. The most detailed treatment of this problem by this kind of approach has been given by Padova³⁸. The extent of solvent electrostriction which such calculations predict is far too large for some ions³⁹ e.g., $-200 \text{ ml}(\text{g ion})^{-1}$ for an ion of the size of Mg^{++} . The principal difficulty here is the use of a continuous integration to obtain the overall extent of electrostriction in the region where discreteness of solvent structure becomes significant.

Normal water is a tetrahedrally co-ordinated liquid having a large structural free volume³⁹. Thus cubically packed water molecules would have a volume of $\sim 12.5 \text{ ml/mole}$ compared with the observed value of 18.07 ml/mole at 25°C and 1 atmosphere. The main contribution to volume change associated with the presence of ions will be that arising from local collapse of the solvent structure, as pointed out by Bernal

and Fowler³⁹. Thus, in an ion-solvent complex, the actual size of the water molecules themselves hardly changes, but the spatial arrangement is modified.

1.6 HYDROPHOBIC EFFECT

When organic compounds containing non-polar residues are introduced into an aqueous solution, large positive deviations from ideality are observed. However, whereas poor solvent properties are normally caused by an unfavourable heat of mixing, the solution of materials such as aliphatic hydrocarbons in water has frequently been found to be exothermic. The poor solubility of nonpolar solutes in water is a consequence of a large negative excess entropy of mixing. Frank and Evans⁴⁰ pointed out that the negative heat of mixing, ΔH_M and negative excess entropy of mixing, ΔS_M^E may be rationalized by assuming that an ice like structure is stabilized in the neighbourhood of nonpolar solvents. Thus the heat evolved may be thought of as due to the latent heat of freezing of "ice bergs" which represent regions of crystalline order and whose formation therefore, leads to a loss of entropy. The tendency of nonpolar solutes aggregate in aqueous media reduces the number of water molecules in their immediate vicinity and leads to "ice berg melting". This provides the driving force towards such aggregation and has been referred to the hydrophobic bond. Frank and Evans⁴⁰ noted that the solution of nonpolar hydrocarbons in water leads generally to a volume contraction in contrast to the expansion observed

when water freezes to ice. They interpreted this discrepancy by assuming that ice bergs may be characterized by a structure which is more efficiently packed than the usual low pressure modification.

When a substance is dissolved in the aqueous medium, it contains not only nonpolar residues but also functional groups which may participate in hydrogen bonding; the situation becomes much more complex and is apparently governed to a considerable extent by geometric factors.

1.7 SOME GENERAL PROPERTIES OF ULTRASONICS

Ultrasonics provide a powerful tool for studying the characteristics of solutions and give valuable information concerning the coulombic interaction between ionogenic groups including their dissociation mechanism. Ultrasonic waves are qualitatively of the same nature as sound waves but they have frequencies higher than those which can be perceived by the human ear. Audible sound waves have frequencies which extend from about 20 c.p.s. to 20,000 cycles per second but the ultrasonic waves can extend to several million cycles per second.

Ultrasonic rays are subject to the laws of geometrical acoustics which are similar to those of geometrical optics. The rays can be reflected, refracted and focussed. The analogy between light and sound rays makes it possible to use the

latter for investigations of processes and phenomena inside optically opaque bodies just as we use light rays in transparent media. It is necessary that the media must be acoustically transparent i.e., absorption and scattering of sound in it is small. This requirement is satisfied by the majority of liquid, almost all metals, various types of ceramic material and a considerable number of plastics. Experimental investigation of the propagation and absorption of ultrasonic waves, the shear and bulk viscosity, and the diffusion coefficient, together provide an opportunity for studying intramolecular processes and the structure of matter. The discovery and investigation of dispersion regions and the anomalous absorption of ultrasonic waves have permitted specific heats, relaxation times and other important physico-chemical quantities to be determined. In recent years ultrasonic technique has been successfully applied in the field of flaw detection in materials, in working of brittle and hard materials, in the cleaning of components, in the facilitation of physico-chemical and technical processes and in the development and invention of ultrasonic based equipments such as power generators, transducers, flaw detectors, measuring equipments and others.

In the work reported in this thesis we are concerned with the study of properties of polymer materials in the solution state. The first step to study the solution properties by

ultrasonics is to determine the velocity in liquid medium. Since ultrasonic waves are smaller, velocity measurements may be carried out with a small amount of substance. Besides that the elaborate corrections which are necessary for larger waves are not required here. Recent development and invention of electronic measuring equipments have greatly helped in this direction. The chief importance of ultrasonic velocity measurements lies in rendering possible the determination of adiabatic compressibility of the medium. The compressibility, β , is defined as the decrease in volume, dv caused by the increase in pressure, dp per unit volume. If the volume is V , then $\beta = -1/V(dv/dp)$. In the liquid media, the pressure changes are so rapid (of the order of twenty thousand to several million times per second), that the in and out flow of heat in the surrounding medium is next to impossible and the compression takes place adiabatically.

The ultrasonic velocity measurements in solution gives us a correlation between compressibility and concentration by which many interesting questions in the theory of electrolytes may be elucidated. In electrolyte solutions a decrease in compressibility with increase in concentration is observed. This may be explained by the Debye's theory of electrolyte. The ions form an ionic atmosphere around it which exerts pressure ($\sim 10,000$ atmospheres) to the surrounding water molecules causing the compression. As ion concentration is increased, the pressure increases and causes further decrease of

compressibility. The Debye-Huckel limiting law predicts that the apparent molal compressibility of solutes $\phi\kappa_2$ is a linear function of the square root of concentration, $c^{1/2}$, in dilute solutions with the same limiting slope for all the salts of the same valency type. In fact, Gucker⁴¹ observed that the apparent molal compressibility of some electrolytes was linearly proportional to the square root of molar concentration i.e.,

$$\phi\kappa_2 = \phi\kappa_2^0 + (d\phi\kappa_2/dc^{1/2}) c^{1/2}$$

Previously most of the work on ultrasonic velocity study was confined to solutions of simple electrolytes which gave information about the structure of solutions as also about the fundamental properties of solutions such as adiabatic compressibility, ratio of specific heats, hydration number, free energy of activation, heat of reaction, activation energy, equilibrium constant, volume change and reaction rates of ionizations going on in solution. In addition to these, it also provided a method of examining implications of the Debye-Huckel interionic attraction theory as has been pointed above and Eucken's aggregate hypothesis. However, recently some work on sound velocity measurements in polymer solutions has been reported in the literature⁴²⁻⁴⁷ but it is confined mainly to the study of uncharged chain molecules in non-aqueous solvents. Apart from the work of Sohma⁴⁴ and lately of Roy-Chowdhury⁴⁸⁻⁵⁰ no systematic study of adiabatic compressibility in dilute aqueous solutions of polyelectrolytes seems to have been reported in the literature.

It is presumed that the molecular properties such as the chain extensions as well as the coulombic interactions of the charged groups in the chain may be related to the compressibility data obtained by sound velocity measurements. A study of adiabatic compressibility of some polyelectrolytes in aqueous solution has been reported in this thesis. In what follows a brief account of some experimental methods of sound velocity measurements.

1.8 EXPERIMENTAL METHODS OF ULTRASONIC VELOCITY MEASUREMENTS

Several methods and techniques have been proposed and used for ultrasonic velocity measurements in liquids which can be classified into three groups: (1) mechanical, (2) optical and (3) electrical. A brief description of some of the methods is given here.

1.8.1 MECHANICAL METHOD

The method first described by Kundt of measuring sound waves made visible by means of fine dust, may also be used in the case of ultrasonics, as long as the waves are not shorter than a few millimeters. Stationary sound waves may be made visible in liquids, if, as by Boyle and Lehmann⁵¹, powdered coke is used, which sinks slowly to the bottom of the liquid, and is driven by the ultrasonic waves to their nodes. A picture of the stationary waves on the bottom of the vessel is observed and its velocity is computed as the product of frequency and wavelength.

Radiation pressure measurements though useful for absorption measurements in liquids are not utilized in velocity measurements.

1.8.2 OPTICAL METHODS

Most optical measurements of ultrasonic velocity have been carried out by means of a method developed by Biquard⁵² based on Debye-Sears effect⁵³. In the Debye-Sears experiment, a light from a narrow slit traverses a beam of ultrasonic rays which is at right angles to the light beam. The light is then focussed on a screen. The successive compressions and rarefactions of the sound beam alter periodically the refractive index of the liquid. Thus the ultrasonic beam acts as a diffraction grating, and a series of parallel diffraction lines are produced on the screen. The greater the intensity of the ultrasonic beam, the more light is diffracted away from the main beam. The fringes are related to the wavelength of sound in the medium. A major disadvantage in this technique is the relatively large sound amplitudes required for sensitivity with the ensuing local heating of the liquid sample and a possible excitation of undesired modes. More recent observers have made improvements in the general techniques. Monochromatic light source and electron multiplier tube have been used so that much narrower light beams and lower acoustic intensities can be used.

1.8.3 ELECTRICAL METHODS

There are two general methods used to determine the ultrasonic velocity (a) Interferometric method and (b) Pulse method.

(a) Interferometric Method

In the basic interferometric method, basically a plane quartz crystal is used as a transducer. A plane reflector is set accurately parallel to the transducer at a distance which can be varied. If sound waves emanate from the transducer, they will be reflected from the reflecting surface. If the reflecting wave returning to the transducer is 180° out of phase with the signal emanating from the crystal, the disturbance at the transducer will be reduced essentially to zero. This will produce a considerable rise in the plate current of the output stage of the driving oscillator (or in the plate current in the tube). Since the problem is essentially one of standing waves, it is clear that a maximum in the plate current will be produced every time the reflector is moved a half-wave length. The velocity is the product of the frequency and wavelength in the medium. The interferometer technique is therefore of great importance in the measurement of the ultrasonic velocity.

Interferometric measurements may be vitiated by defects such as imperfect alignment of the crystal and the reflector plate, error in the precise calibration of the distance

measuring device and the sensitivity of the electronic detecting device. The design of the interferometer cell requires critical control of such factors as cell diameter and form, crystal size, crystal mounting, reflector diameter and crystal reflector separation. In the calculation of the apparent molal compressibility of solutes, the small difference in the compressibilities of the solution and the solvent is the crucial factor. Hence the accuracy in velocity measurements is of prime importance. Del Grosso *et al*⁵⁴ have given a critical discussion on the "Accuracy of ultrasonic interferometer velocity determination". Recently, a frequency modulated ultrasonic interferometer with visual demonstration of the off-balance of signals in an oscilloscope tube has been reported by Gucker *et al*⁵⁵. It has been reported that the standing wave positions could be determined with great accuracy with the above arrangement. We have built an ultrasonic interferometer for our study and this will be described later on.

(b) Pulse Method

Pulse methods usually consist of measuring the time of flight of a pulse by means of a calibrated time delay device on the sweep of a scope. The accuracy of the delay calibration, scope sensitivity and stability are important here, but the relatively large amplitude pulses required are considered to be another draw back because of the possibility of local heating of the liquid sample. The high amplitudes may excite undesired modes of crystal vibration. The selective attenuation

of the high frequency component of the pulse and the resultant distortion of the received pulse are additional sources of error. These difficulties were sufficient indicating not to warrant utilizing this method for precise measurements.

1.9 THE PRESENT INVESTIGATION

Our work is mainly confined to the adiabatic compressibility study of some polyelectrolytes such as poly(acrylic acid), a 1:1 copolymer of styrene and maleic acid and their partially and fully neutralized sodium salts and a few poly-ampholytes in aqueous solution. Since a cationic polymer, poly(4-vinyl N-n butylpyridinium bromide) was studied in this laboratory earlier along with other anionic polymers, we were prompted to make an extension of similar study of synthetic polyelectrolytes to copolymers carrying both anionic and cationic groups in the chain.

The interest in studying synthetic amphoteric polyelectrolytes has been stimulated for the last two decades due to the fact that these polymeric molecules are somewhat similar to many of the biologically important materials such as proteins. They carry 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 and with methacrylic acid which are soluble in aqueous solution. The ultraviolet absorption measurements indicate that these amphoteric polymers in excess KBr solution

absorb halide ions through the formation of charge transfer complex between the halogen ions and the appropriate functional group of the polymer molecule. However this effect is more prominently revealed in adiabatic compressibility data for methacrylic acid containing copolymer rather than in acrylic acid containing copolymer. Besides these two amphoteric polyelectrolytes, we have also studied polyacrylamide, an uncharged polyampholyte. The study of this polymer has been included here because of the fact that poly(acrylic acid) and polyacrylamide are structurally closely related polymers and both of them have functional groups in the monomer which can form a hydrogen bonded structure. Hence their study together may reveal some interesting information about the solution properties of charged and uncharged polymers of similar structure. The corresponding monomers for these two hydrogen bonding polymers have been studied to ascertain the contribution on compressibility data due to their assumption in chain like structure.

The ultrasonic velocity u in aqueous solution was measured using a precision ultrasonic interferometer and the density was measured with Ostwald-type pycnometers. The adiabatic compressibility β_s of the liquid, the apparent molal compressibility, βK_2 and the apparent molal volume ϕV_2 of solute have been computed from the density and velocity data.

The viscosity and the neutralization data for polyacids and polyampholytes were discussed and compared with the compressibility data.

CHAPTER

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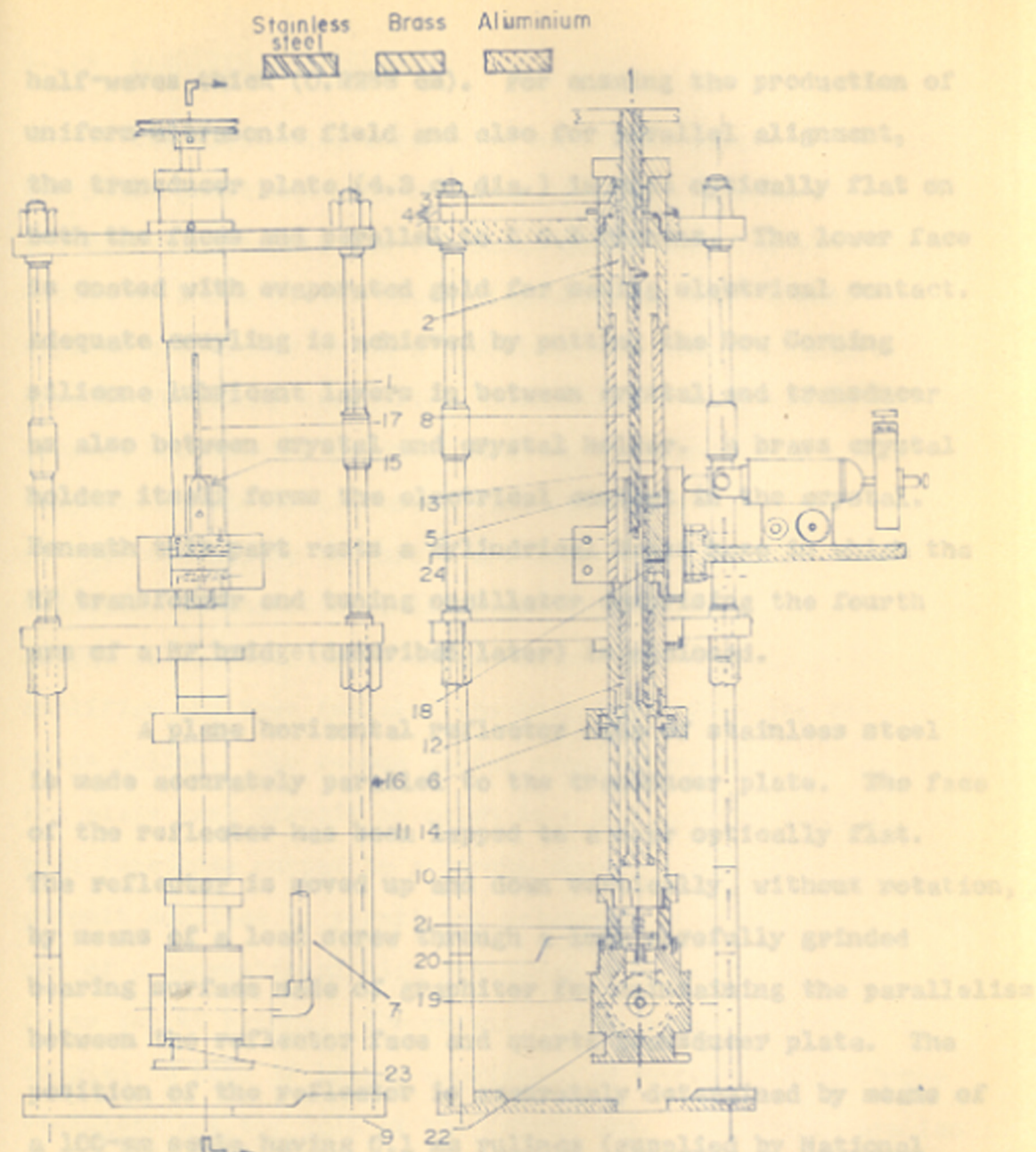
CHAPTER - II

CHAPTER - IIEXPERIMENTAL2.1 ULTRASONIC INTERFEROMETER

The ultrasonic velocities were determined by a precision ultrasonic interferometer⁵⁶ developed in this laboratory. The path length of the cell was varied by movement of a reflector and a fixed frequency of 5 MC/S was employed. The frequency stability of this instrument is $\pm 0.001\%$ (10 ppm) and the reflector position can be determined with an accuracy of ± 1 micron. The electric circuit is sensitive enough to detect the nodal positions with an accuracy of ± 1 micron travel of the reflector beyond the resonance position. No two values of sound velocity determined in this instrument for the same solution differed more than 0.05 m/sec.

2.1.1 INTERFEROMETER CELL

The interferometer cell consists of a stainless steel (Sandvik 10RE21) cylinder, 16 cm long and 3.5 cm in diameter, closed at the bottom by means of a quartz transmission plate below which is a 5-Mc X-cut quartz crystal driven by a suitable oscillator (Fig.2.1). For maximum transmission, the thickness of the transducer plate may be made equal to any integral number, n times of half wave length. The transducer used here is four



- 1 Reflector shaft housing 2 Rotating shaft with collar 3 Ball bearing 4 Thrust bearing
 5 Guide block for reflector shaft 6 Cell cap 7 Water-sealed tube for cable 8 Lead screw
 9 Triangular base 10 Transmission plate 11 Solution holder 12 Graphite bearing
 13 Threaded nut screwed into the reflector shaft 14 Reflector shaft 15 Scale holder
 16 Brass leg 17 Slot for scale travel 18 Guide strip for scale holder 19 Cell base
 20 Threaded bushing with insulation at the centre 21 Crystal holder 22 Brass window
 for electrical connection 23 Brass window for tuning the cell 24 Microscope holder

Fig 2-1 SCHEMATIC DIAGRAM OF THE INTERFEROMETER CELL

half-waves thick (0.2238 cm). For ensuring the production of uniform ultrasonic field and also for parallel alignment, the transducer plate (4.3 cm dia.) is made optically flat on both the faces and parallel to ± 2.5 microns. The lower face is coated with evaporated gold for making electrical contact. Adequate coupling is achieved by putting the Dow Corning silicone lubricant layers in between crystal and transducer as also between crystal and crystal holder. A brass crystal holder itself forms the electrical contact in the crystal. Beneath this part rests a cylindrical brass base in which the RF transformer and tuning oscillator comprising the fourth arm of a RF bridge (described later) is enclosed.

A plane horizontal reflector made of stainless steel is made accurately parallel to the transducer plate. The face of the reflector has been lapped to a near optically flat. The reflector is moved up and down vertically, without rotation, by means of a lead screw through a long carefully grinded bearing surface made of graphitor for maintaining the parallelism between the reflector face and quartz transducer plate. The position of the reflector is accurately determined by means of a 100-mm scale having 0.1 mm rulings (supplied by National Instruments Ltd., Calcutta), fastened to the reflector shaft with a scale holder. The scale is viewed through a microscope (magnification 100 times) fitted with a micrometer eyepiece (supplied by the Andhra Scientific Co., type AS-17161). The position of the reflector could be measured with this arrangement with an accuracy of ± 1 micron or better.

2.1.2 ELECTRICAL CIRCUITS

The electronic circuit is sensitive enough to detect the nodal positions with an accuracy of ± 1 micron travel of the reflector beyond the resonance position. The electronic system is shown on the block diagram (Fig.22). A colpitts crystal oscillator using a 6AU6 tube has been employed for greater frequency stability. However, the 5-Mc quartz crystal (Bharat Electronics product) used in the circuit is a non-temperature controlled unit. The stability characteristics of this oscillator circuit⁵⁷ are such that the frequency tolerance of the circuit is within the $\pm 0.001\%$ (10 ppm). The output of the oscillator is connected to a 2-stage buffer amplifier and thus isolates the oscillator from the circuits which follow. The second buffer stage drives a power amplifier, the plate tank circuit of which is a pie network coupling the high impedance output to a 52-ohm load. A Wheatstone bridge circuit modified to permit the detection of a null without the use of a conventional high frequency shielded transformer etc., forms the RF bridge. The output of the power amplifier is coupled to this RF bridge consisting of three matched 52-ohm resistors and the cell as the fourth arm. The fourth arm (cell) consists of a RF transformer, the primary of which when tuned, has an impedance of 52-Ohms. A movement of the reflector in the cell changes the impedance of this arm of the bridge. The unbalanced voltage at the opposite corners of the bridge is rectified and compared to the rectified and attenuated

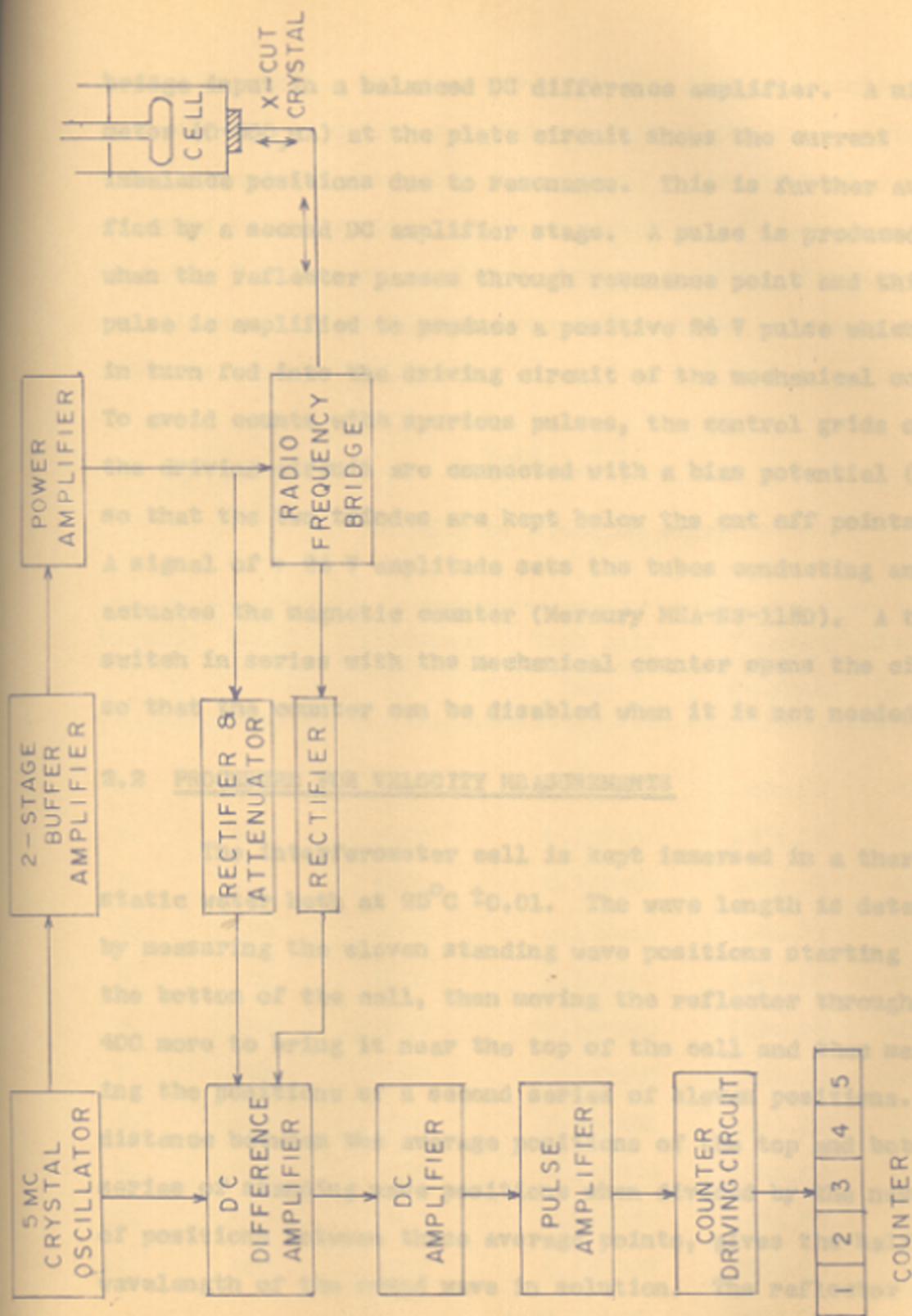


Fig 2.2 BLOCK DIAGRAM OF ULTRASONIC INTERFEROMETER

bridge input in a balanced DC difference amplifier. A micro-meter (0-500 μ A) at the plate circuit shows the current imbalance positions due to resonance. This is further amplified by a second DC amplifier stage. A pulse is produced when the reflector passes through resonance point and this pulse is amplified to produce a positive 24 V pulse which is in turn fed into the driving circuit of the mechanical counter. To avoid counts with spurious pulses, the control grids of the driving circuit are connected with a bias potential (-24V) so that the two triodes are kept below the cut off points. A signal of + 24 V amplitude sets the tubes conducting and actuates the magnetic counter (Mercury MEA-NS-115D). A toggle switch in series with the mechanical counter opens the circuit so that the counter can be disabled when it is not needed.

