COPOLYMERIZATION STUDIES

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by
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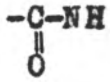
CHAPTER-I

INTRODUCTION

1. INTRODUCTION

1.1 General Introduction

Polyelectrolytes are a broad spectrum of macromolecular compounds carrying pendant ionizable groups. Biologically active macromolecules (proteins, nucleic acids, pectins), synthetic polypeptides (poly α-amino acids such as poly -L-lysine, poly-L-glutamic acid etc.), copolypeptides and some synthetic polymers [poly(acrylic acid), poly (methacrylic acid), poly(vinyl sulphonic acid) etc.] can be classified as polyelectrolytes. The large molecular weights and the interactions between ionised groups impart unique physico-chemical properties which place polyelectrolytes as a separate entity, apart from both electrolytes (like sodium chloride etc.) and unionizing polymers [e.g. poly(acrylamide), poly(N-vinyl pyrrolidone)], despite diversities in their origin and structure.

The first impetus to the study of polyelectrolytes, especially polyampholytes, as simpler analogues of the more complex biomacromolecules was provided by Staudinger[1]. The biological activities of proteins and other biomacromolecules were traced to their stereochemistry and conformation. The physico-chemical studies of polyelectrolytes, which has since become an interdisciplinary domain, reveal their shape and size to be sensitive to the solvent environment, pH and hence the degree of side chain ionisation, ionic strength, temperature, shear force fields, specific and non-specific binding of ions, electrostatic, hydrogen bonded and hydrophobic interactions. The analogy with globular proteins is, however, extremely tenuous since the synthetic polyelectrolytes (with an essentially carbon back-bone) differ from the proteins and polypeptides (with C_α-C, -N-C_α and  $-\underset{\underset{O}{\|}}{C}-NH$ linkages) in their chain flexibility. The conformational changes in synthetic polyelectrolytes arise mainly from the side chain ionisation and hydrophobic interaction, while additional factors like C_α-C and C_α-N bond rotation, intramolecular hydrogen bonding etc., contribute to the conformation of biomacromolecules. It cannot, however, be ruled out that the synthetic polyelectrolytes partially serve as simpler models for the more complex biomacromolecules.

The synthetic polyelectrolytes - polyacids carrying anionic centres, polybases carrying cationic centres and polyampholytes carrying a random distribution of both - ionise in aqueous solutions resulting in electro-static interactions between the charged centres attached to the polymer chain and free ions in the solution. The shape and mean dimensions of the flexible macromolecule assume that of the lowest potential energy. The number of charges on the weak polyelectrolytes like poly(methacrylic acid), poly(vinyl pyridine), which ionise only partially, can be altered by titration with strong base or acid.

Dilution in ion free water leads to increased ionization. The conformational changes effected by changes in ionic strength, concentration of macromolecule, electrostatic, hydrophilic and hydrophobic interactions have been studied exhaustively by potentiometry and viscosity[2-10].

The macroradicals formed during the course of polymerisation of ionic monomers, differ from the polyelectrolytes only in that they carry reactive centres at the growing end and hence are influenced by the same electrostatic and hydrophobic interactions which affect polyelectrolytes. Addition of ionising species considerably affect the rate of chain growth. Kinetic investigations of polymerisation behaviour of ionic monomers have reflected this trend[11-19].

The influences of the electrostatic and hydrophobic interactions on the homopolymerisation rate have also been reflected on the copolymerisation behaviour of ionisable monomers. The rather limited range of investigations in this regard have shown the influence of (i) pH of the medium in aqueous solutions[20-24] and (ii) dielectric constant of the solvent[25-29] even under apolar conditions, on the copolymerisation kinetic parameters, namely, the monomer reactivity ratios.

The present work involves an investigation of two of the factors (pH, ionic strength) that affect the monomer reactivity ratios in binary copolymerizations of ionising monomers (acrylic and methacrylic acids) with neutral water soluble unionizing monomers (N-vinyl pyrrolidone and acrylamide). It has also been shown that a parallel exists between the homopolymerization rates of the ionising monomers and their monomer reactivity ratios in the systems investigated under similar experimental conditions.

The conformation of polymethacrylic acid chain at low pH is the subject of considerable interest in the context of collapsed structure of globular proteins[92]. The compact globular form at low degrees of ionization undergoes a cooperative transition to the expanded structures at high pH. To obtain an insight into the nature of hydrophobic interactions in the chain, a study of the conformational behaviour of the random copolymers of methacrylic acid with a nonionic hydrophilic monomer will be of considerable interest. One such copolymer is investigated in the present work by physico-chemical techniques.

1.2 Copolymerization and Monomer Reactivities

Copolymerization reactions involve the simultaneous incorporation of two or more monomers in the same chain during polymerization. The first attempt at a quantitative, comprehensive theory of copolymerization was made by Dostal[30], later established quantitatively by Mayo and Lewis[31].