2.2 PROCEDURE FOR VELOCITY MEASUREMENTS

The interferometer cell is kept immersed in a thermostatic water bath at $25^{\circ}\text{C} \pm 0.01$. The wave length is determined by measuring the eleven standing wave positions starting from the bottom of the cell, then moving the reflector through about 400 more to bring it near the top of the cell and then measuring the positions of a second series of eleven positions. The distance between the average positions of the top and bottom series of standing wave positions when divided by the number of positions between these average points, gives the half wavelength of the sound wave in solution. The reflector was moved continuously in one direction with a view to minimizing

back-lash error. Two runs were made for each observation. The velocity (u) is computed as the product of the wavelength (λ) measured and the frequency (n), $u = n\lambda$. The typical results of sound velocity measurements in water at 25°C are summarized in Table 2.1. They are numbered chronologically, although the experiments were scattered among those on the solutions and not made consecutively.

Table 2.1

Velocity of sound in water

Experi- ment	Total counts	Frequency (KC/sec)	Mean half wavelengths (mm)	Velocity u (m./sec)	Deviation u (m./sec)
1.	410	5000	0.149607	1496.07	+0.02
2.	410	5000	0.149603	1496.03	-0.02
3.	410	5000	0.149608	1496.08	+0.03
4.	410	5000	0.149611	1496.11	+0.06
5.	410	5000	0.149607	1496.07	+0.02
6.	410	5000	0.149606	1496.06	+0.01
7.	410	5000	0.149610	1496.10	+0.04
8.	410	5000	0.149598	1495.98	-0.07
9.	410	5000	0.149604	1496.04	-0.01
10.	410	5000	0.149600	1496.00	-0.05
11.	410	5000	0.149598	1495.98	-0.07
			Mean value	1496.05,	= 0.044

From the mean value of the velocity, the deviation of the n individual experiments were determined and the standard deviation was calculated by the formula

$$\sigma = \left[\sum \Delta^2 / (n - m) \right]^{1/2}$$

where m is the number of parameter fitted, in this case, one, the mean value.

The velocity of sound in water as measured with this instrument is found to be 1496.05 ± 0.05 m./sec which is comparable with the recent published value 1496.55 m/sec.⁵⁵

2.3 DENSITY MEASUREMENTS

The density of each solution was determined as the mean of three measurements using 30 cc Ostwald-type pycnometers. They were filled carefully to avoid trapping of air bubbles, equilibrated for 20 minutes in a water thermostat at $25^\circ\text{C} \pm 0.01$, capped, washed, dried and equilibrated at room temperature to constant weight. The densities were calculated from the mass of the solution, and the volumes were obtained from the mass of pure solvent they held at 25°C and its density d (see Tables). All weighings were reduced to the vacuum standard.

2.4 COMPUTATION OF ADIABATIC COMPRESSIBILITY, APPARENT MOLAL VOLUME AND APPARENT MOLAL COMPRESSIBILITY OF POLYELECTROLYTES

The adiabatic compressibility β_s of liquid was calculated by the equation of Newton and Laplace,

$$\beta_s = (-\partial \ln V / \partial P)_s = 1/(u^2 d) \quad \dots (8)$$

Here V, P and S are volume, pressure and entropy respectively.

The apparent molal volume of solute, \bar{V}_2 and apparent molal compressibility of solute, \bar{K}_2 were computed by the following equations:

$$\bar{V}_2 = (M_2/d_1) [1 - (100/c)(d - d_1)] \quad \dots (9)$$

$$\bar{K}_2 = M_2 \beta_1 [(100/c)(\beta/\beta_1 - d/d_1)] + 1/d_1 \quad \dots (10)$$

Here M_2 represents the molecular weight of the monomer as well as the polymer repeat unit, c the concentration, expressed in grams per decilitre and d, d_1 , β and β_1 are the density and compressibility of the solution and solvent respectively.

The limiting values of apparent molal compressibility, \bar{K}_2^0 and apparent molal volume, \bar{V}_2^0 of solute in aqueous solution at 25°C were determined by extrapolation of \bar{K}_2 and \bar{V}_2 versus concentration curves to infinite dilution.

2.5 PREPARATION AND PURIFICATION OF POLYELECTROLYTES

2.5.1 POLYACIDS

2.5.1.1 POLY(ACRYLIC ACID)

Poly(acrylic acid), (PAA) was prepared by polymerising freshly distilled monomer (30% w/w), (Fluka AG, Switzerland) in dioxane solution using 0.5% benzoyl peroxide as initiator

at 55°C with constant stirring in nitrogen atmosphere. The product was dissolved in methanol, precipitated with ether and dried in vacuo to constant weight. The unfractionated sample was used for adiabatic compressibility measurements and its molecular weight was found to be 1.504×10^4 . This was computed from the intrinsic viscosity data (1.130 dl/gm), (see Fig.2.3) of the sodium salt in 1.0 M NaCl solution employing the relation⁵⁸

$$[\eta] = 15.47 \times 10^{-5} \bar{M}_v^{0.90}$$

Poly(sodium acrylate) solutions, (PSA) with different degree (25% and 100%) of neutralized products were prepared by adding calculated amounts of sodium hydroxide to the polyacid.

2.5.12 COPOLYMER OF STYRENE AND MALEIC ACID

A 1:1 copolymer of styrene and maleic anhydride was obtained from Dr. V.M. Joshi of this laboratory. It was treated with excess strong ammonia solution (five equivalents) and stirred for one day at room temperature. The clear solution (14% polymer) was filtered and precipitated with absolute alcohol. The ammonium salt of the hydrolysed copolymer was converted to the corresponding acid copolymer by neutralizing it with hydrochloric acid and reprecipitating the acid copolymer from the solution with absolute alcohol. The product was washed several times with absolute alcohol and dried in vacuo to constant weight.

It was assumed that the repeat unit of the styrene-maleic acid copolymer (SY-MA) contained approximately one residue of maleic acid and one of styrene. The average molecular weight of the repeat unit of the acid copolymer as determined by employing the nonaqueous titration technique given by Fritz and Lisicki⁵⁹ was 239 (see Table 2.2). The acid copolymer was dissolved in dimethyl formamide and titrated with sodium methoxide using thymol blue as an indicator. Sodium methoxide was standardized in turn against benzoic acid dissolved in benzene-methanol mixture (3:1).

The sodium salts of the acid copolymer (i.e. Styrene-sodium maleiate copolymer (SY-SMA) with different degrees of neutralization (50% and 100%) were obtained by neutralizing the acid copolymer with calculated amount of sodium hydroxide.

2.5.2 POLYAMPHOLYTES

2.5.21 POLYACRYLAMIDE

Polyacrylamide, (PAAM) was prepared by polymerizing the monomer (10% solution), (Fluka AG, Switzerland) in ethanol solution using azo-bis-isobutyronitrile (0.5%) as initiator at 60°C with constant stirring and bubbling nitrogen throughout. The polymer came out as a precipitate, was washed with fresh alcohol several times and dried in vacuo over P_2O_5 to constant weight. This polymer was very hygroscopic. The molecular weight of the polymer was found to be 2.423×10^4 as computed from the intrinsic viscosity data (0.203 dl/gm) obtained in

aqueous solution at 25°C (Fig. 2.6) employing the relation⁶⁰

$$[\eta] = 6.31 \times 10^{-5} \times \bar{M}_v^{0.80}$$

2.5.22 SYNTHESIS AND PURIFICATION OF AMPHOTERIC POLYELECTROLYTES

(a) Acrylic acid-4-vinyl Pyridine (AA-ViPy) Copolymer

This copolymer was prepared by bulk polymerization of a mixture of freshly distilled monomers of Acrylic acid (50 mole % in monomer) and 4-vinyl pyridine (Koch-Light Laboratories, England) without initiator at 55°C with constant stirring and bubbling with nitrogen for one hour. The reaction was very vigorous and the product left after the reaction was a hard solid mass. This was dissolved in a small amount of benzene-methyl alcohol mixture (40:60) and precipitated with large excess of ethyl acetate and finally dried in vacuo to constant weight. The conversion into polymer was about 82.5%. This copolymer was very hygroscopic.

(b) Methacrylic acid-4-vinyl pyridine (MAA-ViPy) copolymer

This copolymer was prepared in the similar way by bulk polymerization of freshly distilled monomers of methacrylic acid (50 mole % in monomer) and 4-vinyl pyridine by treatment with 0.1% azo-bis-isobutyronitrile at 70°C with constant stirring and bubbling with nitrogen for 6 hours. 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 4-vinyl pyridine groups in the two copolymers were further converted into stronger base by quaternization.

2.5.3 QUATERNIZATION OF THE COPOLYMERS

The pyridine groups of the two copolymers of 4-vinyl pyridine with acrylic acid and methacrylic acid, were quaternized separately with n-butyl bromide by the method of Fuoss and Edelson⁶¹. 16 grams of the fine powder of each copolymer was suspended separately in dimethylformamide (400 cc) and treated with excess (9.65 moles) of n-butyl bromide. The mixture was stirred for 50 hours 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 then precipitated with dioxane. The product was further purified by redissolving in absolute alcohol and precipitating with dry dioxane and finally dried to constant weight. The two amphoteric polyelectrolytes thus obtained were acrylic acid-4-vinyl N-n butylpyridinium bromide (AA-ViBuPyBr) copolymer and methacrylic acid-4-vinyl N-n butylpyridinium bromide (MAA-ViBuPyBr) copolymer.

2.6 DETERMINATION OF THE COMPOSITION OF THE AMPHOTERIC POLYELECTROLYTES

The composition i.e., the molecular weight (or equivalent weight) of the repeat unit of each of the amphoteric polyelectrolytes were determined in the following way:

Electrometric titration permits us the calculation of the number of equivalents of acid or base bound per gram of the copolymer as a function of the pH. The maximum acid or base bound at the extremes of high or low pH would be equal to the number of acid (i.e., acrylic or methacrylic acid) or base (i.e., 4-vinyl N-n butylpyridinium bromide) groups in the copolymer. Since it was not possible to locate the end point sharply at low pH region, where the copolymers were titrated against 0.5 N acid, the method for estimation of base was changed. Two methods were tried, namely the determination of nitrogen content by the Kjeldahl method and the estimation of bromide ions potentiometrically. However, the estimation of nitrogen proved to be erratic and so a simple potentiometric method employing a silver wire as one electrode and a glass electrode as another, was used to estimate the bromide ions⁶² in the amphoteric polyelectrolytes. The copolymers in aqueous solution were titrated against 0.1 M silver nitrate solution and a sharp break accompanied with polarity reversal characterized the end point. The silver nitrate solution in turn was standardized by titration against KBr (B.D.H., Analar) solution potentiometrically in the similar way. As usual, the acid groups were estimated pH-metrically with 0.1 N NaOH. The equivalent weight of the copolymers as obtained by the bromide ions (base group) estimation and by acid group estimation are given in Table 2.2. Comparing the two equivalent weights thus obtained for each amphoteric polyelectrolyte, it was found that the ratios of acid to base group in the polymer chain were

TABLE 2.2

COMPOSITION OF THE COPOLYMERS: EQUIVALENT WEIGHT OR
THE AVERAGE MOLECULAR WEIGHT OF THE COPOLYMER
REPEAT UNIT

Copolymer	cc of C.1 N NaOH consumed per gram of copolymer	Equi. wt. determined on the basis of acid group analysis	cc of 0.1 M AgNO ₃ soln. consumed per gram of copolymer	Equi. wt. determin- ed on the basis of acid group analysis	Ratio of acid to base group in the copolymer
Styrene-maleic acid (SY-MA) copolymer	33.6 ^a	239	-	-	-
Acrylic acid- 4-vinyl N-n butyl pyridinium bromide (AA-ViBuPyBr) copolymer	10.6	943	38.1	262	1:3.6
Methacrylic acid- 4-vinyl N-n butyl pyridinium bromide (MAA-ViBuPyBr) copolymer	6.9	1449	38.8	258	1:5.6

^a Sodium methoxide was used in the nonaqueous titration and the calculation is based on 2 equivalents of alkali used for complete neutralization.

1:3.6 and 1:5.6 for acrylic acid and methacrylic acid containing amphoteric polyelectrolytes respectively.

All calculations regarding the compressibilities and apparent molal properties of amphoteric polyelectrolytes were made taking the equivalent weight determined by the base group analysis. However, the values determined by the acid group analysis may be obtained by multiplying these values with the corresponding ratio of acid to base groups in the polymeric chain.

2.7 PURIFICATION OF SOLVENTS AND PREPARATION OF SOLUTIONS

Double distilled water, degassed by boiling so as to prevent formation of air bubbles in the pycnometers and on the interferometer transducer or reflector was used for the preparation of all solutions. The acid polymers did not dissolve easily and so they were left for several days, to give clear solutions. All solutions were filtered before use and the concentrations were checked by weighing the residue from evaporation. All dilutions were made from the stock solutions by volumetric additions of solvents.

2.8 VISCOSITY MEASUREMENTS

The viscosity measurements for polyelectrolyte solutions were done with two Ubbelohde dilution viscometers. The flow times of water were 66.0 and 234.5 seconds respectively. Highly viscous solutions were measured with the fast

flowing viscometer, and the viscosity, η at 25°C was determined by using the equation

$$\eta = A t - B/t$$

where A and B are two constants and t is the flow time in seconds. The values of constants A and B for this viscometer were determined as 0.016687 and 13.7044 respectively with the help of pure liquids such as pure water and glycerene of known viscosity at 25°C. For the other viscometer, no kinetic energy correction was made as the flow time of solvent was more than 200 seconds. The temperature was controlled by immersing the viscometer in a water thermostat maintained at $25 \pm 0.01^\circ\text{C}$. The data were plotted as reduced viscosity η_{sp}/c versus concentration and extrapolated to infinite dilution where permitted (Figs. 2.3 to 2.7).

The reduced viscosity versus concentration curves for poly(acrylic acid) and its fully neutralized sodium salt in aqueous solution are shown in Figure 2.3. At higher concentrations, the polyelectrolyte showed a normal dependence of reduced viscosity on concentration, whereas at very low ionic strength, strange curvatures were observed (curves 1 and 2). The abnormal decrease of reduced viscosity with increasing concentration is well known and is due to the coiling of the polymer chain effected by the counter ions. The more dilute the solution is, the less is the influence of the counter ions through the repulsive effect of the charged segments of

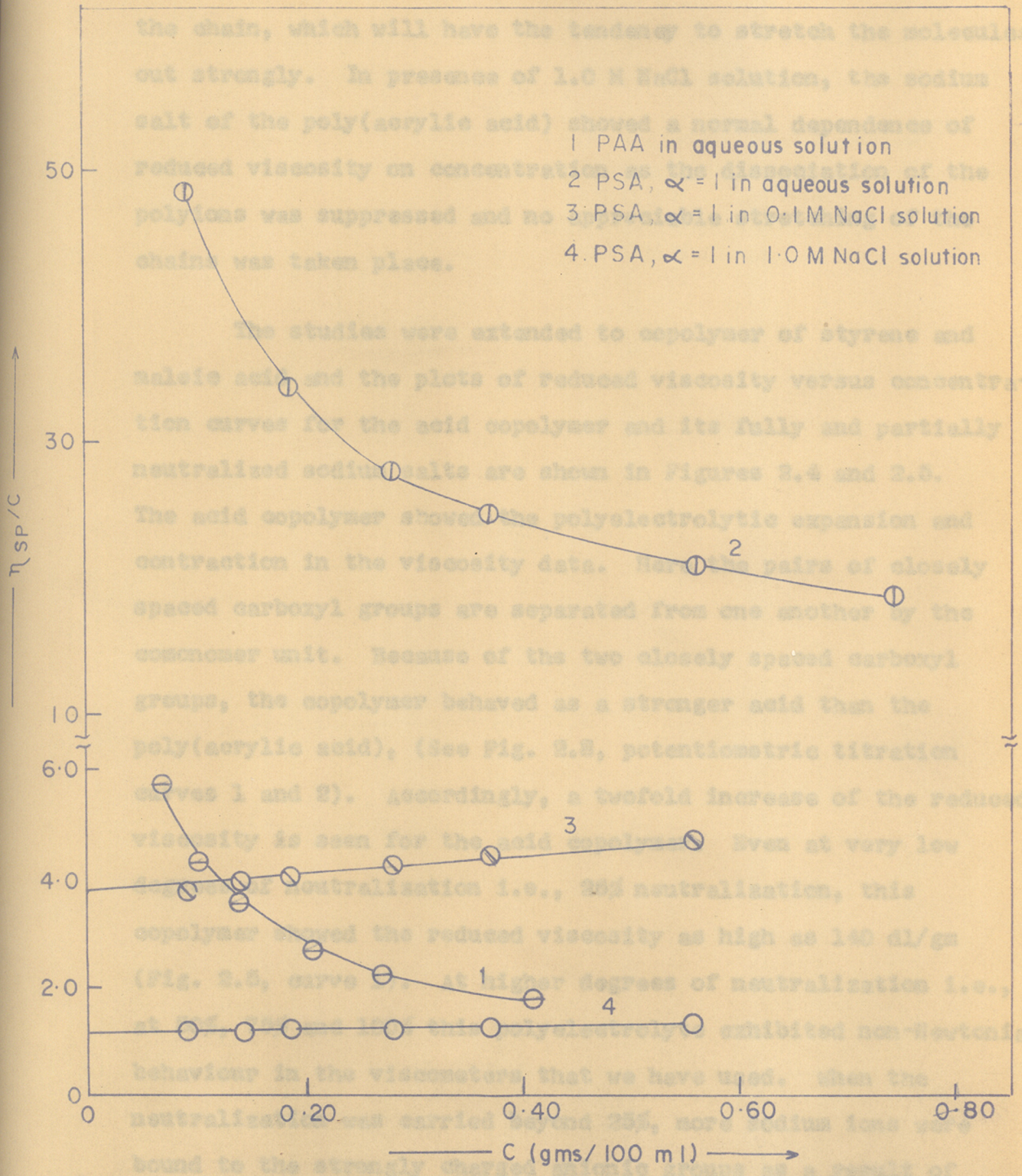


Fig 2-3. PLOTS OF REDUCED VISCOSITY Vs. CONCENTRATION (POLYACRYLIC ACID)

the chain, which will have the tendency to stretch the molecules out strongly. In presence of 1.0 M NaCl solution, the sodium salt of the poly(acrylic acid) showed a normal dependence of reduced viscosity on concentration as the dissociation of the polyions was suppressed and no appreciable stretching of the chains was taken place.

The studies were extended to copolymer of styrene and maleic acid and the plots of reduced viscosity versus concentration curves for the acid copolymer and its fully and partially neutralized sodium salts are shown in Figures 2.4 and 2.5. The acid copolymer showed the polyelectrolytic expansion and contraction in the viscosity data. Here the pairs of closely spaced carboxyl groups are separated from one another by the comonomer unit. Because of the two closely spaced carboxyl groups, the copolymer behaved as a stronger acid than the poly(acrylic acid), (See Fig. 2.8, potentiometric titration curves 1 and 2). Accordingly, a twofold increase of the reduced viscosity is seen for the acid copolymer. Even at very low degrees of neutralization i.e., 25% neutralization, this copolymer showed the reduced viscosity as high as 140 dl/gm (Fig. 2.5, curve 1). At higher degrees of neutralization i.e., at 50%, 75% and 100% this polyelectrolyte exhibited non-Newtonian behaviour in the viscometers that we have used. When the neutralization was carried beyond 25%, more sodium ions were bound to the strongly charged anionic groups as a result of which the charge effect in the chain was reduced more and more

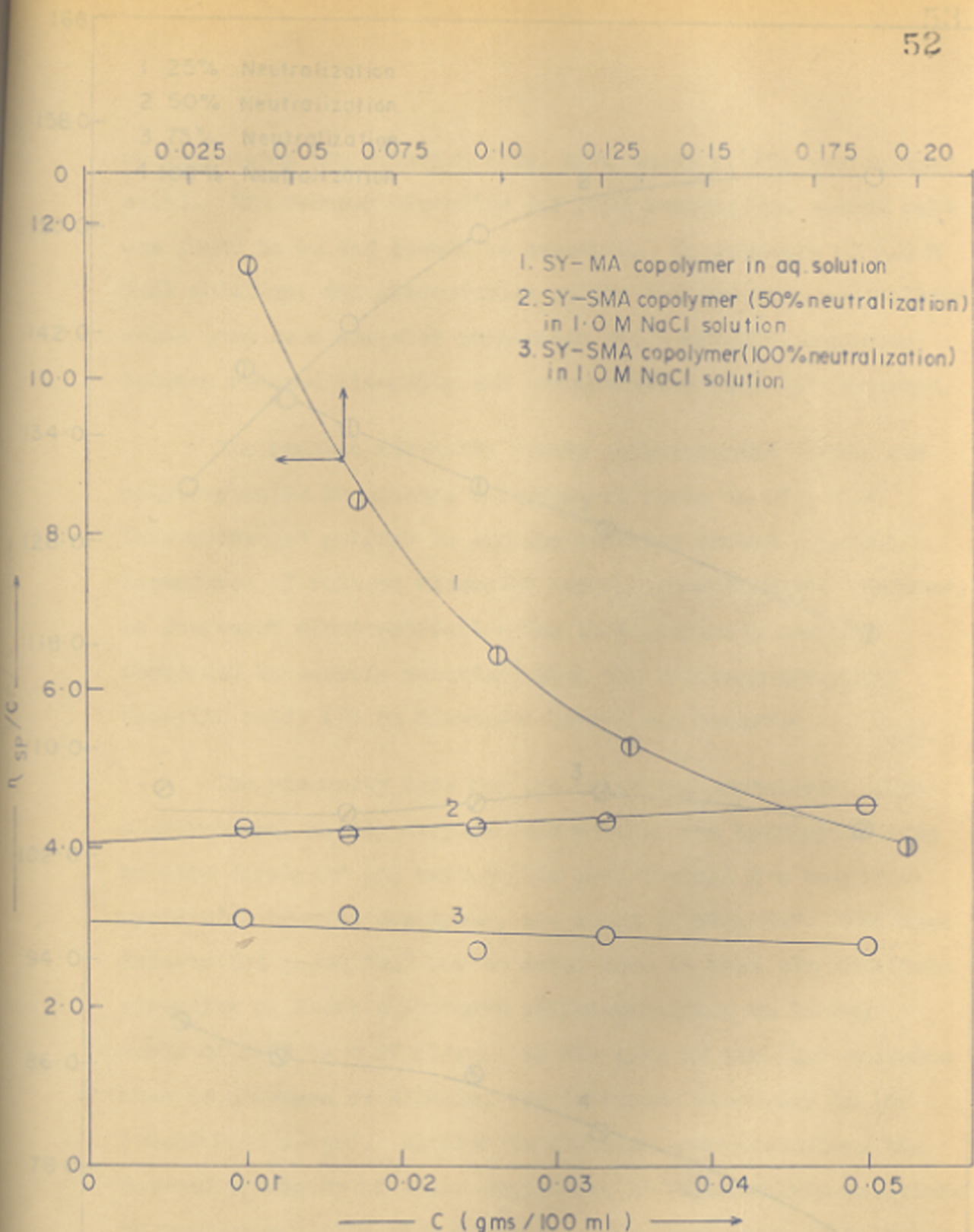


Fig 2.4 PLOTS OF REDUCED VISCOSITY Vs. CONCENTRATION (STYRENE-MALEIC ACID COPOLYMER)

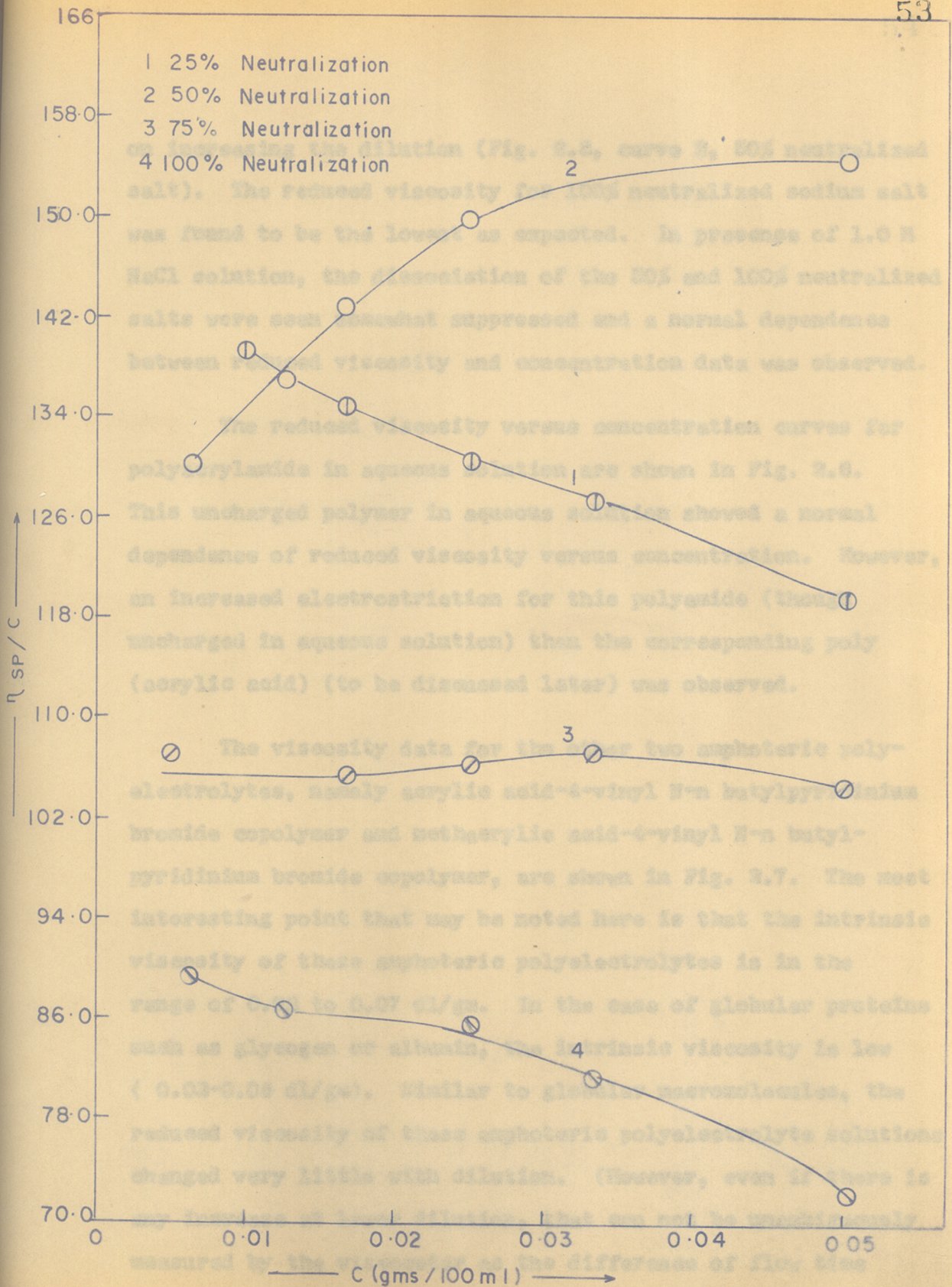


Fig 2-5 PLOTS OF REDUCED VISCOSITY vs. CONCENTRATION (SODIUM SALTS OF STYRENE-MALEIC ACID COPOLYMER IN AQUEOUS SOLUTION)

on increasing the dilution (Fig. 2.5, curve 2, 50% neutralized salt). The reduced viscosity for 100% neutralized sodium salt was found to be the lowest as expected. In presence of 1.0 M NaCl solution, the dissociation of the 50% and 100% neutralized salts were seen somewhat suppressed and a normal dependence between reduced viscosity and concentration data was observed.

The reduced viscosity versus concentration curves for polyacrylamide in aqueous solution are shown in Fig. 2.6. This uncharged polymer in aqueous solution showed a normal dependence of reduced viscosity versus concentration. However, an increased electrostriction for this polyamide (though uncharged in aqueous solution) than the corresponding poly (acrylic acid) (to be discussed later) was observed.

The viscosity data for the other two amphoteric polyelectrolytes, namely acrylic acid-4-vinyl N-n butylpyridinium bromide copolymer and methacrylic acid-4-vinyl N-n butylpyridinium bromide copolymer, are shown in Fig. 2.7. The most interesting point that may be noted here is that the intrinsic viscosity of these amphoteric polyelectrolytes is in the range of 0.03 to 0.07 dl/ga. In the case of globular proteins such as glycogen or albumin, the intrinsic viscosity is low (0.03-0.06 dl/ga). Similar to globular macromolecules, the reduced viscosity of these amphoteric polyelectrolyte solutions changed very little with dilution. (However, even if there is any increase at lower dilution, that can not be unambiguously measured by the viscometer as the difference of flow time

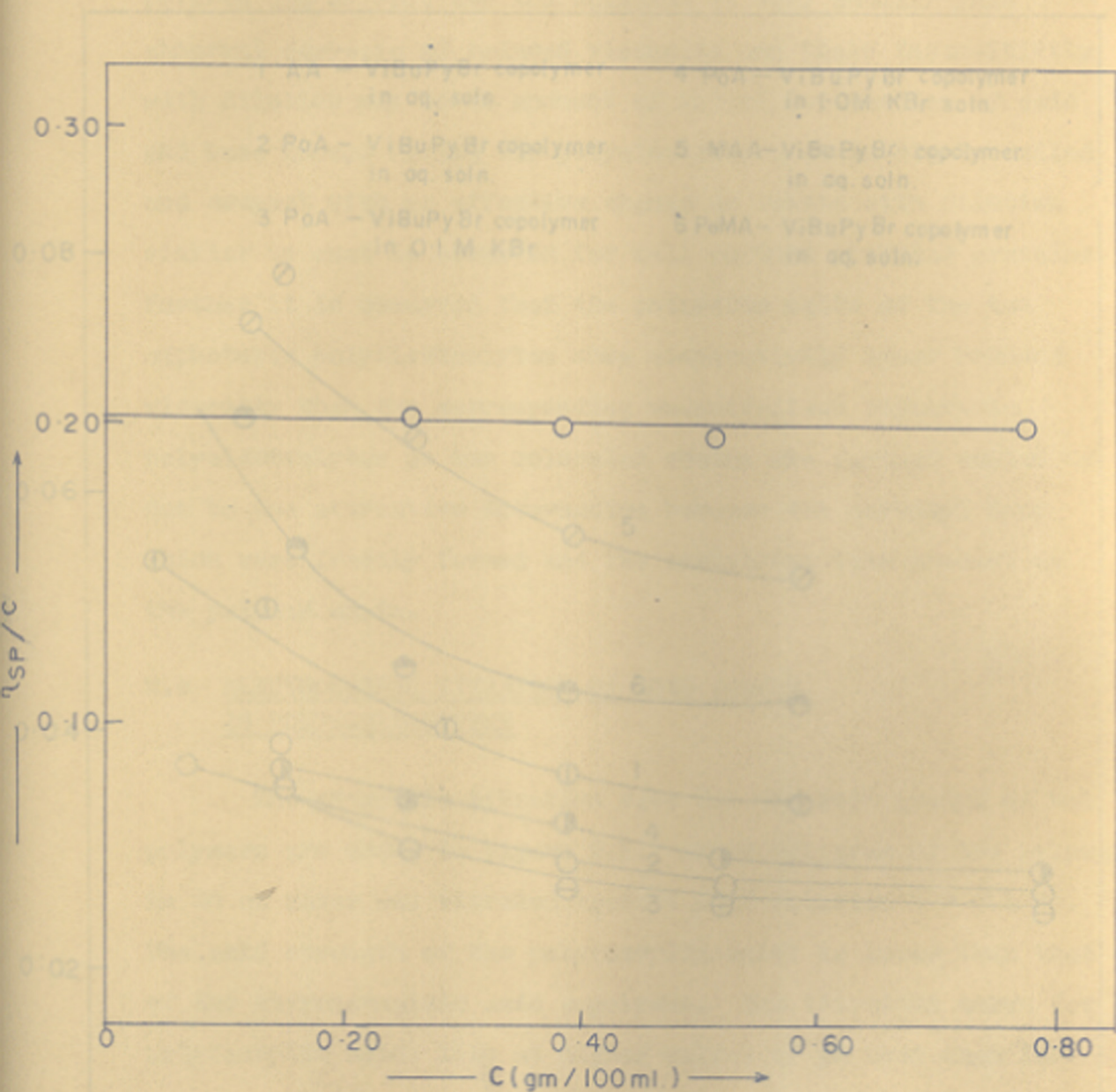


Fig2.6 INTRINSIC VISCOSITY OF POLYACRYLAMIDE IN AQUEOUS SOLUTION

FIG. 2. PLOTS OF REDUCED VISCOSITY VS. CONCENTRATION (POLYAMPHOLYTES)

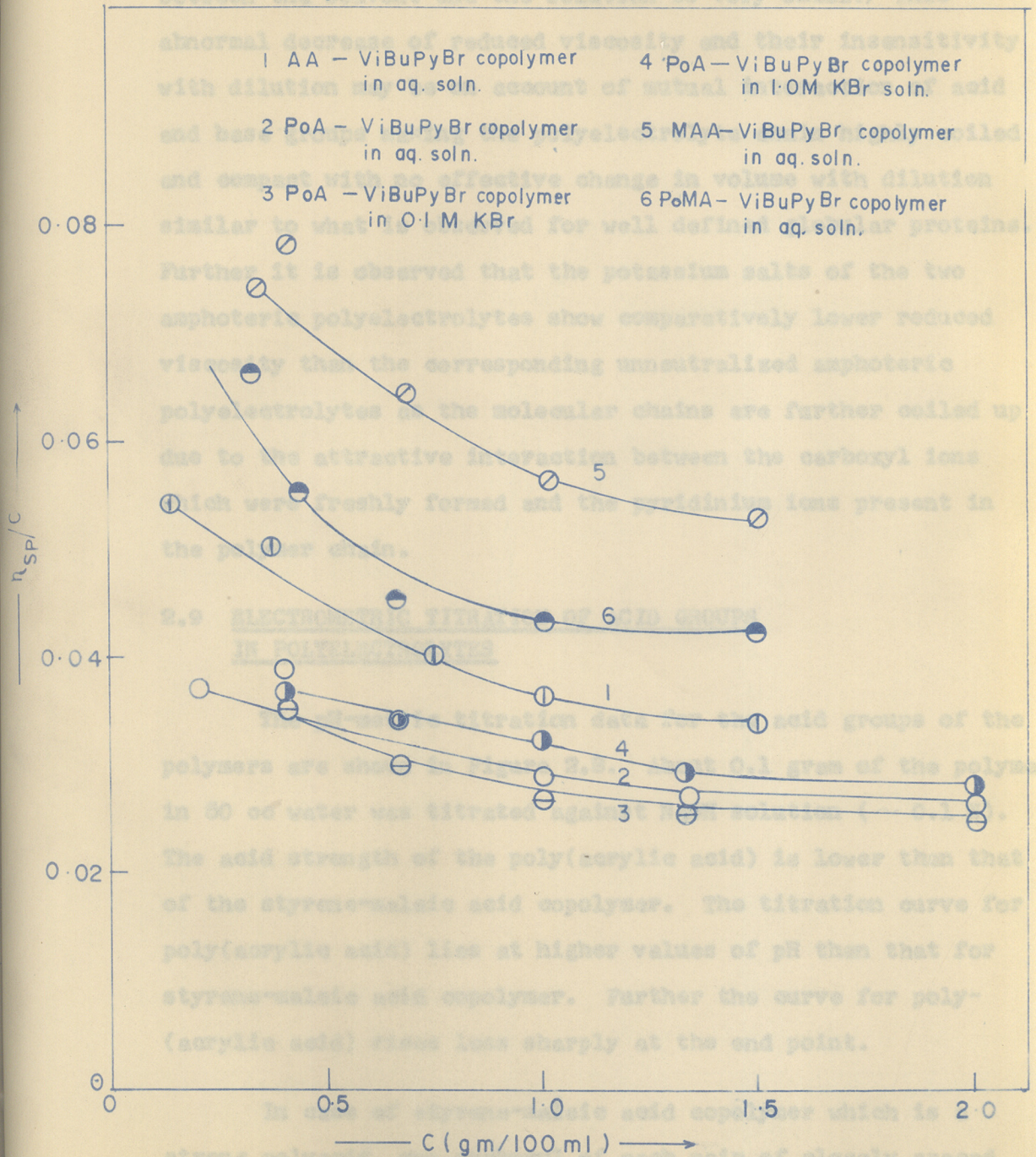


Fig.2.7 PLOTS OF REDUCED VISCOSITY Vs. CONCENTRATION (POLYAMPHOLYTES)

between the solvent and the solution is very small.) This abnormal decrease of reduced viscosity and their insensitivity with dilution may be on account of 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 what is observed for well defined globular proteins. Further it is observed that the potassium salts of the two amphoteric polyelectrolytes show comparatively lower reduced viscosity than the corresponding unneutralized amphoteric polyelectrolytes as the molecular chains are further coiled up due to the attractive interaction between the carboxyl ions which were freshly formed and the pyridinium ions present in the polymer chain.

2.9 ELECTROMETRIC TITRATION OF ACID GROUPS IN POLYELECTROLYTES

The pH-metric titration data for the acid groups of the polymers are shown in Figure 2.8. About 0.1 gram of the polymer in 50 cc water was titrated against NaOH solution (\sim 0.1 N). The acid strength of the poly(acrylic acid) is lower than that of the styrene-maleic acid copolymer. The titration curve for poly(acrylic acid) lies at higher values of pH than that for styrene-maleic acid copolymer. Further the curve for poly-(acrylic acid) rises less sharply at the end point.

In case of styrene-maleic acid copolymer which is a strong polyacid, one carboxyl of each pair of closely spaced carboxyl groups ionized relatively easily. However, when the

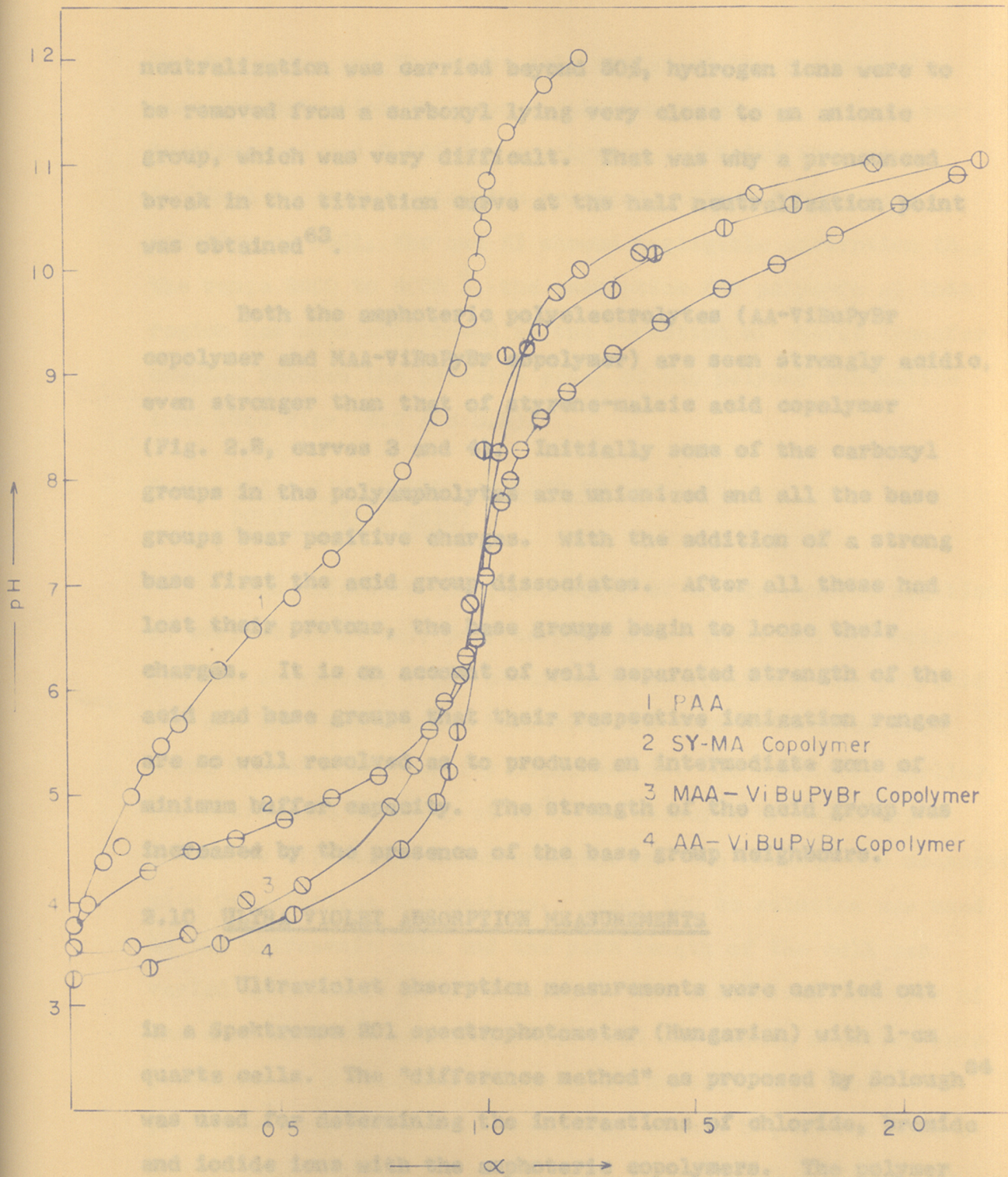


Fig. 2.8 pH METRIC TITRATIONS

neutralization was carried beyond 50%, hydrogen ions were to be removed from a carboxyl lying very close to an anionic group, which was very difficult. That was why a pronounced break in the titration curve at the half neutralization point was obtained⁶³.

Both the amphoteric polyelectrolytes (AA-ViBuPyBr copolymer and MAA-ViBuPyBr copolymer) are seen strongly acidic, even stronger than that of styrene-maleic acid copolymer (Fig. 2.8, curves 3 and 4). Initially some of the carboxyl groups in the polyampholytes are unionized and all the base groups bear positive charges. With the addition of a strong base first the acid group dissociates. After all these had lost their protons, the base groups begin to lose their charges. It is on account of well separated strength of the acid and base groups that their respective ionization ranges are so well resolved as to produce an intermediate zone of minimum buffer capacity. The strength of the acid group was increased by the presence of the base group neighbours.

2.10 ULTRA VIOLET ABSORPTION MEASUREMENTS

Ultraviolet absorption measurements were carried out in a Spektromom 201 spectrophotometer (Hungarian) with 1-cm quartz cells. The "difference method" as proposed by Solough⁶⁴ was used for determining the interactions of chloride, bromide and iodide ions with the amphoteric copolymers. The polymer solution in presence of chloride (1.0 M NaCl), bromide (1.0 M KBr) or iodide (0.001 M or 0.01 M KI) ions was kept in one of

the two cells and the other cell contained the polymer of same concentration in aqueous solution as blank. The concentration used was 0.02% for copolymers and 0.01% for poly-(4-vinyl N-n butylpyridinium bromide). Since the aqueous solution of NaCl, KBr and KI showed negligible absorption in the range 2600 to 4000 \AA , the absorption for polymers at this region has been attributed to the formation of charge transfer complex between the pyridine group of the polymer and halide ions (See Figs. 3.7 and 3.8).

2.11 ADIABATIC COMPRESSIBILITY OF POLY(ACRYLIC ACID)

The adiabatic compressibility of dilute aqueous solutions of acrylic acid (AA), poly(acrylic acid) (PAA) and two poly-(sodium acrylates) (PSA) obtained by neutralizing the polyacid 25% and 100% with sodium hydroxide has been determined from sound velocity and density measurements. So mentioned earlier, the ultrasonic velocity at 25°C was measured by employing a precision ultrasonic interferometer and the density was measured with Ostwald-type pycnometers. About 100 cc solution was used in the ultrasonic cell and the path length of the cell was varied by movement of a reflector. The electrical reaction of the cell upon the oscillator was used for fixing standing wave positions at a standard frequency (5 MC/Sec), and their positions were determined accurately within ± 1 micron with a 100-mm scale having 0.1 mm rulings, fitted with a microscope and a micrometer eyepiece. The cell was kept immersed in a

thermostatic water bath at $25 \pm 0.01^\circ\text{C}$. The measured half wavelengths were averaged out from about 410 counts for each experiment. Two measurements of the wavelengths of sound were made in each instance, and the velocity of sound in solvent and solutions was computed as the product of frequency n and wavelength λ . The two values of sound velocity agreed within 0.05 m/sec with no appreciable systematic difference between them.

The density of each solution was determined as the mean of three measurements by 30 cc pycnometers, and the agreement between the measurements was ± 0.00002 or better. The results of adiabatic compressibility measurements are summarized in Tables 2.3 to 2.8.

2.12 ADIABATIC COMPRESSIBILITY OF STYRENE-MALEIC ACID COPOLYMER

The adiabatic compressibility of a 1:1 copolymer of styrene and maleic acid and of its two, 50% and 100% neutralized, sodium salts was determined in the same way as described earlier. Since the acid copolymer was not much soluble, more than 1% solution was found difficult to prepare. The acid copolymer was left in the solvent for several days to dissolve. Because of the very high viscosity of the sodium salt solutions, the adiabatic compressibility measurements for this case were also limited to 1% concentration. The results of adiabatic compressibility measurements are given in Tables 2.9 to 2.13.

TABLE 2.3

SUMMARY OF RESULTS FOR ACRYLIC ACID IN AQUEOUS SOLUTION

AT 25°C ($M_2 = 72.06$)

c g/dl	d gm/cc	ρV_2 cc/mole	u m/sec	$\beta \times 10^6$ bar ⁻¹	$\frac{\beta}{c} - \beta \times 10^7$	$VK_2 \times 10^4$ cc/bar/mole
0.0000	0.99705	61.7 ^a	1496.05	44.812	-	6.0 ^a
0.1028	0.99720	61.7	1496.42	44.783	2.8	7.3
0.2056	0.99735	61.7	1496.84	44.751	2.9	6.3
0.3084	0.99750	61.7	1497.30	44.717	3.1	5.5
0.4112	0.99765	61.7	1497.63	44.690	2.9	6.4
0.5140	0.99778	62.0	1498.04	44.660	2.9	6.5
0.7457	0.99810	61.8	1498.92	44.593	2.9	6.7
1.0280	0.99855	61.7	1500.03	44.504	3.0	6.1
1.4975	0.99912	62.2	1501.88	44.372	2.9	6.6
1.9833	0.99984	62.1	1503.69	44.234	2.9	6.8

^a Extrapolated value.

TABLE 2.4

SUMMARY OF RESULTS FOR POLY(ACRYLIC ACID) IN AQUEOUS SOLUTION

AT 25°C ($M_2 = 72.06$)

c g/dl	d g/cc	V_{N_2} cc/mole	u m/sec	$\beta \times 10^6$ bar ⁻¹	$\frac{\beta}{1-\beta} \times 10^7$	$V_{N_2} \times 10^4$ cc/bar/mole
0.0000	0.99705	46.7 ^a	1496.05	44.812	-	0.85 ^a
0.0942	0.99737	47.7	1496.26	44.785	2.9	0.85
0.1884	0.99773	46.6	1496.41	44.759	2.8	0.85
0.3015	0.99813	46.9	1496.64	44.728	2.7	0.79
0.4020	0.99847	46.7	1496.84	44.701	2.8	1.05
0.5034	0.99885	46.4	1497.01	44.673	2.8	1.08
0.8054	0.99993	46.4	1497.69	44.585	2.8	0.51
1.2886	1.00169	46.2	1498.59	44.483	2.8	0.69
1.7182	1.00326	46.1	1499.33	44.340	2.7	0.89

^a Extrapolated value.

TABLE 2.5

SUMMARY OF RESULTS FOR POLY(SODIUM ACRYLATE), $\alpha = 0.25$,
 IN AQUEOUS SOLUTION AT 25°C ($M_2 = 77.56$)

c gm/dl	d gm/cc	ρV_2 cc/mole	u m/sec	$\beta \times 10^6$ bar ⁻¹	$\frac{\beta_1 - \beta}{c} \times 10^7$	$\rho V_2 \times 10^4$ cc/bar/mole
0.0000	0.99705	45.5 ^a	1496.05	44.812	-	-14.0 ^a
0.0949	0.99743	46.7	1496.61	44.761	5.3	-20.4
0.1899	0.99783	45.8	1496.74	44.735	4.0	-10.5
0.3165	0.99836	45.6	1497.55	44.663	4.7	-15.9
0.4114	0.99876	45.5	1497.77	44.632	4.4	-13.4
0.6330	0.99970	45.2	1498.83	44.527	4.5	-14.6
0.7815	1.00032	45.2	1499.31	44.471	4.4	-13.5
1.0159	1.00141	44.4	1500.62	44.345	4.6	-15.7
1.5630	1.00366	44.9	1502.94	44.115	4.4	-14.4

^a Extrapolated value.

TABLE 2.6

SUMMARY OF RESULTS FOR POLY(SODIUM ACRYLATE), $\alpha = 1.0$,IN AQUEOUS SOLUTION AT 25°C ($M_2 = 94.04$)

c gm/dl	d gm/cc	M_2 cc/mole	u m/sec	$\beta \times 10^6$ bar ⁻¹	$\frac{\beta}{c} \frac{1-\beta}{c} \times 10^7$	$M_2 \times 10^4$ cc/bar/mole
0.0000	0.99705	37.0 ^a	1496.05	44.812	-	-50.5 ^a
0.1024	0.99769	35.4	1496.82	44.739	7.3	-52.8
0.2049	0.99832	37.2	1497.57	44.664	7.2	-51.7
0.3013	0.99888	37.0	1498.28	44.596	7.1	-50.5
0.3964	0.99945	37.2	1499.00	44.528	7.1	-50.6
0.4955	1.00005	37.2	1499.76	44.456	7.2	-50.7
0.7743	1.00174	37.2	1501.70	44.267	7.0	-49.5
1.0188	1.00325	36.9	1503.86	44.073	7.2	-51.6
1.4982	1.00624	36.5	1507.09	43.754	7.1	-50.0
1.9976	1.00914	37.2	1511.10	43.397	7.1	-49.9
2.6635	1.01331	36.7	1516.26	42.925	7.1	-50.1

^a Extrapolated value.

TABLE 2.7

SUMMARY OF RESULTS FOR POLY(SODIUM ACRYLATE), $\alpha = 1.0$,
 IN 0.1 M HCl SOLUTION AT 25°C ($M_2 = 94.04$)

c gm/dl	d gm/cc	V_2 cc/mole	u m/sec	$\beta \times 10^6$ bar ⁻¹	$\frac{\beta_1 - \beta}{c} \times 10^7$	$V_2 \times 10^4$ cc/bar/mole
0.0000	1.00115	37.1 ^a	1502.30	44.257	-	-49.5 ^a
0.0877	1.00170	36.0	1503.01	44.191	7.5	-55.2
0.1755	1.00222	36.7	1503.76	44.124	7.6	-55.2
0.2581	1.00272	36.8	1504.29	44.071	7.2	-51.6
0.3396	1.00322	36.7	1504.87	44.015	7.1	-50.8
0.5306	1.00435	37.3	1506.37	43.978	7.1	-50.7
0.7185	1.00551	36.9	1507.58	43.757	7.0	-49.0
0.9580	1.00691	37.3	1509.43	43.590	7.0	-49.0
1.4739	1.01003	37.3	1512.57	43.275	6.7	-46.2
2.2109	1.01442	37.6	1515.64	42.744	6.8	-47.8

^a Extrapolated value.

TABLE 2.3

SUMMARY OF RESULTS FOR POLY(SODIUM ACRYLATE), $\alpha = 1.0$,
 IN 1.0 M NaCl SOLUTION AT 25°C ($M_2 = 94.04$)

c	d	ρV_2	u	$\beta \times 10^6$	$\frac{\beta_1 - \beta}{c} \times 10^7$	$\rho V_2 \times 10^4$
gm/dl	gm/cc	cc/mole	m/sec	bar ⁻¹		cc/bar/mole
0.0000	1.03709	42.8 ^a	1557.30	39.759	-	-33.0 ^a
0.1059	1.03765	42.7	1558.06	39.699	5.7	-36.7
0.2118	1.03820	43.1	1558.65	39.648	5.3	-32.3
0.3025	1.03870	42.4	1559.26	39.598	5.3	-33.3
0.4033	1.03923	42.6	1559.99	39.541	5.4	-34.0
0.5378	1.03992	43.0	1560.84	39.471	5.3	-33.3
0.7683	1.04125	41.6	1562.07	39.359	5.2	-32.5
1.0976	1.04302	41.7	1564.54	39.168	5.4	-34.1
1.6886	1.04614	42.1	1568.43	38.858	5.3	-33.5

^a Extrapolated value.

TABLE 2.9

SUMMARY OF RESULTS FOR THE COPOLYMER OF STYRENE-MALEIC ACID
 IN AQUEOUS SOLUTION AT 25°C ($M_2 = 239$)

c	d	\bar{V}_2	u	$\times 10^6$	$\frac{1}{c} \times 10^7$	$\beta K_2 \times 10^4$
gm/dl	gm/cc	cc/mole	m/sec	bar ⁻¹		cc/bar/mole
0.0000	0.99705	172.4 ^a	1496.05	44.812	-	11.0 ^a
0.0987	0.99732	174.1	1496.30	44.784	2.7	11.9
0.1974	0.99761	171.7	1496.54	44.757	2.8	10.8
0.2961	0.99788	172.5	1496.81	44.729	2.8	10.5
0.4491	0.99832	171.9	1497.17	44.688	2.8	11.1
0.6416	0.99889	171.0	1497.73	44.629	2.8	8.6
0.9870	0.99987	171.2	1498.45	44.542	2.7	11.5

^a Extrapolated value.

TABLE 2.10

SUMMARY OF RESULTS FOR SODIUM SALT OF STYRENE-MALEIC ACID COPOLYMER
(50% NEUTRALIZED) IN AQUEOUS SOLUTION AT 25°C ($M_2 = 261$)

c g/dl	d g/cc	βV_2 cc/mole	u m/sec	$\beta \times 10^6$ bar ⁻¹	$\frac{\beta}{c} \frac{1-\beta}{c} \times 10^7$	$\beta K_2 \times 10^4$ cc/bar/mole
0.0000	0.99705	160.0 ^a	1496.05	44.812	-	-57.0 ^a
0.1000	0.99744	159.7	1496.58	44.762	5.0	-58.1
0.2000	0.99783	159.7	1497.22	44.713	4.9	-57.5
0.3000	0.99822	159.7	1497.67	44.662	5.0	-58.9
0.4000	0.99860	160.3	1498.17	44.615	4.9	-56.7
0.5000	0.99899	160.2	1498.73	44.565	4.9	-57.2
0.7500	0.99998	159.5	1499.98	44.446	4.9	-55.9
1.0000	1.00097	159.2	1501.34	44.322	4.9	-56.6

^a Extrapolated value.

TABLE 2.11

SUMMARY OF RESULTS FOR SODIUM SALT OF STYRENE-MALEIC ACID COPOLYMER
(100% NEUTRALIZED) IN AQUEOUS SOLUTION AT 26°C ($M_2 = 283$)

c gm/dl	d gm/cc	\bar{V}_2 cc/mole	u m/sec	$\beta \times 10^6$ bar ⁻¹	$\frac{\beta_1 - \beta}{c} \times 10^7$	$\beta \kappa_2 \times 10^4$ cc/bar/mole
0.0000	0.99705	140.3 ^a	1496.05	44.812	-	-100.0 ^a
0.1029	0.99757	140.4	1496.65	44.752	5.8	-102.0
0.2059	0.99809	140.5	1497.24	44.694	5.7	- 98.8
0.3088	0.99861	140.5	1497.87	44.634	5.8	- 99.1
0.5018	0.99960	139.6	1499.00	44.521	5.8	-101.5
0.7721	1.00097	139.7	1500.55	44.369	5.7	- 99.8
1.0294	1.00225	140.4	1502.09	44.221	5.7	- 99.5

^a Extrapolated value.

TABLE 2.12

SUMMARY OF RESULTS FOR SODIUM SALT OF STYRENE-MALEIC ACID COPOLYMER
(50 % NEUTRALIZED) IN 1.0 M NaCl SOLUTION AT 25°C ($M_2 = 261$)

c	d	\bar{V}_2	u	$\beta \times 10^6$	$\frac{\beta}{c} \times 10^7$	$\beta K_2 \times 10^4$
gm/dl	gm/cc	cc/mole	m/sec	bar ⁻¹		cc/bar/mole
0.0000	1.03709	158.2 ^a	1557.30	39.759	-	-44.0 ^a
0.1000	1.03746	158.5	1557.82	39.719	4.0	-42.1
0.2000	1.03783	158.5	1558.35	39.677	4.1	-43.7
0.3000	1.03821	157.7	1558.90	39.635	4.1	-45.2
0.4000	1.03857	158.5	1559.40	39.596	4.1	-43.4
0.5250	1.03903	158.7	1560.06	39.545	4.1	-43.2
0.7500	1.03989	157.7	1561.19	39.455	4.1	-43.1
1.0000	1.04079	158.5	1562.42	39.358	4.0	-41.7
1.5000	1.04269	157.7	1564.83	39.166	4.0	-40.5

^a Extrapolated value.

TABLE 2.13

SUMMARY OF RESULTS FOR SODIUM SALT OF STYRENE-MALEIC ACID COPOLYMER
(100% NEUTRALIZED) IN 1.0 M NaCl SOLUTION AT 25°C ($M_2 = 233$)

c gm/dl	d gm/cc	βV_2 cc/mole	u m/sec	$\rho \times 10^6$ bar ⁻¹	$\frac{\beta}{c} \frac{1-\beta}{c} \times 10^7$	$\beta K_2 \times 10^4$ cc/bar/mole
0.0000	1.03709	161.6 ^a	1557.30	39.759	-	-46.0 ^a
0.0984	1.03749	161.9	1557.75	39.721	3.9	-45.9
0.1967	1.03789	161.9	1558.21	39.682	3.9	-46.5
0.2951	1.03829	161.9	1558.66	39.644	3.9	-45.9
0.3934	1.03872	160.4	1559.11	39.605	3.9	-46.3
0.4918	1.03910	161.3	1559.56	39.566	3.9	-46.8
0.7462	1.04013	161.7	1560.59	39.473	3.8	-45.2
0.9836	1.04110	161.6	1561.83	39.377	3.9	-45.7
1.4754	1.04313	161.2	1563.77	39.203	3.8	-42.5
1.9246	1.04494	161.6	1566.17	39.015	3.9	-45.1

^a Extrapolated value.

2.13 THE ADIABATIC COMPRESSIBILITY OF POLYACRYLAMIDE

The adiabatic compressibility for polyacrylamide and its monomer have been determined in aqueous solution at 25°C. This is an uncharged polymer with amphoteric groups in the chain. However, polyacrylamide and poly(acrylic acid) are structurally closely related and both of them have functional groups in the monomer which form a hydrogen bonded structure. The results of adiabatic compressibility measurements are given in Tables 2.14 and 2.15.

2.14 THE ADIABATIC COMPRESSIBILITY OF AMPHOTERIC POLYELECTROLYTES

The adiabatic compressibility studies were extended to two amphoteric polyelectrolytes namely acrylic acid-4-vinyl N-n butylpyridinium bromide copolymer and methacrylic acid-4-vinyl N-n butylpyridinium bromide copolymer. The ultrasonic velocity and density of solutions were measured in the similar way. The results are summarized in Tables 2.16 to 2.25.

TABLE 2.14

SUMMARY OF RESULTS FOR ACRYLAMIDE IN AQUEOUS SOLUTION

AT 25°C ($M_2 = 71.08$)

c gm/dl	d gm/cc	\bar{V}_2 cc/mole	u m/sec	$\beta \times 10^6$ bar ⁻¹	$\frac{\beta(1-\beta)}{c} \times 10^7$	$\bar{V}_2 \times 10^4$ cc/bar/mole
0.0000	0.99705	65.5 ^a	1496.05	44.812	-	5.0 ^a
0.10005	0.99713	65.6	1496.57	44.777	3.5	5.5
0.2001	0.99722	65.2	1497.10	44.741	3.5	4.9
0.3001	0.99729	65.6	1497.56	44.711	3.4	5.5
0.4000	0.99738	65.4	1498.19	44.669	3.6	3.9
0.5002	0.99747	65.3	1498.59	44.630	3.6	3.4
1.0001	0.99790	65.2	1500.51	44.484	3.3	5.9
1.5001	0.99832	65.2	1503.61	44.305	3.4	5.3
2.0001	0.99877	65.2	1505.97	44.147	3.3	5.6

^a Extrapolated value.

TABLE 2.15

SUMMARY OF RESULTS FOR POLYACRYLAMIDE IN AQUEOUS SOLUTION AT

25°C (M₂ = 71.08)

c	d	WV ₂	u	$\beta \times 10^6$	$\frac{\beta}{c} \times 10^7$	$\frac{\beta K_2}{c} \times 10^4$
gm/dl	gm/cc	cc/mole	u/sec	bar ⁻¹		cc/bar/mole
0.0000	0.99705	50.9 ^a	1496.05	44.812	-	-3.0 ^a
0.1035	0.99735	50.6	1496.46	44.774	3.6	-3.4
0.2670	0.99764	51.0	1496.88	44.735	3.7	-3.6
0.3105	0.99793	51.1	1497.25	44.700	3.6	-2.7
0.4140	0.99825	50.1	1497.67	44.661	3.6	-3.1
0.5175	0.99855	50.6	1498.14	44.620	3.7	-3.7
0.7752	0.99925	51.1	1498.95	44.540	3.5	-2.1
1.0336	1.00000	51.3	1500.10	44.438	3.6	-2.8
1.5493	1.00149	50.9	1502.13	44.252	3.6	-2.9
2.0657	1.00297	51.0	1504.15	44.069	3.6	-2.3

^a Extrapolated value.

TABLE 2.16

SUMMARY OF RESULTS FOR COPOLYMER OF ACRYLIC ACID AND 4-VINYL
N-T BUTYLPYRIDINIUM BROMIDE IN AQUEOUS SOLUTION

AT 25°C (N₂ = 262)

c gm/dl	d gm/cc	βV_2 cc/mole	u m/sec	$\beta \times 10^6$ bar ⁻¹	$\frac{\beta \gamma - \beta}{c} \times 10^7$	$\beta K_2 \times 10^4$ cc/bar/mole
0.0000	0.99705	183.9 ^a	1496.05	44.812	-	-7.0 ^a
0.1000	0.99735	183.9	1496.40	44.777	3.5	-9.0
0.2000	0.99765	183.9	1496.75	44.743	3.4	-7.9
0.3000	0.99796	183.1	1497.07	44.710	3.4	-7.1
0.4000	0.99826	183.3	1497.41	44.676	3.4	-7.0
0.5000	0.99856	183.4	1497.79	44.640	3.4	-7.9
0.7500	0.99930	183.9	1498.61	44.558	3.4	-6.4
1.0000	1.00005	183.9	1499.50	44.472	3.4	-6.7
1.5000	1.00154	184.1	1501.29	44.300	3.4	-6.9
2.0000	1.00302	184.3	1503.03	44.132	3.4	-6.5

^a Extrapolated value.

TABLE 2.17

SUMMARY OF RESULTS FOR ACRYLIC ACID-4-VINYL N-N BUTYLPYRIDINIUM
BROMIDE COPOLYMER IN 1.0 M KBr SOLUTION AT 25°C ($M_2 = 262$)

c gm/dl	d gm/cc	\bar{V}_2 cc/mole	u m/sec	$\beta \times 10^6$ bar ⁻¹	$\frac{\beta(1-\beta)}{c} \times 10^7$	$\bar{V}_2 \times 10^4$ cc/bar/mole
0.0000	1.08054	184.3 ^a	1513.80	40.385	-	7.0 ^a
0.1000	1.08078	184.3	1514.13	40.369	2.6	6.9
0.2000	1.08102	184.3	1514.42	40.334	2.6	8.0
0.3000	1.08126	184.3	1514.76	40.307	2.6	6.2
0.4000	1.08151	183.7	1515.08	40.281	2.6	5.9
0.5000	1.08176	183.3	1515.36	40.257	2.6	6.9
0.7500	1.08237	183.3	1516.16	40.191	2.6	6.4
1.0000	1.08293	184.5	1516.97	40.128	2.6	7.2
1.5000	1.08411	184.8	1518.60	39.998	2.6	7.1
2.0000	1.08522	185.7	1520.17	39.875	2.6	8.2

^a Extrapolated value.

TABLE 2.18

SUMMARY OF RESULTS FOR POTASSIUM SALT (100% NEUTRALIZED) OF
ACRYLIC ACID-4-VINYL N-N BUTYLPIRIDINIUM BROMIDE COPOLYMER
IN AQUEOUS SOLUTION AT 25°C ($M_2 = 273$)

c gm/dl	d gm/cc	ρV_2 cc/mole	u m/sec	$\beta \times 10^6$ bar ⁻¹	$\frac{\beta}{c} \frac{1-\beta}{c} \times 10^7$	$\beta K_2 \times 10^4$ cc/bar/mole
0.0000	0.99705	184.4 ^a	1496.05	44.812	-	-23.0 ^a
0.1000	0.99738	183.4	1496.45	44.773	3.9	-24.1
0.2000	0.99770	184.8	1496.85	44.734	3.9	-23.5
0.3000	0.99803	184.4	1497.25	44.696	3.9	-22.9
0.4000	0.99836	184.1	1497.63	44.658	3.8	-22.6
0.5000	0.99868	184.5	1498.04	44.620	3.8	-22.1
0.7500	0.99950	184.4	1499.04	44.524	3.8	-22.3
1.0000	1.00032	184.3	1499.67	44.450	3.6	-16.3
1.5000	1.00191	185.1	1501.91	44.247	3.8	-19.9
1.9941	1.00346	185.8	1503.64	44.077	3.8	-17.4

^a Extrapolated value.

TABLE 2.19

SUMMARY OF RESULTS FOR POTASSIUM SALT (100% NEUTRALIZED) OF
 ACRYLIC ACID-4-VINYL N-n BUTYLPYRIDINIUM BROMIDE COPOLYMER
 IN 0.1 M KBr SOLUTION AT 25°C ($n_D = 273$)

c g/dl	d g/cc	βV_2 cc/mole	u m/sec	$\beta \times 10^6$ bar ⁻¹	$\frac{\beta \Gamma^{\beta}}{c} \times 10^7$	$\beta K_2 \times 10^4$ cc/bar/mole
0.0000	1.00552	184.6 ^a	1497.94	44.322	-	-18.0 ^a
0.1000	1.00594	184.6	1498.32	44.285	3.7	-20.0
0.2000	1.00616	184.6	1498.70	44.249	3.6	-18.2
0.3000	1.00648	184.6	1499.08	44.212	3.7	-18.0
0.4000	1.00680	184.6	1499.48	44.175	3.7	-18.5
0.6136	1.00749	184.3	1500.28	44.097	3.7	-18.5
0.7500	1.00793	184.3	1500.78	44.049	3.6	-17.8
1.0000	1.00872	184.6	1501.74	43.958	3.6	-17.5
1.5000	1.01030	185.0	1503.63	43.779	3.6	-16.8
2.0000	1.01188	185.2	1505.60	43.596	3.6	-17.0

^a Extrapolated value.

TABLE 2.20

SUMMARY OF RESULTS FOR POTASSIUM SALT (100% NEUTRALIZED) OF
 ACRYLIC ACID-4-VINYL N-n BUTYLPYRIDINIUM BROMIDE COPOLYMER
 IN 1.0 M KBr SOLUTION AT 25°C ($M_2 = 273$)

c gm/dl	d gm/cc	ρV_2 cc/mole	u m/sec	$\beta \times 10^6$ bar ⁻¹	$\frac{\beta \bar{1} - \beta}{c} \times 10^7$	$\beta K_2 \times 10^4$ cc/bar/mole
0.0000	1.08054	184.8 ^a	1513.80	40.385	-	-4.0 ^a
0.1000	1.08081	184.4	1514.15	40.356	2.9	-4.9
0.2000	1.08108	184.4	1514.53	40.326	2.9	-6.0
0.3000	1.08134	185.3	1514.86	40.299	2.9	-3.4
0.4000	1.08162	184.4	1515.20	40.270	2.9	-4.1
0.5000	1.08188	184.9	1515.56	40.241	2.9	-4.0
0.7500	1.08255	184.9	1516.47	40.163	2.9	-4.2
1.0000	1.08321	185.2	1517.37	40.096	2.9	-4.1
1.5000	1.08454	185.3	1519.17	39.952	2.9	-3.9
2.0000	1.08578	186.4	1521.00	39.811	2.9	-3.1

^a Extrapolated value.

TABLE 2.21

SUMMARY OF RESULTS FOR THE COPOLYMER OF METHACRYLIC ACID AND
4-VINYL N-m BUTYLPYRIDINIUM BROMIDE IN AQUEOUS SOLUTION

AT 25°C ($M_2 = 253$)

c gm/dl	d gm/cc	V_2 cc/mole	η ml/sec	$\beta \times 10^6$ bar ⁻¹	$\frac{\beta_1 - \beta}{c} \times 10^7$	$\beta M_2 \times 10^4$ cc/bar/mole
0.0000	0.99708	184.6 ^a	1496.05	44.812	-	-3.0 ^a
0.1030	0.99734	185.9	1496.40	44.778	3.3	-1.9
0.2060	0.99764	184.6	1496.76	44.743	3.3	-3.6
0.3090	0.99794	184.2	1497.12	44.708	3.4	-4.1
0.4028	0.99820	184.9	1497.43	44.677	3.3	-3.4
0.5035	0.99849	184.8	1497.79	44.643	3.4	-3.7
0.7552	0.99922	184.4	1498.65	44.599	3.3	-3.9
1.0299	0.99999	184.9	1499.56	44.471	3.3	-2.6
1.4876	1.00132	184.5	1501.12	44.320	3.3	-2.6
2.0189	1.00279	185.2	1503.01	44.143	3.3	-2.5

^a Extrapolated value.

TABLE 2.22

SUMMARY OF RESULTS FOR METHACRYLIC ACID-4-VINYL N- α BUTYLPIRIDINIUM
BROMIDE COPOLYMER IN 1.0 M KBr SOLUTION AT 25°C ($M_2 = 258$)

c gm/dl	d gm/cc	\bar{V}_2 cc/mole	u m/sec	$\beta \times 10^6$ bar ⁻¹	$\frac{\beta(1-\beta)}{c} \times 10^7$	$\bar{V}_2 \times 10^4$ cc/bar/mole
0.0000	1.08054	188.6 ^a	1513.80	40.385	-	13.0 ^a
0.1000	1.08075	188.6	1514.11	40.361	2.4	15.2
0.2000	1.08096	188.6	1514.42	40.336	2.4	13.1
0.3000	1.08117	188.6	1514.74	40.311	2.5	12.7
0.4000	1.08137	189.2	1515.07	40.287	2.4	13.1
0.5000	1.08159	188.6	1515.41	40.260	2.5	11.6
0.7500	1.08214	187.8	1516.14	40.201	2.4	12.5
1.0000	1.08263	188.9	1516.87	40.144	2.4	14.1
1.5000	1.08370	188.5	1518.41	40.023	2.4	13.9
2.0000	1.08476	188.4	1520.00	39.901	2.4	13.6

^a Extrapolated value.

TABLE 2.23

SUMMARY OF RESULTS FOR POTASSIUM SALT (100% NEUTRALIZED) OF
 METHACRYLIC ACID-4-VINYL N-n BUTYLPYRIDINIUM BROMIDE COPOLYMER
 IN AQUEOUS SOLUTION AT 25°C ($M_2 = 268$)

c g/dl	d gm/cc	ρV_2 cc/mole	u m/sec	$\beta \times 10^6$ bar ⁻¹	$\frac{\beta}{c} \frac{1-\beta}{c} \times 10^7$	$\rho M_2 \times 10^4$ cc/bar/mole
0.0000	0.99705	176.6 ^a	1496.05	44.812	-	-24.0 ^a
0.0876	0.99734	177.8	1496.41	44.777	4.0	-20.9
0.1753	0.99764	176.3	1496.73	44.741	4.0	-23.6
0.2630	0.99793	176.8	1497.13	44.707	4.0	-20.3
0.3944	0.99837	176.8	1497.61	44.659	3.9	-23.6
0.4931	0.99870	176.8	1498.04	44.619	3.9	-24.4
0.6574	0.99927	176.0	1498.63	44.555	3.9	-24.9
0.8765	1.00000	176.3	1499.57	44.470	3.9	-24.4
1.3148	1.00142	177.4	1501.31	44.304	3.9	-22.9
1.7530	1.00234	178.0	1503.34	44.122	3.9	-24.5

^a Extrapolated value.

TABLE 2.24

SUMMARY OF RESULTS FOR POTASSIUM SALT (100% NEUTRALIZED) OF
 METHACRYLIC ACID-4-VINYL N-T BUTYLPYRIDINIUM BROMIDE COPOLYMER
 IN 0.1 M KBr SOLUTION AT 25°C ($N_2 = 265$)

c gm/dl	d gm/cc	ρV_2 cc/mole	u m/sec	$\beta \times 10^6$ bar ⁻¹	$\frac{\beta \lambda^{-\beta}}{c} \times 10^7$	$\rho V_2 \times 10^4$ cc/bar/mole
0.0000	1.00552	179.5 ^a	1497.94	44.322	-	-18.0 ^a
0.1013	1.00584	180.3	1498.33	44.285	3.7	-17.7
0.2027	1.00617	179.0	1498.72	44.247	3.7	-18.8
0.3040	1.00649	179.4	1499.11	44.210	3.7	-18.0
0.4028	1.00680	179.8	1499.49	44.174	3.7	-17.6
0.5067	1.00713	179.8	1499.90	44.136	3.7	-17.6
0.7506	1.00791	179.6	1500.82	44.047	3.7	-17.6
1.0008	1.00873	179.0	1501.79	43.955	3.7	-17.8
1.5687	1.01056	178.9	1504.11	43.740	3.7	-19.1

^a Extrapolated value.

TABLE 2.25

SUMMARY OF RESULTS FOR POTASSIUM SALT (100% NEUTRALIZED) OF
 METHACRYLIC ACID-4-VINYL N-T BUTYLPYRIDINIUM BROMIDE COPOLYMER
 IN 1.0 M KBr SOLUTION AT 25°C ($M_2 = 265$)

c	d	ρV_2	u	$\beta \times 10^6$	$\frac{\beta_1 - \beta}{c} \times 10^7$	$\beta K_2 \times 10^4$
g/dl	g/cc	cc/mole	cm/sec	bar ⁻¹	g	cc/bar/mole
0.0000	1.08054	165.5 ^a	1513.80	40.385	-	-20.0 ^a
0.1000	1.08057	164.3	1514.20	40.352	3.3	-20.8
0.2000	1.08119	165.5	1514.59	40.319	3.3	-20.3
0.3000	1.08152	165.1	1514.99	40.285	3.3	-21.9
0.4000	1.08194	165.5	1515.38	40.253	3.3	-20.5
0.5000	1.08217	165.3	1515.78	40.219	3.3	-21.2
0.7500	1.08298	165.5	1516.68	40.141	3.2	-19.4
1.0002	1.08390	165.3	1517.73	40.055	3.3	-20.7
1.4128	1.08514	165.4	1519.21	39.928	3.2	-19.0
1.8543	1.08658	165.4	1520.91	39.786	3.2	-18.8

^a Extrapolated value.

CHAPTER - III

CHAPTER - III

DISCUSSION

From the results (Tables 2.3 to 2.25) it is evident that the density and ultrasonic velocity increase linearly and accordingly the adiabatic compressibility decreases with the increase in concentration. When a solute is dissolved in a solvent, the variation of ultrasonic velocity is phenomenologically dependent upon two factors viz., the change of density and the compressibility. For small changes, it follows from the equation of ultrasonic velocity

$$u^2 = 1/(\beta d)$$

that

$$\Delta v/v = -\frac{1}{2} (\Delta d/d + \Delta\beta/\beta)$$

On adding solute to the solvent, the density increases, that is, Δd is generally positive. Therefore, the variation in density causes the sound velocity to decrease. It is seen from the results that the ultrasonic velocity increases as the concentration increases. This result tells us that the decrease in the compressibility has a greater effect on velocity than does the negative contribution of the density. It is visualized that the coulombic force or other intermolecular forces may influence the structure of the liquid and also association of the ions significantly. These forces

will thus affect the compressibility of the solution so much so that compressibility may be considered as a more suitable parameter to analyse than the ultrasonic velocity for studying the influence of the ions on the solution.

3.1 ADIABATIC COMPRESSIBILITY

The plots of adiabatic compressibility as a function of concentration are shown in Figure 3.1. It is observed that the total adiabatic compressibility of polyacrylic acid and styrene-maleic acid copolymer are more or less the same (curves 1 and 4). Further the 50% and 100% neutralized sodium salts of styrene-maleic acid copolymer (curves 5 and 6) show comparatively higher compressibilities than those of the corresponding sodium salts of poly(acrylic acid) (curve 3). It may be pointed out that the reduced viscosity for the acid and the sodium salts of styrene-maleic acid copolymer showed a similar trend i.e., higher reduced viscosity than those of the corresponding acid and salts of poly(acrylic acid) (Figures 2.3 to 2.5).

The decrease of compressibility for electrolytes is due to the action on water of the electric field around each ion. The electrostatic pressure causes an additional contraction of the water in the same way as is caused by increasing external pressure. However, the comparatively larger decrease in compressibility in case of polyacrylamide (curve 7), an uncharged polymer in water with respect to polyacids, may be

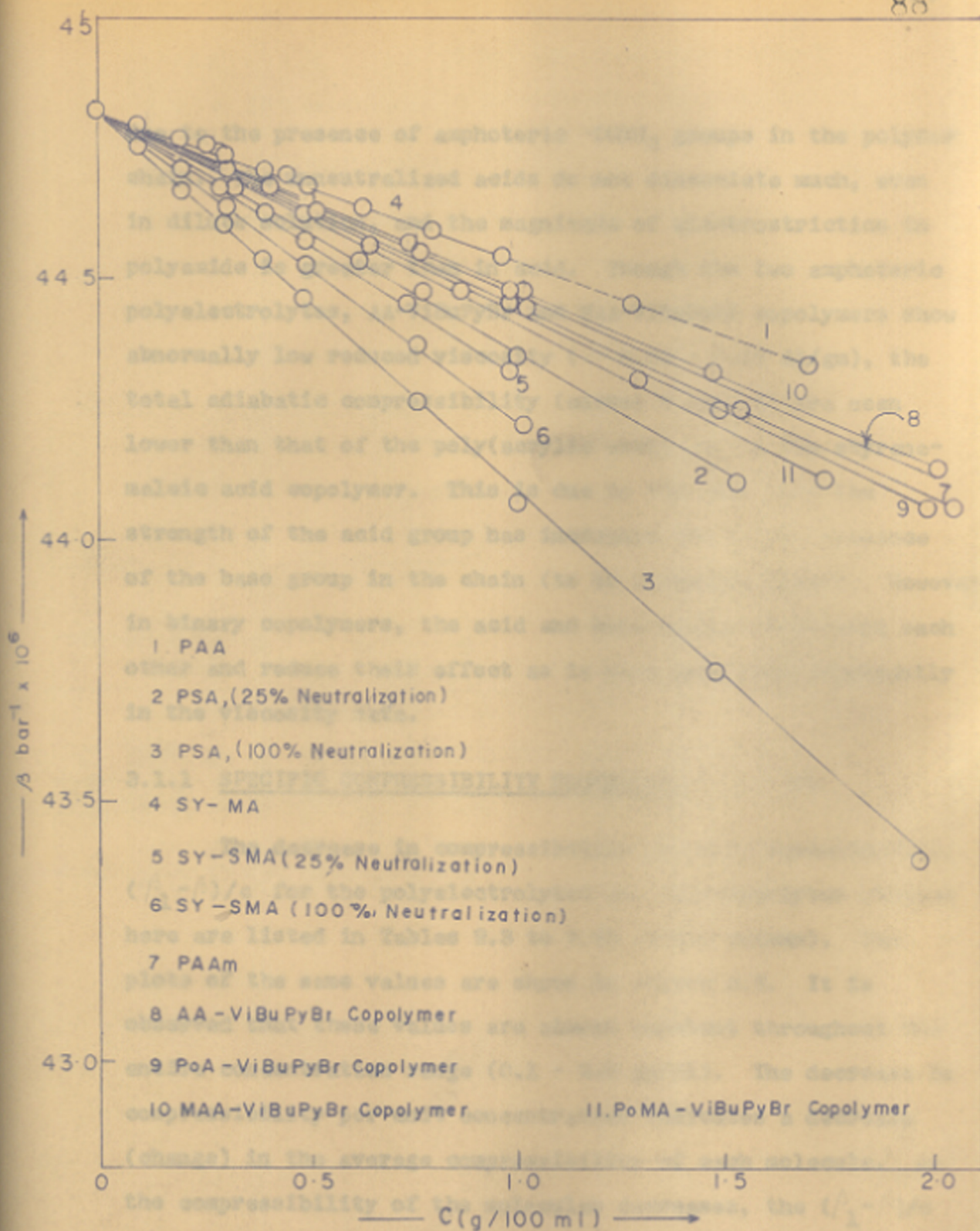


Fig 3.1 ADIABATIC COMPRESSIBILITY IN AQUEOUS SOLUTION AT 25°C

due to the presence of amphoteric $-\text{CONH}_2$ groups in the polymer chain. The unneutralized acids do not dissociate much, even in dilute solution, and the magnitude of electrostriction in polyamide is greater than in acid. Though the two amphoteric polyelectrolytes, AA-ViBuPyBr and MAA-ViBuPyBr copolymers show abnormally low reduced viscosity ($\sim 0.03 - 0.07$ dl/ga), the total adiabatic compressibility (curves 8 and 10) are seen lower than that of the poly(acrylic acid) and so the styrene-maleic acid copolymer. This is due to the fact that the strength of the acid group has increased due to the presence of the base group in the chain (to be discussed later). However, in binary copolymers, the acid and base groups react with each other and reduce their effect as is seen here very prominently in the viscosity data.

3.1.1 SPECIFIC COMPRESSIBILITY DECREMENT, $(\beta_1 - \beta)/c$

The decrease in compressibility per unit concentration, $(\beta_1 - \beta)/c$ for the polyelectrolytes and polyampholytes studied here are listed in Tables 2.3 to 2.25 (sixth column). The plots of the same values are shown in Figure 3.2. It is observed that these values are almost constant throughout the entire concentration range (0.1 - 2.0 ga/dl). The decrease in compressibility per unit concentration indicates a decrease (change) in the average compressibility of each molecule. As the compressibility of the molecules decreases, the $(\beta_1 - \beta)/c$ value increases and vice versa. The partially and fully

- | | |
|----------------------------|---------------------------------|
| 1 PAA | 5 SY-SMA (50% neutralization) |
| 2 PSA, 25% neutrllization | 6. SY-SMA (100% neutralization) |
| 3 PSA, 100% neutralization | 7. PAA m |
| 4 SY-MA | 8. AA-ViBuPyBr Copolymer |
| | 9. PoA-ViBuPyBr copolymer |
| | 10 MAA-ViBu Py Br copolymer |
| | 11 PoMA-ViBuPyBr copolymer |

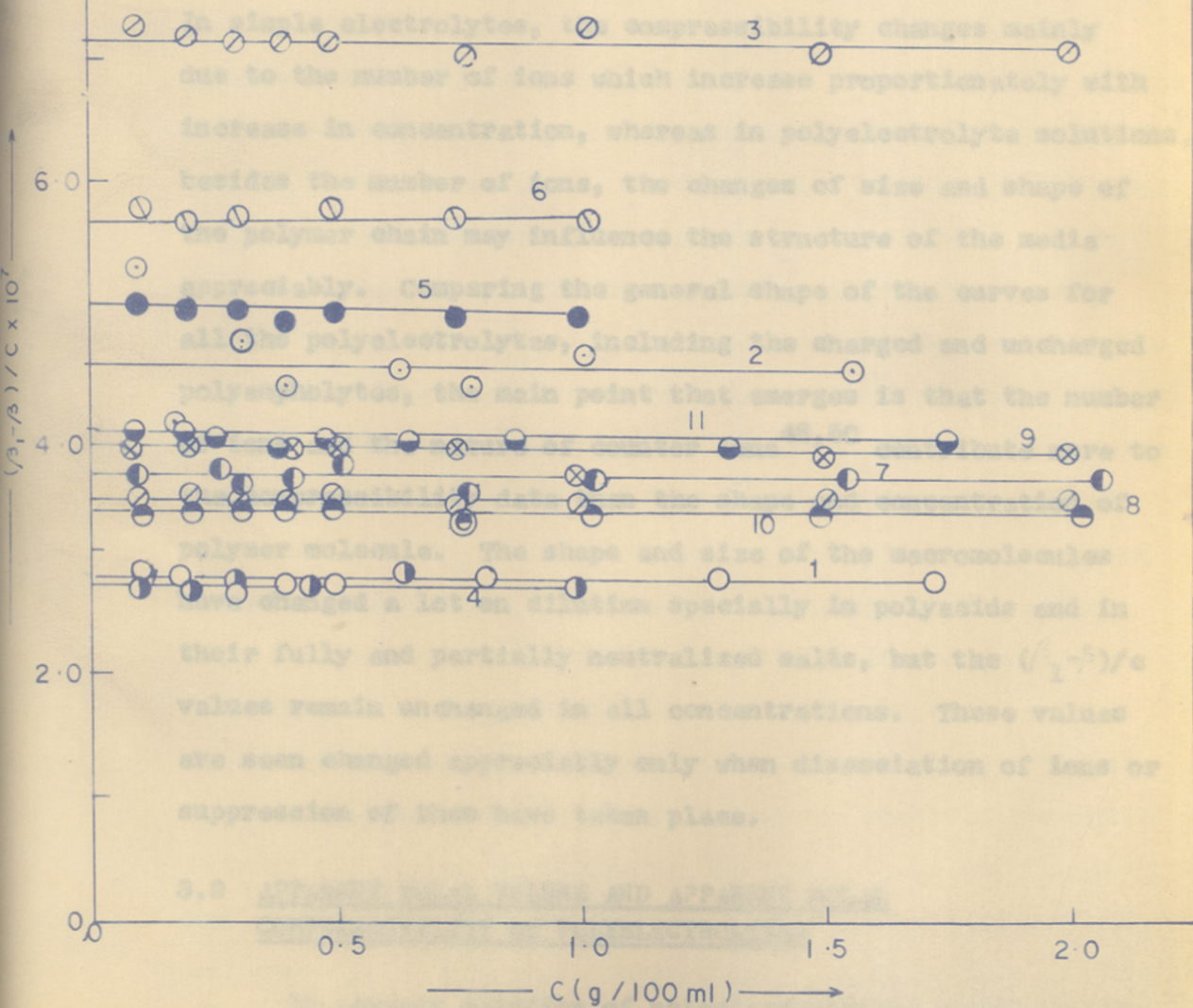


Fig 3:2 PLOTS OF COMPRESSIBILITY DECREMENT Vs. CONCENTRATION IN AQUEOUS SOLUTION

neutralized sodium salts are seen to have higher values of $(\beta_1 - \beta)/c$ than that of the corresponding polyacids. On neutralization of the carboxyl groups in amphoteric polyelectrolytes with KOH, the compressibility decreases but the $(\beta_1 - \beta)/c$ values are not increased so high in these cases as the carboxyl groups are only ~15-20% in the molecular chain. In simple electrolytes, the compressibility changes mainly due to the number of ions which increase proportionately with increase in concentration, whereas in polyelectrolyte solutions, besides the number of ions, the changes of size and shape of the polymer chain may influence the structure of the media appreciably. Comparing the general shape of the curves for all the polyelectrolytes, including the charged and uncharged polyampholytes, the main point that emerges is that the number of ions and the nature of counter ions^{48,50} contribute more to the compressibility data than the shape and concentration of polymer molecule. The shape and size of the macromolecules have changed a lot on dilution specially in polyacids and in their fully and partially neutralized salts, but the $(\beta_1 - \beta)/c$ values remain unchanged in all concentrations. These values are seen changed appreciably only when dissociation of ions or suppression of them have taken place.

3.2 APPARENT MOLAL VOLUME AND APPARENT MOLAL COMPRESSIBILITY OF POLYELECTROLYTES

In aqueous solution of polyelectrolytes, there are two

types of solute-solvent interaction: (1) the electrostrictional hydration by electric charges of gegenion or macroion i.e., the charge effect and (2) the hydrophobic structural enhancement or "ice berg" formation by hydrophobic parts of the electrolytes, i.e., the hydrophobic effect. Both the electrostrictional effect and the hydrophobic effect have a large influence on the solution density and compressibility. The data for apparent molal volume and apparent molal compressibility of the polymers are given in Tables 2.3 to 2.25. The plots of \bar{V}_2 and \bar{K}_2 versus c are shown in Figures 3.3 to 3.6. The \bar{V}_2 and \bar{K}_2 values for monomers and polymers are found to be concentration independent. The insensitivity of the \bar{V}_2 and \bar{K}_2 values toward concentration are also seen for the sodium salts of poly(acrylic acid) and styrene-maleic acid copolymer as well as for the two amphoteric polyelectrolytes and their potassium salts. According to Wen and Saito⁶⁵ the hydrophobic effect tends to lower \bar{V}_2 with concentration while the charge effect tends to increase \bar{V}_2 with concentration, especially with smaller electrolytes³⁴. The insensitivity toward concentration in case of some large tetraalkyl ammonium salts was described as a delicate balancing between these two effects. In fact Ise and Okubo⁶⁶ have explained the observed insensitivity of \bar{V}_2 toward concentration in case of poly(acrylic acid) and other poly(sodium acrylates) as a result of balancing of two opposite effects i.e., hydrophobic effect and charge effect. Two types of polymers have been studied here, the two polyacids and three polyampholytes. Polyacrylamide is an uncharged

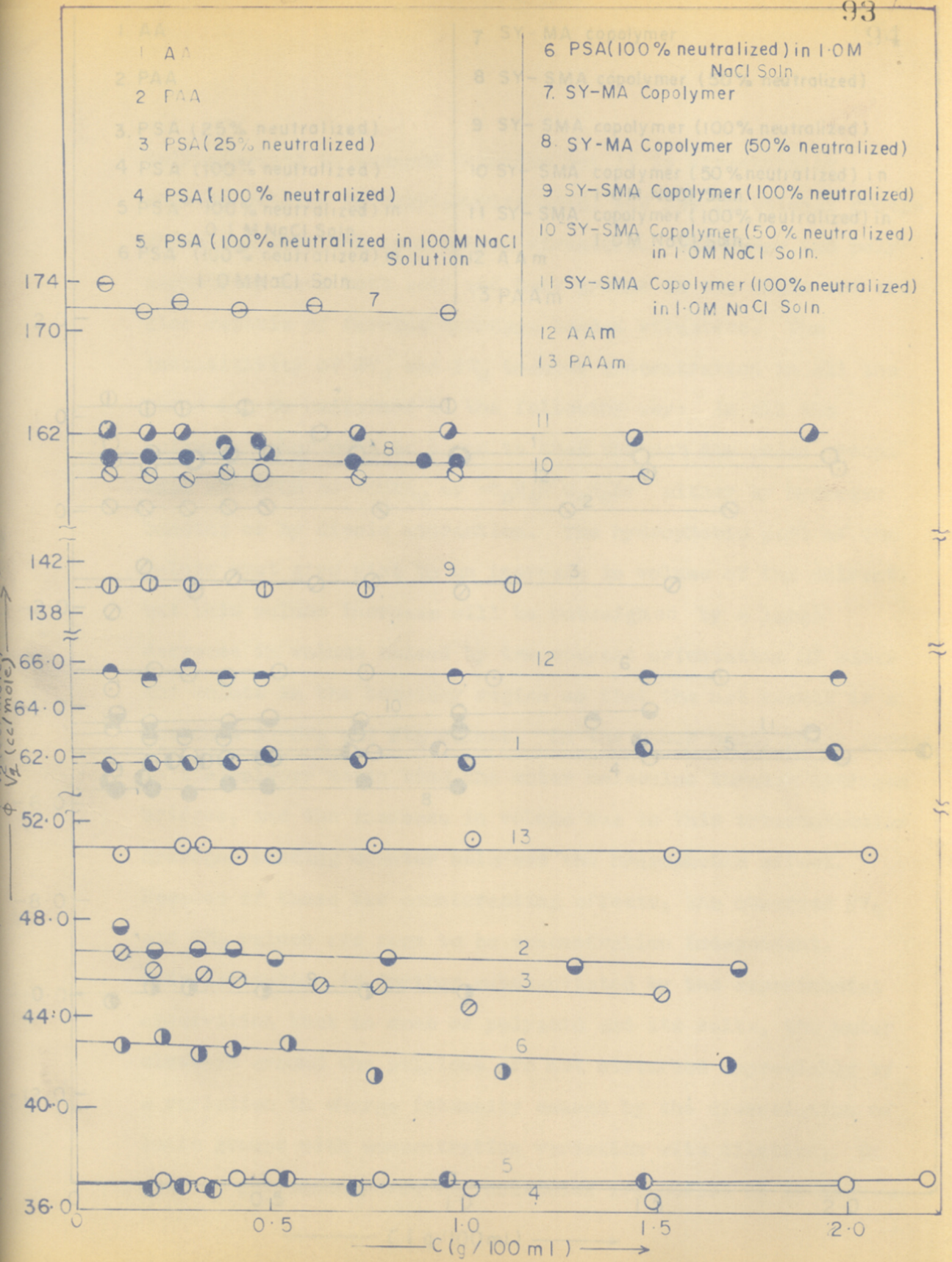


Fig 3.3 APPARENT MOLAL VOLUME Vs CONCENTRATION CURVES IN AQUEOUS SOLUTION

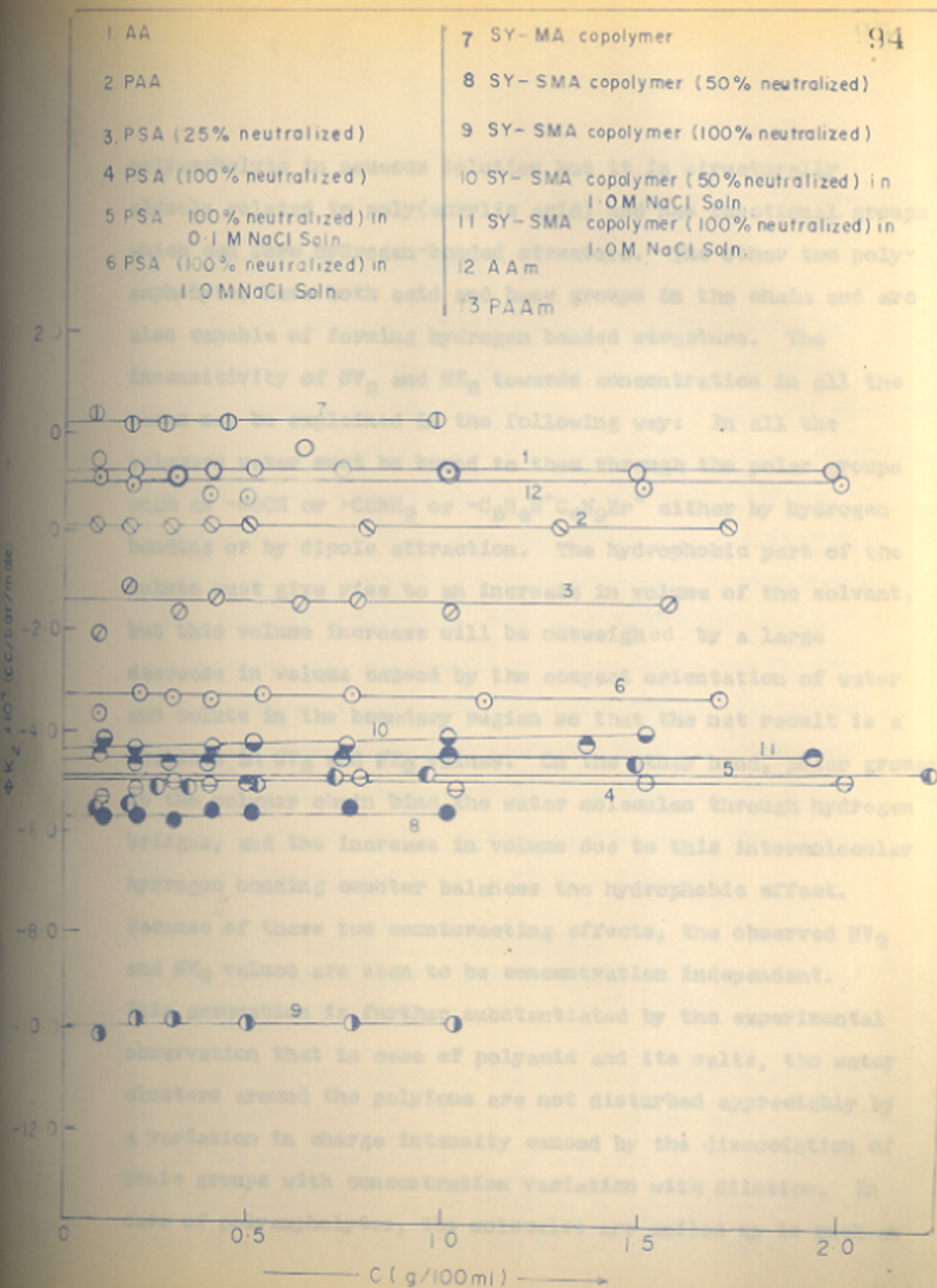


Fig 3.4 ADIABATIC COMPRESSIBILITY Vs CONCENTRATION CURVES IN AQUEOUS SOLUTION

polyampholyte in aqueous solution but it is structurally closely related to poly(acrylic acid) and has functional groups which can form hydrogen-bonded structure. The other two polyampholytes have both acid and base groups in the chain and are also capable of forming hydrogen bonded structure. The insensitivity of ∂V_2 and ∂K_2 towards concentration in all the cases may be explained in the following way: In all the polymers water must be bound to them through the polar groups such as $-\text{COOH}$ or $-\text{CONH}_2$ or $-\text{C}_5\text{H}_4\text{N}^+\text{C}_4\text{H}_9\text{Br}^-$ either by hydrogen bonding or by dipole attraction. The hydrophobic part of the solute must give rise to an increase in volume of the solvent, but this volume increase will be outweighed by a large decrease in volume caused by the compact orientation of water and solute in the boundary region so that the net result is a decrease in ∂V_2 and ∂K_2 values. On the other hand, polar groups in the polymer chain bind the water molecules through hydrogen bridges, and the increase in volume due to this intermolecular hydrogen bonding counter balances the hydrophobic effect. Because of these two counteracting effects, the observed ∂V_2 and ∂K_2 values are seen to be concentration independent. This assumption is further substantiated by the experimental observation that in case of polyacid and its salts, the water clusters around the polyions are not disturbed appreciably by a variation in charge intensity caused by the dissociation of ionic groups with concentration variation with dilution. In case of polyampholytes, the molecules are coiled up to such an

extent that dilution of the polymers do not permit any appreciable change of their shapes and sizes (see viscosity curves).

3.3 ELECTROSTRICTIONAL EFFECT

In 100% neutralized polyacids, the dissociation of counterions is complete and the magnitude of electrostriction effect is highest so that lowest \bar{v}_2 and $\beta\bar{\kappa}_2$ values are observed. For poly(sodium acrylate) and styrene-sodium maleate copolymer these values are observed as ~ 37.0 cc/mole and -50.5×10^{-4} cc/bar/mole, and 140.3 cc/mole and -100.0×10^{-4} cc/bar/mole respectively. By suppression of dissociation of counterions, as was produced effectively with 1.0 M NaCl solution (in 0.1 M NaCl solution, the suppression of dissociation was marginal), the magnitude of electrostriction was somewhat reduced and accordingly, the values were increased to 42.8 cc/mole and -33.0×10^{-4} cc/bar/mole, and 161.6 cc/mole and -46.0×10^{-4} cc/bar/mole respectively. (The potassium salts for two amphoteric polyelectrolytes will be discussed later).

3.4 LIMITING VALUES OF APPARENT MOLAL COMPRESSIBILITY AND APPARENT MOLAL VOLUME OF SOLUTE

At infinite dilution, the apparent molal volume \bar{v}_2^0 and the compressibility $\beta\bar{\kappa}_2^0$ of the solute and the partial molal volume \bar{v}_2^0 and the compressibility $\bar{\kappa}_2^0$ of the solute are identical. The limiting values for solutes obtained by extrapolation of \bar{v}_2 versus c and $\beta\bar{\kappa}_2$ versus c curves to infinite dilution at 25°C

are listed in Table 3.1. The limiting values for methacrylic acid and methacrylamide along with their corresponding polymers⁴⁹ and poly(4-vinyl N-n butylpyridinium bromide)⁵⁰ are listed in the same table for comparison.

3.5 CHANGE OF COMPRESSIBILITY DUE TO POLYMERIZATION

Poly(acrylic acid), polyacrylamide, poly(methacrylic acid) and polymethacrylamide are structurally closely related polymers. The values of apparent molal volume and compressibility for these four polymers are found to differ widely from those of the corresponding monomers. The polymers show a decrease of $\sim 15.0-19.5$ cc/mole for δV_2^0 and of $\sim 5.15 \times 10^{-4}$ to 3.0×10^{-4} cc/bar/mole for $\delta \kappa_2^0$ over the monomer values. It is interesting to note (Table 3.1) that δV_2^0 and $\delta \kappa_2^0$ per methyl group decrease as the molecules grew in size on polymerization. For example, in the case of monomers at 25°C, δV_2^0 and $\delta \kappa_2^0$ per methyl group are 16.9 cc/mole and 0.8×10^{-4} cc/bar/mole respectively in going from acrylic to methacrylic acid and are 16.5 cc/mole and -0.5×10^{-4} cc/bar/mole respectively in going from acrylamide to methacrylamide. While for polymers, δV_2^0 and $\delta \kappa_2^0$ per methyl group are 13.3 cc/mole and 0.25×10^{-4} cc/bar/mole in going from polyacrylic to poly(methacrylic acid), and are 11.6 cc/mole and -0.13×10^{-4} cc/bar/mole in going from polyacrylamide to polymethacrylamide. The lower values of δV_2^0 and $\delta \kappa_2^0$ per methyl group in case of polymers (average 16.7 cc/mole) further substantiate the observation made by Wen and Saito⁶⁵ that water clusters become stronger and better formed

TABLE 3.1

LIMITING VALUES OF APPARENT MOLAL COMPRESSIBILITY AND
APPARENT MOLAL VOLUME OF SOLUTES IN AQUEOUS SOLUTION

AT 25°C

Materials	M_2	Molar volume cc/mole	βV_2^0 cc/mole	$\beta K_2^0 \times 10^4$ cc/bar/mole
Acrylic acid	72.06	63.56 ^a	61.7	6.0
Poly(acrylic acid)	72.06	-	46.7	0.85
Acrylamide	71.03	63.35 ^a	65.5	5.0
Polyacrylamide	71.03	-	50.9	- 3.0
Poly(sodium acrylate) 25% neutralized	77.56	-	45.5	-14.0
Poly(sodium acrylate) 100% neutralized	94.04	-	37.0	-50.5
Poly(sodium acrylate) 100% neutralized, in 0.1 M NaCl solution	94.04	-	37.1	-49.5
Poly(sodium acrylate) 100% neutralized, in 1.0 M NaCl solution	94.04	-	42.8	-33.0

contd.....

Materials	M_2	Molar volume cc/mole	\bar{V}_2^0 cc/mole	$\beta V_2^0 \times 10^4$ cc/bar/mole
Methacrylic acid ^b	86.09	84.79 ^a	78.6	6.8
Poly(methacrylic acid) ^b	86.09	-	60.0	1.1
Methacrylamide ^b	86.116	76.75 ^c	82.0	4.5
Polymethacrylamide ^b	86.116	-	62.5	- 2.37
Styrene-maleic acid copolymer	239	-	172.4	11.0
Styrene-sodium maleate copolymer 50% neutralized	261	-	160.0	-57.5
Styrene-sodium maleate copolymer 100% neutralized	283	-	140.3	-100.0
Styrene-sodium maleate copolymer in 1.0 M NaCl (50% neutralized)	261	-	158.2	-44.0
Styrene-sodium maleate copolymer in 1.0 M NaCl (100% neutralized)	283	-	161.6	-46.0
Acrylic acid-4-vinyl N-n butyl- pyridinium bromide copolymer	262	-	183.9	- 7.0
Acrylic acid-4-vinyl N-n butyl- pyridinium bromide copolymer in 1.0 M KBr solution	262	-	184.3	-23.0

contd.....

Table 3.1 contd.

Materials	H_2	Molar volume cc/mole	\bar{V}_2^0 cc/mole	$\beta_{H_2}^C \times 10^4$ cc/bar/mole
Potassium acrylate-4-vinyl N-n butylpyridinium bromide copolymer	273	-	134.4	-23.0
Potassium acrylate-4-vinyl N-n butylpyridinium bromide copolymer in 0.1 M KBr solution	273	-	134.6	-13.0
Potassium acrylate-4-vinyl N-n butylpyridinium bromide copolymer in 1.0 M KBr solution	273	-	134.8	- 4.0
Methacrylic acid-4-vinyl N-n butylpyridinium bromide copolymer	268	-	134.6	- 3.0
Methacrylic acid-4-vinyl N-n butylpyridinium bromide copolymer in 1.0 M KBr solution	268	-	133.6	13.0
Potassium methacrylate-4-vinyl N-n butylpyridinium bromide copolymer	265	-	176.6	-24.0
Potassium methacrylate-4-vinyl N-n butylpyridinium bromide copolymer in 0.1 M KBr solution	265	-	179.5	-13.0

contd.....

Table 3.1 contd.

Materials	M ₂	Molar volume cc/mole	ρV_2^0 cc/mole	$\rho K_2^0 \times 10^4$ cc/bar/mole
Potassium methacrylate-4-vinyl N-n butylpyridinium bromide copolymer in 1.0 M KBr solution	265	-	165.5	-20.0
Poly(4-vinyl N-n butylpyridinium bromide) ^d	242.17	-	180.1	5.0

a Density obtained from Brandrus and Immergut⁶⁷

b Data from Roy-Chowdhury⁴⁹

c Density of methacrylamide was not available in the literature, therefore value determined in this laboratory i.e. 1.122 gm/cc at 25°C was used.

d Data from Roy-Chowdhury⁵⁰

as the molecules grow larger and larger. They observed, in the case of five tetraalkyl ammonium salts (methyl to pentyl) at 25°C, that ΔV_2^0 per methyl group is an average of 15.7 cc/mole compared to the average of 23.75 cc/mole obtained by Masterion⁶⁸ for aliphatic hydrocarbons in water at 23°C.

Acrylic acid and methacrylic acid (both liquid at room temperature) with molar volumes of 68.56 and 84.79 cc respectively⁶⁷, when dissolved to form an infinitely dilute solution are found (Table 3.1) to decrease in volume by 6.86 and 6.19 cc respectively. This decrease is due to electrostriction. Uncharged molecules, such as acrylamide and methacrylamide (both solids at room temperature) with molar volumes 63.35 and 76.75 cc respectively, when dissolved to form an infinitely dilute solution are found to increase in volume by 2.15 and 5.25 cc respectively, which seems to compare with the usually observed phenomenon of expansion on melting of a solid. If the usual expansion on melting is considered as 10%, the observed volume increase is lower as this may be partly due to electrostrictional effect because of the presence of amphoteric $-\text{CONH}_2$ groups.

3.6 AMPHOTERIC POLYELECTROLYTES

The two amphoteric polyelectrolytes, acrylic acid-4-vinyl N-n butyl pyridinium bromide copolymer and methacrylic acid-4-vinyl N-n butylpyridinium bromide copolymer, are seen strongly acidic. The 0.2% aqueous solutions for AA-ViPy copolymer and MAA-ViPy copolymer were found to have pH of 4.8

and 5.2 respectively. After quaternization, the same copolymers at the same concentration (0.2%) showed the pH as 3.3 and 3.5 respectively. The pH for 0.2% aqueous solution of poly(acrylic acid), poly(methacrylic acid) and poly(4-vinyl N-n butylpyridinium bromide) were measured as 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 neighbours and this behaviour was also observed by Alfrey et al⁶⁹ in the study of a series of amphoteric polyelectrolytes made by copolymerizing N-dialkyl aminoethyl acrylates and methacrylates with acrylic, methacrylic and itaconic acids. During titration the two polyampholytes show good buffer capacity (Titration curves, Figure 3.8) and the water solubility of the ampholytes even in the isoelectric range indicates that the polymers are zwitterionic since it is known that the zwitterionic materials are much more water soluble than their uncharged isomers⁷⁰.

The plots of ϕV_2 and ϕK_2 versus concentration are shown in Figures 3.5 and 3.6 respectively. The ϕK_2 and ϕV_2 values are found as concentration independent. The dissociation of Br^- ions and H^+ ions (only those which were free) were suppressed in excess KBr solution and accordingly the ϕK_2 and ϕV_2 values have increased (Tables 2.17 and 2.22). 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

- 1 AA - ViBu PyBr Copolymer
- 2 PoA - ViBu PyBr Copolymer
- 3 PoA - ViBu PyBr Copolymer in 0.1M KBr Soln
- 4 PoA - ViBu PyBr Copolymer in 1.0M KBr Soln
- 5 MAA - ViBu PyBr Copolymer
- 6 PoMA - ViBu PyBr Copolymer
- 7 PoMA - ViBu PyBr Copolymer in 0.1M KBr Soln
- 8 PoMA - ViBu PyBr Copolymer in 1.0M KBr Soln

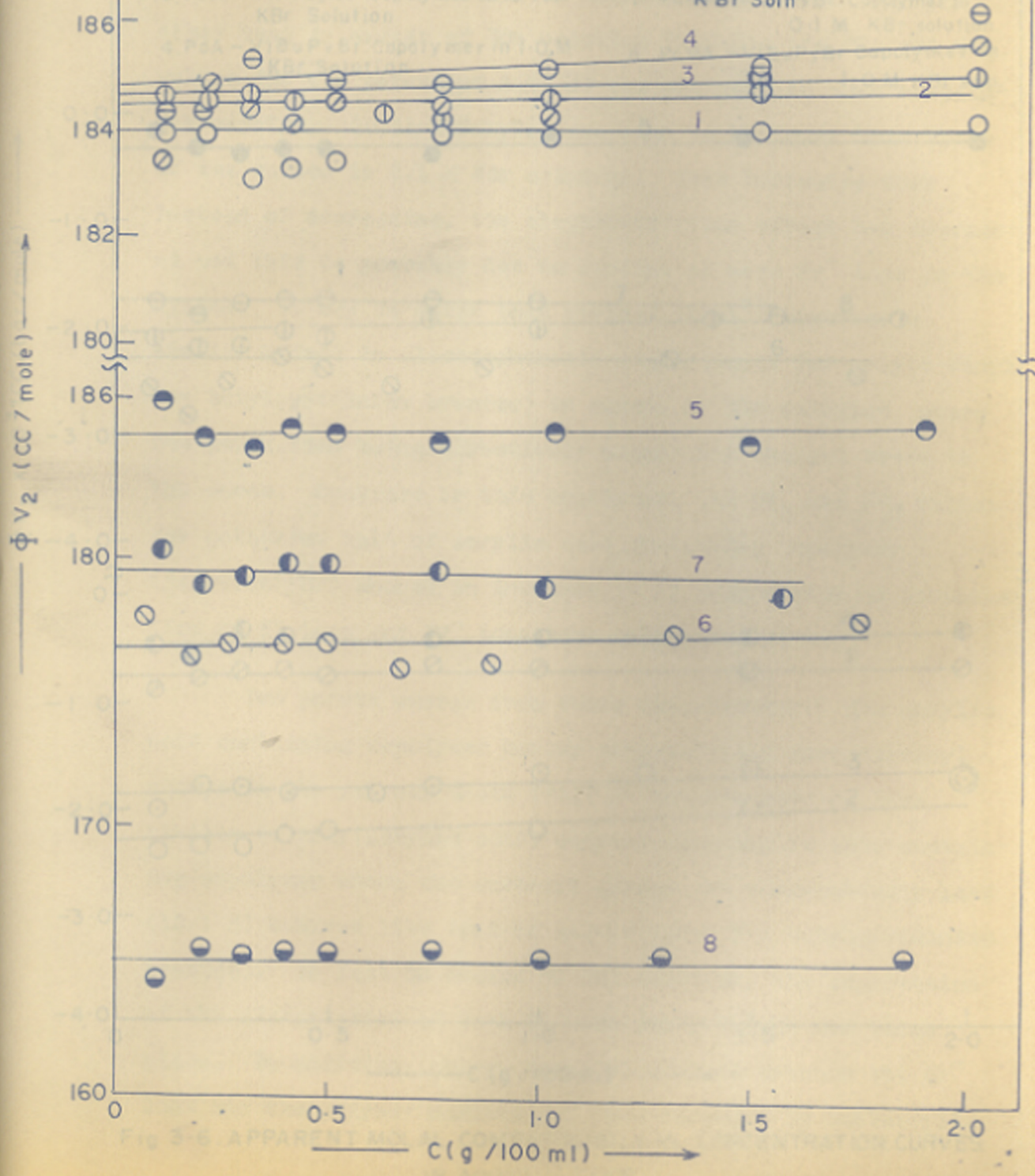


Fig 3-5 APPARENT MOLAL VOLUME Vs. CONCENTRATION CURVES IN AQUEOUS SOLUTION

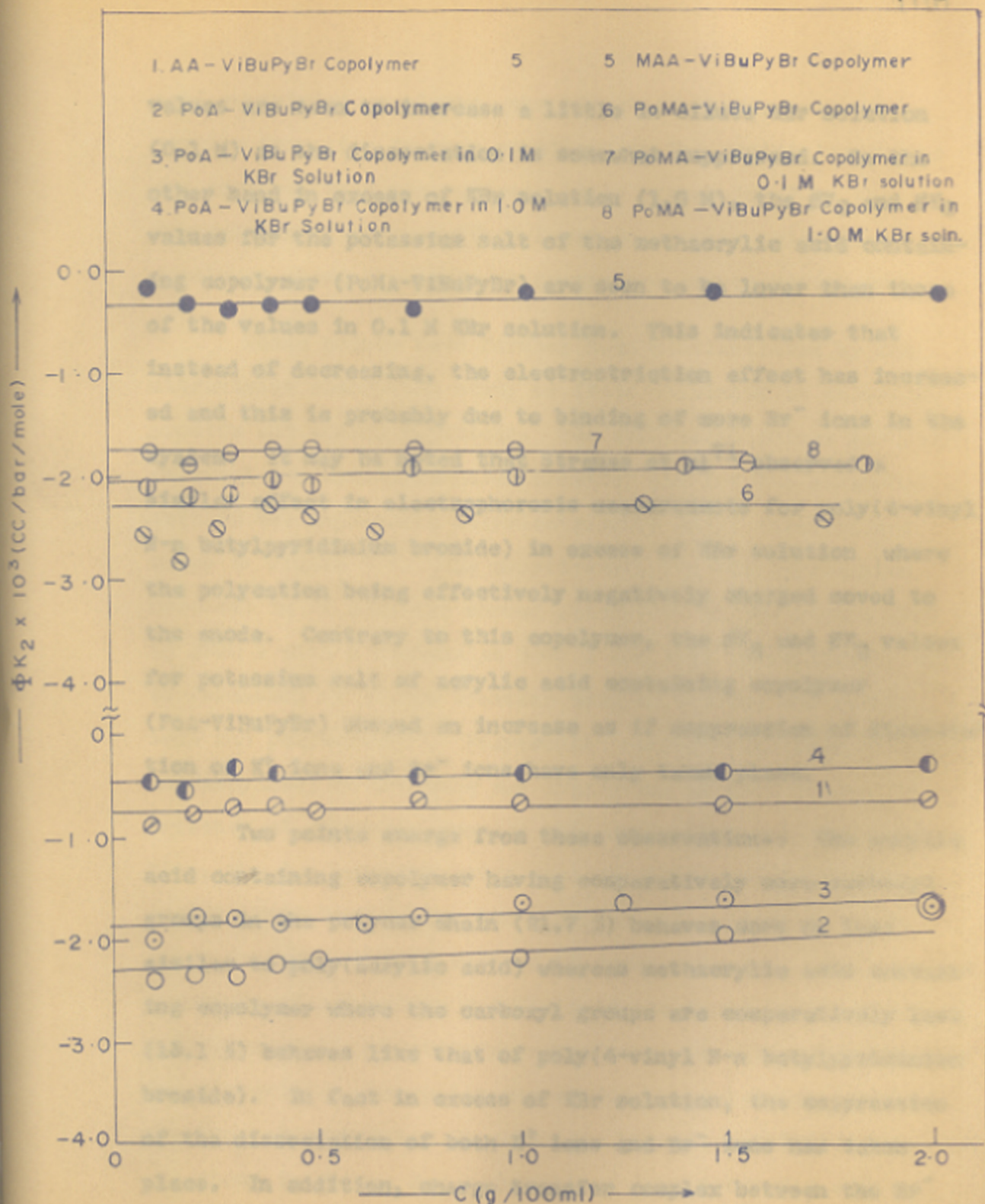


Fig 3.6. APPARENT MOLAL COMPRESSIBILITY Vs. CONCENTRATION CURVES IN AQUEOUS SOLN.

values are seen to increase a little in dilute KBr solution (0.1 M) as the dissociation is somewhat suppressed. On the other hand in excess of KBr solution (1.0 M), the ϕV_2 and ϕK_2 values for the potassium salt of the methacrylic acid containing copolymer (PoMA-ViBuPyBr) are seen to be lower than those of the values in 0.1 M KBr solution. This indicates that instead of decreasing, the electrostriction effect has increased and this is probably due to binding of more Br^- ions in the system. It may be noted that Strauss et al.⁷¹ observed a similar effect in electrophoresis measurements for poly(4-vinyl N-n butylpyridinium bromide) in excess of 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 suppression of dissociation of K^+ ions and Br^- ions have only taken place.

Two points emerge from these observations: The acrylic acid containing copolymer having comparatively more carboxyl groups in the polymer chain (21.7 %) behaves more or less similar to poly(acrylic acid) whereas methacrylic acid containing copolymer where the carboxyl groups are comparatively less (15.1 %) behaves like that of poly(4-vinyl N-n butylpyridinium bromide). In fact in excess of KBr solution, the suppression of the dissociation of both K^+ ions and Br^- ions has taken place. In addition, charge transfer complex between the Br^- ions and the polymer nucleus has been formed. In methacrylic

acid containing copolymer, the effect of charge transfer complex formation is more prominent as the pyridinium groups are comparatively more whereas it is overshadowed by the suppression of charge effect found in acrylic acid containing copolymer where the carboxyl groups are comparatively more.

These points have further been 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 3.7. 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 formation of charge transfer complex between the iodide ions and polycation⁶⁴. Poly(sodium acrylate and poly(sodium methacrylate) do not show any absorption in this region in presence of chloride, bromide and iodide ions. In KI solution, the two polyampholytes also show absorption in the same region, 2700-3800 Å, but the magnitude of extinction coefficient is found greatly reduced in these polymers. The magnitude of extinction coefficients are found in the order of poly(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 3.8. Absorption does occur for each of the polyampholytes due to charge transfer complex formation in

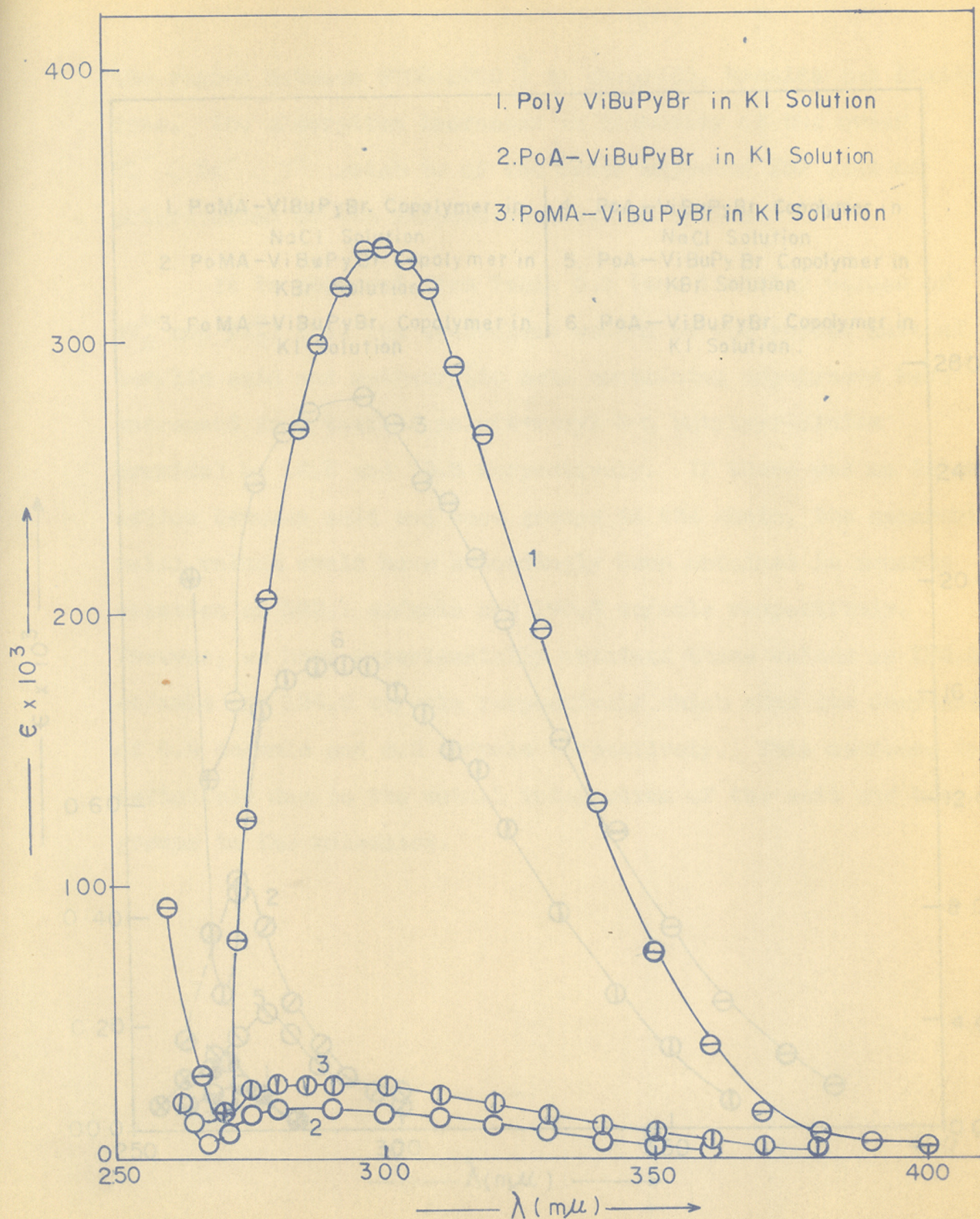
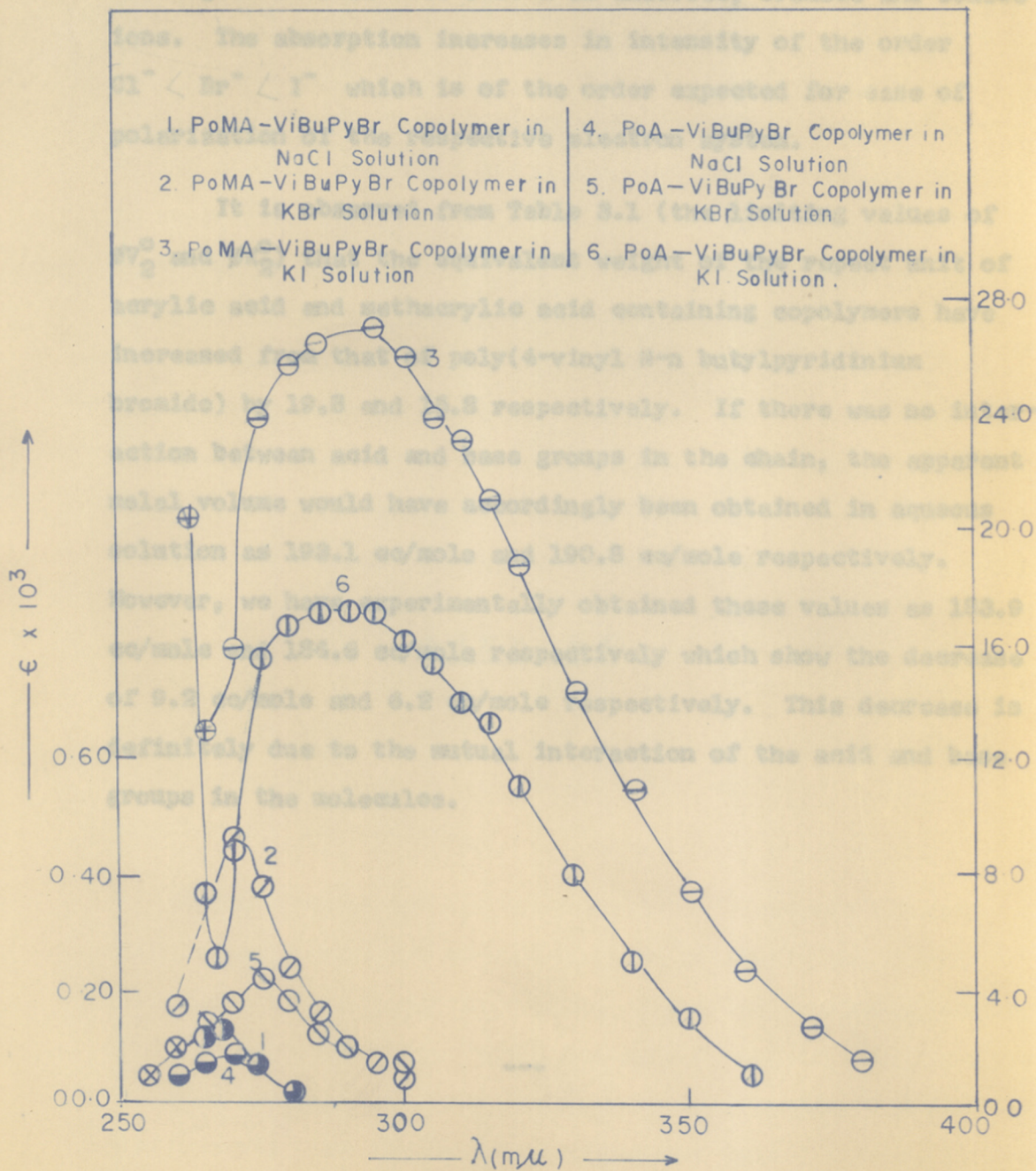


Fig 3.7 ULTRAVIOLET ABSORPTION CURVES

Fig 3.8 ULTRAVIOLET ABSORPTION CURVES

the region between 2700-3800 \AA in chloride, bromide and iodide ions. The absorption increases in intensity of the order $\text{Cl}^- < \text{Br}^- < \text{I}^-$ which is of the order expected for ease of polarization of the respective electron system.

It is observed from Table 3.1 (the limiting values of \bar{v}_2^0 and \bar{v}_2^c) that the equivalent weight of the repeat unit of acrylic acid and methacrylic acid containing copolymers have increased from that of poly(4-vinyl N-n butylpyridinium bromide) by 19.8 and 15.8 respectively. If there was no interaction between acid and base groups in the chain, the apparent molal volume would have accordingly been obtained in aqueous solution as 193.1 cc/mole and 190.3 cc/mole respectively. However, we have experimentally obtained these values as 183.9 cc/mole and 184.6 cc/mole respectively which show the decrease of 9.2 cc/mole and 6.2 cc/mole respectively. This decrease is definitely due to the mutual interaction of the acid and base groups in the molecules.

S U M M A R Y

S U M M A R Y

The studies have been made on the adiabatic compressibility of some polyacids and a few amphoteric polyelectrolytes in aqueous solution. The materials used were poly(acrylic acid) and polyacrylamide along with their corresponding monomers, two poly(sodium acrylates) obtained by neutralizing the polyacid to the extent 25% and 100% with sodium hydroxide, a 1:1 copolymer of styrene and maleic acid and two of their 50% and 100% neutralized sodium salts and two synthetic amphoteric polyelectrolytes obtained as the copolymers of 4-vinyl N-n butylpyridinium bromide with acrylic acid and methacrylic acid.

The adiabatic compressibility has been determined from the ultrasonic velocity and density data. The ultrasonic velocity at 25°C was measured by employing a precision ultrasonic interferometer and the density was measured with Ostwald-type pycnometers.

The density and ultrasonic velocity increase linearly with concentration and accordingly the adiabatic compressibility decreases with concentration. The total adiabatic compressibility of poly(acrylic acid) and styrene-maleic acid copolymer are more or less the same. Similar to the results of viscosity measurements, the sodium salts of styrene-maleic acid copolymers showed comparatively higher compressibilities than those of the corresponding poly(sodium acrylates). The decrease of compressibility for electrolytes is due to the action on water of the

electric field around each ion. The comparatively larger decrease in compressibility in case of polyacrylamide, an uncharged polymer with respect to polyacids may be due to the presence of amphoteric $-\text{CONH}_2$ groups in the polymer chain. The two amphoteric polyelectrolytes acrylic acid-4-vinyl N-n butylpyridinium bromide copolymer and methacrylic acid-4-vinyl N-n butylpyridinium bromide copolymer show abnormally low reduced viscosity (0.03-0.07 dl/gm), the total adiabatic compressibility of them is seen lower than that of polyacrylic acid and styrene-maleic acid copolymer.

The compressibility decrement per unit concentration $(\beta_1 - \beta)/c$ are seen almost constant for all the polymers studied throughout the entire concentration range. On neutralization of the carboxyl groups in amphoteric polyelectrolytes with potassium hydroxide, the $(\beta_1 - \beta)/c$ values are not increased as high as is found in case of poly(sodium acrylates) or of sodium salts of styrene-maleic acid copolymer and this is because of the fact that the carboxyl groups in polyampholytes are only 15-20%. It has been observed that the number and nature of ions contribute more to the compressibility data than the shape and size of the molecules. In case of polyacids and their partially and fully neutralized salts, the $(\beta_1 - \beta)/c$ values remain unchanged in all concentrations even though the shape and size of the molecules have changed considerably on dilution. Only when dissociation or suppression of ions takes place, the $(\beta_1 - \beta)/c$ value changes.

The apparent molal volume ϕV_2 and apparent molal compressibility βK_2 for monomers and polymers are seen to be almost concentration independent and so are the sodium salts of the polyacids. The ϕV_2 and βK_2 values for the two amphoteric polyelectrolytes and their potassium salts obtained by neutralizing them (100%) with potassium hydroxide, are also seen concentration independent. In aqueous solution two types of solute-solvent interaction, the charge effect and the hydrophobic effect have taken place. Poly(acrylic acid) and polyacrylamide are structurally closely related polymers and water must be bound to them through polar groups either by hydrogen bonding or by dipole attraction. The two amphoteric polyelectrolytes have $-\text{COOH}$ and $-\text{C}_5\text{H}_4\text{N}^+\text{C}_4\text{H}_9\text{Br}^-$ groups in the chain and are capable of forming hydrogen bonded structure. The hydrophobic part of the solute because of compact orientation of water and solute in the boundary region, causes a decrease in solvent volume and therefore in the values of ϕV_2 and βK_2 . On the other hand, intermolecular hydrogen bonding between the polar groups increases the volume and counter balances the hydrophobic effect. Because of these two counteracting effects, the observed ϕV_2 and βK_2 values are seen to be concentration independent. In 100% neutralized polyacids, the dissociation of counterions is complete and the magnitude of electrostriction is highest so that lowest ϕV_2 and βK_2 values are observed. For poly(sodium acrylate) and styrene-sodium maleate copolymer these values are observed as 37.0 cc/mole and -50.5×10^{-4} cc/bar/mole, and 140.3 cc/mole and -100.0×10^{-4} cc/bar/mole

respectively. However, the dissociation and therefore the magnitude of electrostriction are somewhat reduced in presence of 1.0 M NaCl solution, and accordingly the values increase to 42.8 cc/mole and -33.0×10^{-4} cc/bar/mole, and 161.6 cc/mole and -46.0×10^{-4} cc/bar/mole respectively. The limiting values for the apparent molal volume and apparent molal compressibility for polymers show a considerable decrease over those of the monomers. The values of ϕV_2^0 and ϕK_2^0 per methyl group are less in the polymers than in monomers, and this has been attributed to water clusters that become stronger and better formed as the molecules grow larger and larger. The molar volumes of acrylic acid and methacrylic acid are decreased, while those of acrylamide and methacrylamide are increased when dissolved in water to form an infinitely dilute solution.

The two amphoteric polyelectrolytes are seen strongly acidic and the strength of the acid group has been increased by the presence of the base group neighbours. In binary copolymers, the acid and base groups interact with each other and reduce their effect as is seen very prominently in the viscosity data. The potassium salts for these amphoteric polyelectrolytes showed lowest ϕV_2 and ϕK_2 values as the electrostriction is highest here and these values showed a slight increase in presence of dilute KBr solution (0.1 M) as the dissociation is somewhat reduced. However, in excess KBr solution (1.0 M) the acrylic acid containing copolymer having comparatively more carboxyl groups (21.7 %) in the polymer chain

behaves more or less similar to poly(acrylic acid), whereas the poly(methacrylic acid) containing copolymer with only 15.1% carboxyl groups behaves closely to that of poly(4-vinyl N-n butylpyridinium bromide). These amphoteric polyelectrolytes showed optical absorption in the region 2700 to 3800 Å in presence of chloride, bromide and iodide ions which are due to the formation of charge transfer complex between the halide ions and the polymer nucleus. The magnitude of extinction coefficient for these two polyampholytes is much lower than that of poly(4-vinyl N-n butylpyridinium bromide). The limiting values of apparent molal volume, \bar{v}_2^0 for acrylic and methacrylic acid containing copolymers are seen 183.9 cc/mole and 184.6 cc/mole respectively. These experimentally determined values fall short of 9.2 cc/mole and 6.2 cc/mole from the calculated values (if no interaction between acid and base groups is assumed) which are due to mutual interaction of acid and base groups in the polymer chain.

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ACKNOWLEDGEMENTS

It gives me immense pleasure to record my deep sense of gratitude to Dr. Phanibhusan Roy-Chowdhury for his meticulous planning of this investigation and methodical guidance which made this work possible.

I am thankful to Dr. H.B. Mathur, Assistant Director, National Chemical Laboratory, Poona, for his constant encouragement.

My sincere thanks are due to the Director, Explosives Research and Development Laboratory, Poona-21, for his permission to undertake this research work. Thanks are due to Dr. E.S. Jog of E.R.D.L., Poona-21 for his encouragement.

I am also thankful to the M.E.S. College of Arts & Sciences authorities for allowing me to continue this work and adjusting my work schedule suitably during the course of this investigation.

Heartly thanks are due to Shri V.P. Shiralkar, National Chemical Laboratory, Poona-8 for his cooperation.

I am grateful to the Director, National Chemical Laboratory, Poona-8 for allowing me to use the facilities of the Laboratory and submit this investigation in the form of a thesis.

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The Adiabatic Compressibility of Poly(acrylic Acid) and Polyacrylamide in Aqueous Solution

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Synopsis

The results of adiabatic compressibility measurements of poly(acrylic acid) and polyacrylamide along with their corresponding monomers and two poly(sodium acrylates) obtained by neutralizing the polyacid 25% and 100% with sodium hydroxide have been described. The total adiabatic compressibility of poly(acrylic acid) solution is higher than that of the corresponding salt solutions or of polyacrylamide solutions. The unneutralized acid does not dissociate much, even in dilute solution, and the magnitude of electrostriction in polyamide is greater than in acid. The ΦV_2 and ΦK_2 values for monomers and polymers are seen to be almost concentration independent, and so are the sodium salts of the polyacid. Poly(acrylic acid) and poly(acrylamide) are structurally closely related polymers, and water must be bound to them through polar groups either by hydrogen bonding or by dipole attraction. The hydrophobic part of the solute, because of compact orientation of water and solute in the boundary region, causes a decrease in solvent volume and therefore in the values of ΦV_2 and ΦK_2 . On the other hand, intermolecular hydrogen bonding between the polar groups increases the volume and counterbalances the hydrophobic effect. Because of these two counteracting effects, the observed ΦV_2 and ΦK_2 values are seen to be concentration independent. Contrary to the observation with poly(methacrylic acid)¹ and its sodium salts, the solvated counter-ions in case of poly(sodium acrylates) make no special contribution in the dilute region. In 100% neutralized polyacid, the dissociation of counterions is complete, and the magnitude of electrostriction is highest in this case. Accordingly, lowest ΦV_2 and ΦK_2 values (37.0 cc/mole and -50.50×10^{-3} cc bar⁻¹ mole⁻¹) are observed. However, the dissociation and therefore the magnitude of electrostriction are somewhat reduced in the presence of 1.0M NaCl solution; and, accordingly, the values increase to 42.80 cc/mole and -33.0×10^{-3} cc bar⁻¹ mole⁻¹, respectively. The limiting values for the apparent molal volume and the apparent molal compressibility for the polymers show a considerable decrease over those of the monomers. The values of ΦV_2^0 and ΦK_2^0 per methyl group are less in the polymers than in the monomers, and this has been attributed to water clusters that become stronger and better formed as the molecules grow larger and larger. The molar volumes of acrylic acid and methacrylic acid are decreased, while those of acrylamide and methacrylamide are increased when dissolved in water to form an infinitely dilute solution.

INTRODUCTION

In a program for the systematic study of adiabatic compressibility of polyelectrolytes in aqueous solution in this laboratory, the results for poly(methacrylic acid) and poly(methacrylamide) along with those for their monomers were reported in earlier papers.^{1,2} However, poly(methacrylic

acid), poly(methacrylamide), poly(acrylic acid), and polyacrylamide are structurally closely related and they have functional groups which can form a hydrogen-bonded structure. Silberberg and co-workers³ have studied the temperature dependence of the 90-degree scattering of light and of the viscosity of the dilute aqueous solutions of these four hydrogen-bonding polymers and observed that the results of poly(methacrylic acid) were at variance with those of the other three. Besides, the statistical chain element length for poly(methacrylic acid) and poly(methacrylamide) was found to be half that of poly(acrylic acid) under corresponding condition. It was explained that, because of the presence of a methyl group in the α -position, intramolecular hydrogen bonding may probably have taken place. Since the adiabatic compressibility data of the last two polymers, i.e., poly(acrylic acid) and polyacrylamide, and of their monomers have not been reported so far, the results obtained by us are reported in this paper.

EXPERIMENTAL

The apparatus and technique were essentially the same as previously described,¹ i.e., the ultrasonic velocities were measured by an ultrasonic interferometer and the density with Ostwald-type pycnometers. The adiabatic compressibility β_s of the liquid was obtained by the relation

$$\beta_s = \frac{1}{u^2 d}$$

where u and d are velocity and density, respectively.

Poly(acrylic acid) was prepared by polymerizing freshly distilled monomer (30% w/w) in dioxane solution using 0.5% benzoyl peroxide as initiator at 55°C with constant stirring in nitrogen atmosphere. The product was dissolved in methanol, precipitated with ether, and dried in vacuo to constant weight. The unfractionated sample was used for adiabatic compressibility measurements; it had a molecular weight of 1.504×10^4 as determined from the intrinsic viscosity data of the sodium salt in 1.0M NaCl solution.⁴

Poly(sodium acrylate) solutions with different degrees (25% and 100%) of neutralized products were prepared by adding calculated amounts of sodium hydroxide to the polyacid.

Polyacrylamide was prepared by polymerizing the monomer (10% solution) in ethanol solution using azobisisobutyronitrile (0.5%) as initiator at 60°C with constant stirring and bubbling nitrogen throughout. The polymer precipitated out, was washed with fresh alcohols several times, and was dried in vacuo over P_2O_5 to constant weight. This polymer was very hygroscopic. The molecular weight of the sample was 2.423×10^4 as obtained by measuring the intrinsic viscosity in aqueous solution.⁵

RESULTS AND DISCUSSION

The results of the adiabatic compressibility measurements are summarized in Tables I to VIII. The materials used were the two monomers, acrylic acid (AA) and acrylamide (AAm), with their corresponding polymers, poly(acrylic acid) (PAA) and polyacrylamide (PAAm), and two sodium salts of poly(acrylic acid) (PSA) obtained by neutralizing the polyacid to different extents. Tables I and II give the data for acrylic acid and acrylamide, while Tables III and IV give similar data for the corresponding polymers in aqueous solution. It is observed that the total adiabatic

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

c , g/dl	d , g/cm ³	ΦV_2 , cm ³ /mole	u , m/sec	β , bar ⁻¹ $\times 10^6$	$(\beta_1 - \beta)/c$ $\times 10^7$	ΦK_2 , cm ³ bar ⁻¹ mole ⁻¹ $\times 10^4$
0.0000	0.99705	61.70 ^a	1496.05	44.812	—	6.00 ^a
0.1028	0.99720	61.728	1496.42	44.783	2.811	7.257
0.2056	0.99735	61.728	1496.84	44.751	2.952	6.315
0.3084	0.99750	61.728	1497.30	44.717	3.080	5.478
0.4112	0.99765	61.728	1497.63	44.690	2.952	6.394
0.5140	0.99778	62.009	1498.04	44.660	2.951	6.503
0.7437	0.99810	61.778	1498.92	44.593	2.937	6.682
1.0280	0.99855	61.728	1500.08	44.504	2.990	6.127
1.4875	0.99912	62.216	1501.88	44.372	2.954	6.575
1.9833	0.99984	62.106	1503.69	44.234	2.914	6.825

^a Extrapolated value.

TABLE II
Summary of Results for Acrylamide in Aqueous Solution
at 25°C ($M_2 = 71.08$)

c , g/dl	d , g/cm ³	ΦV_2 , cm ³ /mole	u , m/sec	β , bar ⁻¹ $\times 10^6$	$(\beta_1 - \beta)/c$ $\times 10^7$	ΦK_2 , cm ³ bar ⁻¹ mole ⁻¹ $\times 10^4$
0.0000	0.99705	65.50 ^a	1496.05	44.812	—	5.00 ^a
0.10005	0.99713	65.600	1496.57	44.777	3.488	5.480
0.2001	0.99722	65.233	1497.10	44.741	3.523	4.864
0.3001	0.99729	65.589	1497.56	44.711	3.365	5.522
0.4000	0.99738	65.409	1498.19	44.669	3.572	3.919
0.5002	0.99747	65.304	1498.59	44.630	3.624	3.421
1.0001	0.99790	65.231	1500.51	44.484	3.276	5.925
1.5001	0.99832	65.255	1503.61	44.305	3.374	5.277
2.0001	0.99877	65.160	1505.97	44.147	3.321	5.603

^a Extrapolated value.

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

c , g/dl	d , g/cm ³	ΦV_2 , cm ³ /mole	u , m/sec	β , bar ⁻¹ $\times 10^6$	$(\beta_1 - \beta)/c$ $\times 10^7$	ΦK_2 , cm ³ bar ⁻¹ mole ⁻¹ $\times 10^4$
0.0000	0.99705	46.70 ^a	1496.05	44.812	—	0.85 ^a
0.0942	0.99737	47.722	1496.26	44.785	2.866	0.850
0.1884	0.99773	46.571	1496.41	44.759	2.813	0.850
0.3015	0.99813	46.864	1496.64	44.728	2.687	0.792
0.4020	0.99847	46.744	1496.84	44.701	2.761	1.059
0.5034	0.99885	46.430	1497.01	44.673	2.761	1.083
0.8054	0.99993	46.429	1497.69	44.585	2.817	0.512
1.2886	1.00169	46.193	1498.59	44.453	2.786	0.687
1.7182	1.00326	46.109	1499.33	44.340	2.747	0.888

^a Extrapolated value.

TABLE IV
Summary of Results for Polyacrylamide in Aqueous Solution
at 25°C ($M_2 = 71.08$)

c , g/dl	d , g/cm ³	ΦV_2 , cm ³ /mole	u , m/sec	β , bar ⁻¹ $\times 10^6$	$(\beta_1 - \beta)/c$ $\times 10^7$	ΦK_2 , cm ³ bar ⁻¹ mole ⁻¹ $\times 10^4$
0.0000	0.99705	50.90 ^a	1496.05	44.812	—	-3.00 ^a
0.1035	0.99735	50.627	1496.46	44.774	3.652	-3.445
0.2670	0.99764	50.971	1496.88	44.735	3.691	-3.599
0.3105	0.99793	51.086	1497.25	44.700	3.581	-2.727
0.4140	0.99825	50.627	1497.67	44.661	3.638	-3.137
0.5175	0.99855	50.627	1498.14	44.620	3.708	-3.691
0.7752	0.99925	51.058	1498.95	44.540	3.505	-2.075
1.0336	1.00000	51.288	1500.10	44.438	3.613	-2.846
1.5493	1.00149	50.860	1502.13	44.252	3.609	-2.860
2.0657	1.00297	51.032	1504.15	44.069	3.597	-2.763

^a Extrapolated value.

compressibility of poly(acrylic acid) solution is higher than that of the corresponding salt solutions or of polyacrylamide solutions. The data for 25% and 100% neutralized poly(acrylic acid) solutions are given in Tables V and VI, respectively. The decreased compressibility of electrolytes is due to the action on water of the electric field around each ion; the electrostatic pressure causes an additional contraction of the water in the same way as is caused by increasing external pressure. However, the comparatively larger decrease in compressibility in case of polyamide with respect to polyacid may be due to the presence of amphoteric $-\text{CONH}_2$ groups in the polymer chain. The unneutralized acid does not dissociate much, even in

TABLE V
Summary of Results for Poly(sodium Acrylate), $\alpha = 0.25$,
in Aqueous Solution at 25°C ($M_2 = 77.56$)

c , g/dl	d , g/cm ³	ΦV_2 , cm ³ /mole	u , m/sec	β , bar ⁻¹ $\times 10^6$	$(\beta_1 - \beta)/c$ $\times 10^7$	ΦK_2 , cm ³ bar ⁻¹ mole ⁻¹ $\times 10^4$
0.0000	0.99705	45.50 ^a	1496.05	44.812	—	-14.00 ^a
0.0949	0.99743	46.658	1496.61	44.761	5.329	-20.41
0.1899	0.99783	45.839	1496.74	44.735	4.018	-10.53
0.3165	0.99836	45.593	1497.55	44.663	4.689	-15.87
0.4114	0.99876	45.461	1497.77	44.632	4.361	-13.38
0.6330	0.99970	45.224	1498.83	44.527	4.493	-14.61
0.7815	1.00032	45.241	1499.31	44.471	4.357	-13.48
1.0159	1.00141	44.403	1500.62	44.345	4.591	-15.71
1.5630	1.00366	44.893	1502.84	44.115	4.455	-14.42

Extrapolated value.

TABLE VI
Summary of Results for Poly(sodium Acrylate), $\alpha = 1.0$,
in Aqueous Solution at 25°C ($M_2 = 94.04$)

c , g/dl	d , g/cm ³	ΦV_2 , cm ³ /mole	u , m/sec	β , bar ⁻¹ $\times 10^6$	$(\beta_1 - \beta)/c$ $\times 10^7$	ΦK_2 , cm ³ bar ⁻¹ mole ⁻¹ $\times 10^4$
0.0000	0.99705	37.00 ^a	1496.05	44.812	—	-50.50 ^a
0.1024	0.99769	35.369	1496.82	44.739	7.305	-52.80
0.2049	0.99832	37.240	1497.57	44.664	7.213	-51.72
0.3013	0.99888	37.032	1498.28	44.596	7.142	-50.46
0.3964	0.99945	37.213	1499.00	44.528	7.149	-50.65
0.4955	1.00005	37.213	1499.76	44.456	7.169	-50.69
0.7743	1.00174	37.189	1501.70	44.267	7.036	-49.49
0.0188	1.00325	36.920	1503.86	44.073	7.247	-51.59
0.4982	1.00624	36.463	1507.09	43.754	7.058	-50.02
0.9976	1.00914	37.234	1511.10	43.397	7.077	-49.88
0.6635	1.01331	36.740	1516.26	42.925	7.083	-50.13

Extrapolated value.

in solution, and the magnitude of electrostriction in polyamide is greater than in acid. Accordingly, the apparent molal compressibility of amide is slightly negative, in contrast to that of the polyacid, which is positive in dilute solution.

The apparent molal volume of the solute, ΦV_2 , and its apparent molal compressibility, ΦK_2 , have been computed by the following equations:

$$\Phi V_2 = (M_2/d_1)[1 - (100/c)(d - d_1)]$$

$$\Phi K_2 = M_2\beta_1\{(100/c)[(\beta/\beta_1) - (d/d_1)] + (1/d_1)\}$$

TABLE VII
Summary of Results for Poly(sodium Acrylate), $\alpha = 1.0$,
in 0.1M NaCl Solution at 25°C ($M_2 = 94.04$)

c , g/dl	d , g/cm ³	ΦV_2 , cm ³ /mole	u , m/sec	β , bar ⁻¹ $\times 10^6$	$(\beta_1 - \beta)/c$ $\times 10^7$	ΦK_2 , cm ³ bar ⁻¹ mole ⁻¹ $\times 10^4$
0.0000	1.00115	37.10 ^a	1502.30	44.257	—	-49.50 ^a
0.0877	1.00170	35.023	1503.01	44.191	7.537	-55.24
0.1755	1.00222	36.663	1503.76	44.124	7.578	-55.18
0.2581	1.00272	36.794	1504.29	44.071	7.210	-51.63
0.3396	1.00322	36.677	1504.87	44.015	7.140	-50.83
0.5306	1.00435	37.282	1506.37	43.878	7.145	-50.75
0.7185	1.00551	36.932	1507.58	43.757	6.959	-49.04
0.9580	1.00691	37.259	1509.43	43.590	6.972	-48.97
1.4739	1.01003	37.340	1512.57	43.275	6.668	-46.19
2.2109	1.01442	37.553	1518.64	42.744	6.847	-47.77

^a Extrapolated value.

TABLE VIII
Summary of Results for Poly(sodium Acrylate), $\alpha = 1.0$,
in 1.0M NaCl Solution at 25°C ($M_2 = 94.04$)

c , g/dl	d , g/cm ³	ΦV_2 , cm ³ /mole	u , m/sec	β , bar ⁻¹ $\times 10^6$	$(\beta_1 - \beta)/c$ $\times 10^7$	ΦK_2 , cm ³ bar ⁻¹ mole ⁻¹ $\times 10^4$
0.0000	1.03709	42.80 ^a	1557.30	39.759	—	-33.00 ^a
0.1059	1.03765	42.727	1558.06	39.699	5.685	-36.68
0.2118	1.03820	43.154	1558.65	39.648	5.255	-32.26
0.3025	1.03870	42.416	1559.26	39.598	5.335	-33.29
0.4033	1.03923	42.562	1559.99	39.541	5.420	-34.03
0.5378	1.03992	42.961	1560.84	39.471	5.351	-33.26
0.7683	1.04125	41.580	1562.07	39.359	5.210	-32.47
1.0976	1.04302	41.687	1564.54	39.168	5.385	-34.09
1.6886	1.04614	42.079	1568.43	38.858	5.338	-33.47

^a Extrapolated value.

where M_2 is the molecular weight of the monomer as well as the polymer repeat unit; c is the concentration expressed in g/dl; and d , d_1 , β , and β_1 are the density and compressibility of the solution and solvent, respectively.

The plots of ΦV_2 and ΦK_2 versus concentration are shown in Figures 1 and 2, respectively. The ΦV_2 and ΦK_2 values for monomers and polymers are seen to be almost concentration independent. The insensitivity of the ΦV_2 and ΦK_2 values toward concentration are also seen for the sodium salt of poly(acrylic acid). According to Wen and Saito,⁶ the hydrophobic effect tends to lower ΦV_2 with concentration, while the charge effect tends to increase ΦV_2 with concentration, especially with smaller electrolytes;⁷ the

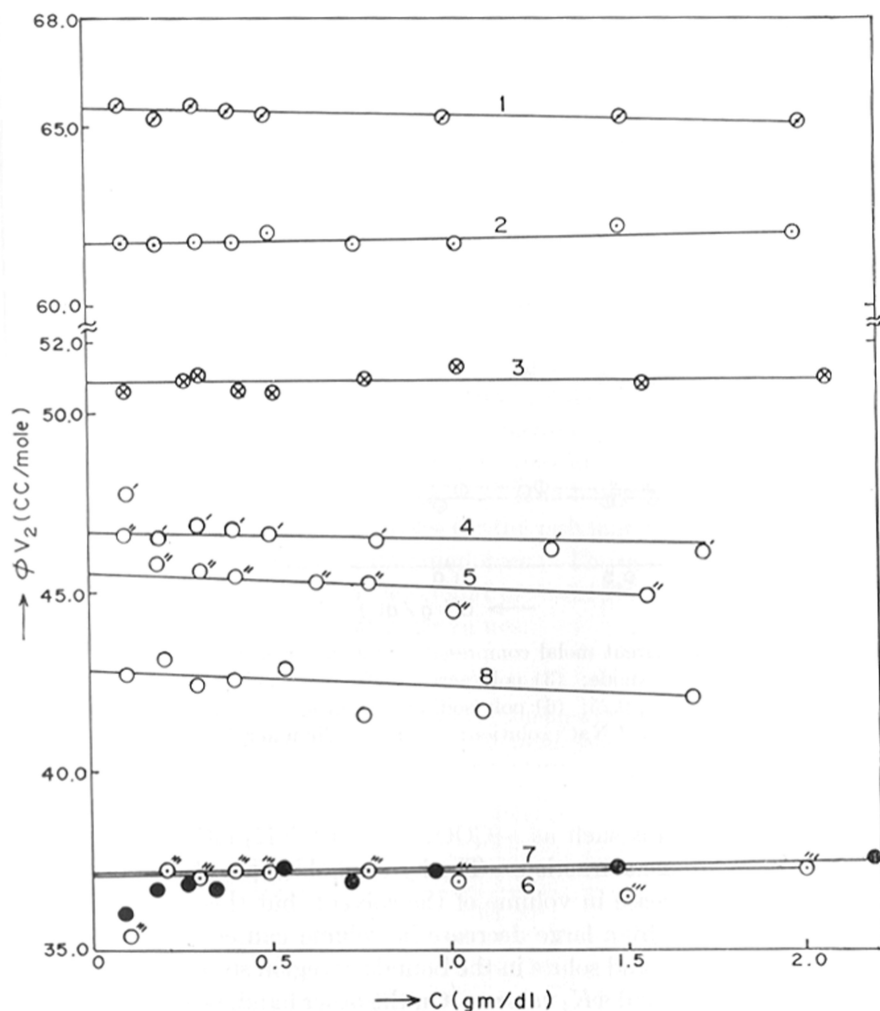


Fig. 1. Plots of apparent molal volume as a function of concentration: (1) acrylamide; (2) acrylic acid; (3) polyacrylamide; (4) poly(acrylic acid); (5) poly(sodium acrylate), $\alpha = 0.25$; (6) poly(sodium acrylate), $\alpha = 1.0$; (7) poly(sodium acrylate), $\alpha = 1.0$ 0.1M NaCl solution; (8) poly(sodium acrylate), $\alpha = 1.0$ in 1.0M NaCl solution.

sensitivity toward concentration in case of some large tetraalkylammonium salts was described as a delicate balancing between these two effects. In fact, Ise and Okubo⁸ have explained the observed insensitivity of ΦV_2 toward concentration in case of poly(acrylic acid) and other poly(diodium acrylates) as the result of balancing of two opposite effects, i.e., hydrophobic effect and charge effect. However, the insensitivity of ΦV_2 and \bar{v}_2 toward concentration in case of uncharged polyamides (and also poly(acrylic acid) and its partially and fully neutralized sodium salts) may be explained in the following way: poly(acrylic acid) and polyacrylamide are actually closely related polymers, and water must be bound to them

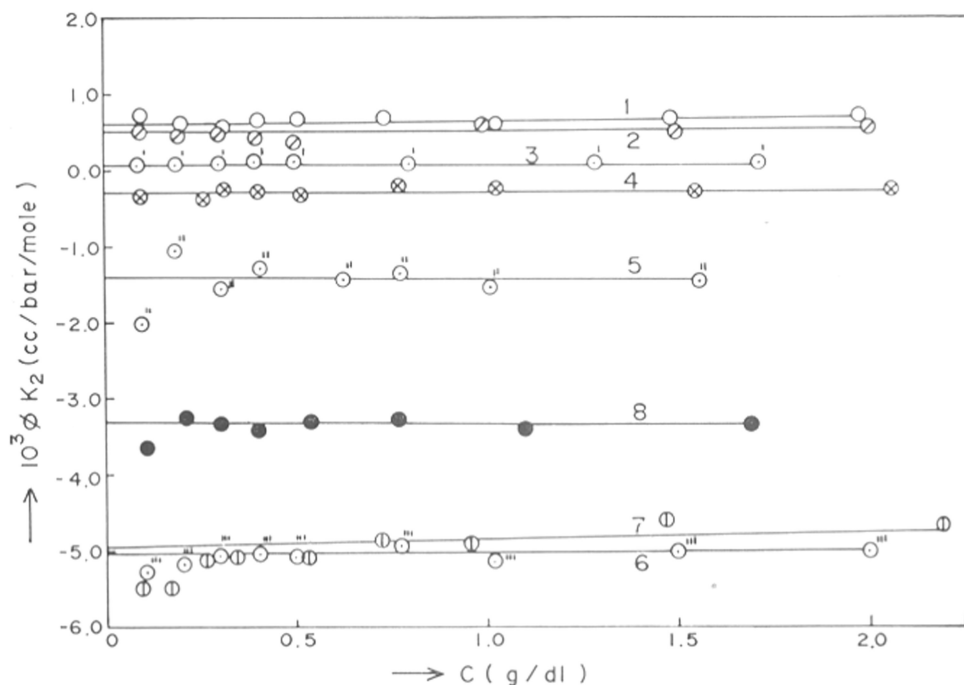


Fig. 2. Plots of apparent molal compressibility as a function of concentration: (1) acrylic acid; (2) acrylamide; (3) poly(acrylic acid); (4) polyacrylamide; (5) poly(sodium acrylate), $\alpha = 0.25$; (6) poly(sodium acrylate), $\alpha = 1.0$; (7) poly(sodium acrylate), $\alpha = 1.0$ in $0.1M$ NaCl solution; (8) poly(sodium acrylate), $\alpha = 1.0$ in $1.0M$ NaCl solution.

through polar groups such as $-\text{COOH}$ or $-\text{CONH}_2$ either by hydrogen bonding or by dipole attraction. The hydrophobic part of the solute must give rise to an increase in volume of the solvent, but this volume increase will be outweighed by a large decrease in volume caused by the compact orientation of water and solute in the boundary region so that the net result is a decrease in ΦV_2 and ΦK_2 values. On the other hand, polar groups in the polymer chain bind the water molecules through hydrogen bridges, and the increase in volume due to this intermolecular hydrogen bonding counterbalances the hydrophobic effect. Because of these two counteracting effects, the observed ΦV_2 and ΦK_2 values are seen to be concentration independent. This assumption is further substantiated by the experimental observation that in case of polyacid and its salts, the water clusters around the polyions are not disturbed appreciably by a variation in charge intensity caused by dissociation of ionic groups with concentration variation upon dilution. Contrary to the observations with poly(methacrylic acid) and its sodium salt, the solvated counterions in poly(acrylic acid) or poly(sodium acrylate) make no special contribution in dilute regions. Perhaps a methyl group in the α -position is responsible for these peculiarities. Both the ion-solvent interactions (electrostrictive effect) and the effect of the water structure due to solute addition (structural effect) must influence the adiabatic compressibility—the two effects generally cause a reduction in volume

and therefore in compressibility. In 100% neutralized polyacid, the dissociation of counterions is complete and the magnitude of electrostriction is highest, so that lowest ΦV_2 and ΦK_2 values (~ 37.0 cc/mole and -50.5×10^{-4} cc bar $^{-1}$ mole $^{-1}$, respectively) are observed in this case. By suppression of dissociation of counterions, as was produced effectively with 1.0M NaCl solution (in 0.1M NaCl, the suppression of dissociation was marginal), the magnitude of electrostriction was somewhat reduced, and accordingly the values were increased to 42.80 cc/mole and -33.0×10^{-4} cc bar $^{-1}$ mole $^{-1}$, respectively. The data for 100% neutralized poly(acrylic acid) in 0.1M and 1.0M NaCl solution are given in Tables VII and VIII, respectively.

At infinite dilution, the apparent molal volume ΦV_2^0 and the compressibility ΦK_2^0 of the solute and the partial molal volume \bar{V}_2^0 and the compressibility \bar{K}_2^0 of the solute are identical. The limiting values for solutes at 25°C are listed in Table IX. The limiting values for methacrylic acid and methacrylamide along with their corresponding polymers² are listed in the same table for comparison. The values for the polymer are found to differ widely from that of the corresponding monomer. The polymers show a decrease of ~ 15.0 – 19.5 cc/mole for ΦV_2^0 and of $\sim 5.15 \times 10^{-4}$ – 8.0×10^{-4} cc bar $^{-1}$ mole $^{-1}$ for ΦK_2^0 over the monomer values.

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

Materials	M_2	Molar volume, cc/mole	ΦV_2^0 , cc/mole	ΦK_2^0 , cc bar $^{-1}$ mole $^{-1}$ $\times 10^4$
Acrylic acid	72.06	68.56 ^a	61.7	6.00
Poly(acrylic acid)	72.06		46.7	0.85
Acrylamide	71.08	63.35 ^a	65.5	5.00
Polyacrylamide	71.08		50.9	-3.00
Poly(sodium acrylate), $\alpha = 0.25$	77.56		45.5	-14.00
Poly(sodium acrylate), $\alpha = 1.0$	94.04		37.0	-50.50
Poly(sodium acrylate), $\alpha = 1.0$, in 0.1M NaCl solution	94.04		37.1	-49.50
Poly(sodium acrylate), $\alpha = 1.0$, in 1.0M NaCl solution	94.04		42.80	-33.00
Methacrylic acid ^b	86.09	84.79 ^a	78.6	6.80
Poly(methacrylic acid) ^b	86.09		60.0	4.10
Methacrylamide ^b	86.116	76.75 ^c	82.0	4.50
Poly(methacrylamide) ^b	86.116		62.5	-2.87

^a Density obtained from Brandrup and Immergut.¹⁰

^b Data from Roy-Chowdhury.²

^c Density of methacrylamide was not available in literature; therefore value determined in this laboratory was used, 1.122 g/cc at 25°C.

It is interesting to note (Table IX) that ΦV_2^0 and ΦK_2^0 per methyl group are decreased as the molecules grew in size on polymerization. For example, in the case of monomers at 25°C, ΦV_2^0 and ΦK_2^0 per methyl group are 16.9 cc/mole and 0.8×10^{-4} cc bar⁻¹ mole⁻¹, respectively, in going from acrylic to methacrylic acid and are 16.5 cc/mole and -0.50×10^{-4} cc bar⁻¹ mole⁻¹, respectively, in going from acrylamide to methacrylamide; while for polymers, ΦV_2^0 and ΦK_2^0 per methyl group are 13.3 cc/mole and 0.25×10^{-4} cc bar⁻¹ mole⁻¹ in going from polyacrylic to poly(methacrylic acid) and are 11.6 cc/mole and -0.13×10^{-4} cc bar⁻¹ mole⁻¹ in going from polyacrylamide to poly(methacrylamide). The lower values of ΦV_2^0 and ΦK_2^0 per methyl group in the case of polymers (average $\Phi V_2^0 = 12.45$ cc/mole) compared to monomers (average $\Phi V_2^0 = 16.7$ cc/mole) further substantiate the observation made by Wen and Saito⁶ that water clusters become stronger and better formed as the molecules grow larger and larger. They observed, in the case of five tetraalkylammonium salts (methyl to pentyl) at 25°C, that ΦV_2^0 per methyl group is an average of 15.7 cc/mole compared to the average of 23.75 cc/mole obtained by Masterlon⁹ for aliphatic hydrocarbons in water at 23°C.

Acrylic acid and methacrylic acid (both liquids at room temperature) with molar volumes of 68.56 and 84.79 cc, respectively,¹⁰ when dissolved to form an infinitely dilute solution are found (Table IX) to decrease in volume by 6.86 and 6.19 cc, respectively. This decrease is due to electrostriction. Uncharged molecules, such as acrylamide and methacrylamide (both solids at room temperature) with molar volumes 63.35 and 76.75 cc, respectively, when dissolved to form an infinitely dilute solution are found to increase in volume by 2.15 and 5.25 cc, respectively, which corresponds to the expansion of solids on melting to some extent. Considering the usual expansion on melting as 10%, the observed lesser volume increase may be partly due to electrostrictional decrease because of the presence of amphoteric —CONH₂ groups.

Sincerest thanks are due to Professor A. B. Biswas, Indian Institute of Technology, Bombay, for encouragement and helpful suggestions.

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Received May 6, 1970