In binary free radical copolymerizations the following four principal, mutually competitive, propagation reactions are well recognized[36-38].

$$
\begin{array}{lcl}
\sim\!\sim M_1\cdot + M_1 & \xrightarrow{k_{11}} & \sim\!\sim M_1\text{–}M_1\cdot \\
\sim\!\sim M_1\cdot + M_2 & \xrightarrow{k_{12}} & \sim\!\sim M_1\text{–}M_2\cdot \\
\sim\!\sim M_2\cdot + M_1 & \xrightarrow{k_{21}} & \sim\!\sim M_2\text{–}M_1\cdot \\
\sim\!\sim M_2\cdot + M_2 & \xrightarrow{k_{22}} & \sim\!\sim M_2\text{–}M_2\cdot
\end{array}
\qquad (1)
$$

where M_1 and M_2 are the monomers and $\sim\!\sim M_1\cdot$ and $\sim\!\sim M_2\cdot$ the corresponding growing polymer radicals with the terminal groups M_1 and M_2 carrying the free radical centre. The differential form of the polymer composition equation is then arrived at, assuming a steady state for the free radical concentration[31,36-38].

$$
\frac{d[M_1]}{d[M_2]} = \frac{[M_1]}{[M_2]} \; \frac{r_1[M_1]+[M_2]}{r_2[M_2]+[M_1]} \simeq \frac{m_1}{m_2} \qquad (2)
$$

where the monomer reactivity ratios r_1 $(= k_{11}/k_{12})$ and $r_2 (= k_{22}/k_{21})$ are the kinetic parameters which measure the relative rate of addition of a radical to its own monomer and the addition of the same radical to the comonomer. $[M_1]$ and $[M_2]$ are the molar concentrations of the two monomers in the feed and $d[M_1]\,/\,d[M_2]$ is the relative rate of addition of the two monomers to the chain. For low conversions the latter quantity may be approximated to the mole ratio of the respective monomer in the copolymer. The differential form of the copolymer composition equation has also been derived on the basis of probability of monomer addition[39]. This is suggestive of the correctness of the four basic competitive reactions assumed in the kinetic treatment of binary copolymerizations.

The probability of addition of monomer M_1 to a chain radical $\sim\!\sim\!\sim M_1^{\bullet}$ is:

$$P_{11} = \frac{K_{11}[M_1^{\bullet}][M_1]}{K_{11}[M_1^{\bullet}][M_1]+K_{12}[M_1^{\bullet}][M_2]} = \frac{r_1[M_1]}{r_1[M_1]+[M_2]} = [1-P_{12}] \qquad (3)$$

Similarly

$$P_{12} = \frac{[M_2]}{r_1[M_1]+[M_2]} = [1-P_{11}] \qquad (4)$$

$$P_{21} = \frac{[M_1]}{[M_1]+r_2[M_2]} = [1-P_{22}] \qquad (5)$$

$$P_{22} = \frac{r_2[M_2]}{[M_1]+r_2[M_2]} = [1-P_{21}] \qquad (6)$$

The probability of occurrence of a sequence of 'n' molecules of species M_1 in a copolymer chain is:

$$P_{M_1} = P_{11}^{n-1}\, P_{12} \qquad (7)$$

The weight fraction of all M_1 sequences is:

$$W_1 = \frac{P_{12}}{P_{11}} \sum_{n=1} n\, P_{11}^{n} = 1/P_{12} \qquad (8)$$

Likewise, the weight fraction of all M_2 sequences is:

$$W_2 = 1/P_{21} \qquad (9)$$

The composition of the copolymer is given by:

$$\frac{d[M_1]}{d[M_2]} = \frac{W_1}{W_2} = \frac{1/P_{12}}{1/P_{21}}$$

$$= \frac{r_1[M_1]+[M_2]}{[M_2]} \Big/ \frac{r_2[M_2]+[M_1]}{[M_1]}$$

$$= \frac{[M_1]}{[M_2]}\,\frac{r_1[M_1] + [M_2]}{r_2[M_2] + [M_1]} \qquad (2)$$

The binary copolymerization equation correctly predicts the composition of the initial copolymer formed, from a knowledge of the monomer feeds and monomer reactivity ratios. The copolymer composition equation is mostly employed to determine the monomer reactivity ratios for low conversion copolymerizations. The copolymerization systems are characterized by their monomer reactivity ratios under particular set of conditions (solvent, temperature etc.). Different methods, varying in accuracy and ease of operation, have come into existance for their determination[31,40-51] and excellent reviews[47,51] have appeared recently. For low conversions (<5%), the differential equation is approximated to:

$$\frac{m_1}{m_2} = \frac{[M_1]}{[M_2]} \quad \frac{r_1[M_1] + [M_2]}{r_2[M_2] + [M_1]} \tag{2}$$

where $[M_1]$ and $[M_2]$ are the molar concentrations in the feed and m_1 and m_2 in the copolymer. The differential form of Mayo and Lewis equation[31] is generally used in the form:

$$r_2 = \frac{[M_1]}{[M_2]} \left[\frac{m_2}{m_1} \left(1 - \frac{r_1[M_1]}{[M_2]} \right) - 1 \right] \tag{10}$$

in which each experimental point of monomer feed-copolymer composition yields a straight line of r_2 as a function of r_1. The coordinates of the best weighted point of intersection of several experimental lines represent r_1 and r_2. This is known as the intersection method of Mayo-Lewis plot[31]. The 'best point of intersection' is invariably spread over an area and large uncertainities lie in the evaluation of r_1 and r_2. The better known Fineman and Ross procedure[41] linearizes the differential equation into the forms (11) and (12):

$$\frac{f-1}{F} = r_1 - r_2 \frac{f}{F^2} \tag{11}$$

$$\frac{F(1-f)}{f} = r_2 - \frac{F^2}{f} r_1 \tag{12}$$

where $F = [M_1]/[M_2]$ and $f = m_1/m_2$.

F and f are computed from the monomer feed, and copolymer composition data respectively. Plots of $(f-1)/F$ against f/F^2 (11) and $F(1-f)/f$ against F^2/f (12) yield r_2 and r_1, and r_1 and r_2 from slope and intercept respectively. These equations are unsymmetrical with respect to r_1 and r_2 and the experimental data are unequally weighted. The data obtained under extreme experimental conditions [very low $[M_2]$ in (11) and very low $[M_1]$ in (12)] have the greatest influence on the slopes of the lines drawn. An improved form of the differential method was provided by the YBR procedure[45], which eliminated the unsymmetrical nature of the Fineman-Ross equations (11) and (12). TheYBR method combines both the unsymmetrical equations of Fineman-Ross to yield a symmetrical equation:

$$\frac{F}{f^{\frac{1}{2}}} r_1 - \frac{f^{\frac{1}{2}}}{F} r_2 = f^{\frac{1}{2}} - \frac{1}{f^{\frac{1}{2}}} \tag{13}$$

where F and f have the same significance as in Fineman-Ross equations. The method yields r_1 and r_2 values which are very reliable even at conversions as high as 20%, if 'average monomer feed' (computed from the initial and final monomer concentrations, the copolymer composition and weight fraction conversion) is used in the calculation[46]. The shortcomings of the various differential methods have been well brought out by Tidwell and Mortimer[47] and the use of a nonlinear least squares procedure[47,51] has been suggested.

The copolymerisation equation has been integrated by

Mayo-Lewis[31] and Stockmeyer[52] for binary systems, later extended to ternary systems by Walling and Briggs[53] and to multicomponent systems by Skeist[54]. The numerical computations involved in the integrated equation are quite tedious and its use has now come to practice with the availability of computers to handle the massive calculations. Montgomery and Fry[55] illustrated that the classical methods of determining the monomer reactivity ratios from the differential copolymer composition equation are erroneous. The low molecular weight species formed by termination through side reactions and impurities, and the handling of small quantities of the copolymer magnify the errors. Purification by dissolution and precipitation entails loss of the low molecular weight species. The polymer conversions are also generally high, violating the low conversion requirement. The differential form of the copolymer composition equation does not take into consideration the drift in the monomer feed, due to the unequal reactivities of the monomers with conversion. The copolymers obtained at high conversions are the true representatives of the reaction dictated by the monomer reactivity ratios, while the initial copolymers are governed to a large extent by the monomer feed.

The integrated copolymer composition equation[31] is rearranged as:

$$r_2 = \frac{\log\left[\frac{M_2^0}{M}\right] - \frac{1}{P}\log\left[\frac{1-P(M_1/M_2)}{1-P(M_1^0/M_2^0)}\right]}{\log\frac{[M_1^0]}{[M_1]} + \log\left[\frac{1-P(M_1/M_2)}{1-P(M_1^0/M_2^0)}\right]} \qquad (14)$$

where M_1^0 and M_2^0 refer to the moles of the monomers 1 and 2 present initially, and M_1 and M_2 to the moles of the monomers remaining unreacted at the stoppage of the reaction. The integrated equation corrects for the drift in the monomer feed at every instant, using the conversion data. P is an integration variable, expressed as a function of the reactivity ratios $P = (1-r_1)/(1-r_2)$. The integrated equation procedure of Montgomery and Fry has been applied to styrene-m-divinyl benzene and p-divinyl benzene systems carried to high conversions and the variations in the monomer reactivity ratios with conversion has been well brought out[56].

Recently a linear graphically evaluable equation reported by Kelen and Tüdös[49] has been tested for a number of cationic copolymerization systems by Kennedy[50]. This semi-empirical equation overcomes the shortcomings of the Fineman and Foss linearization and provides accurate values of r_1 and r_2. The equation may be represented as:

$$\eta = [r_1 + r_2/\alpha]\,\xi - r_2/\alpha \qquad (15)$$

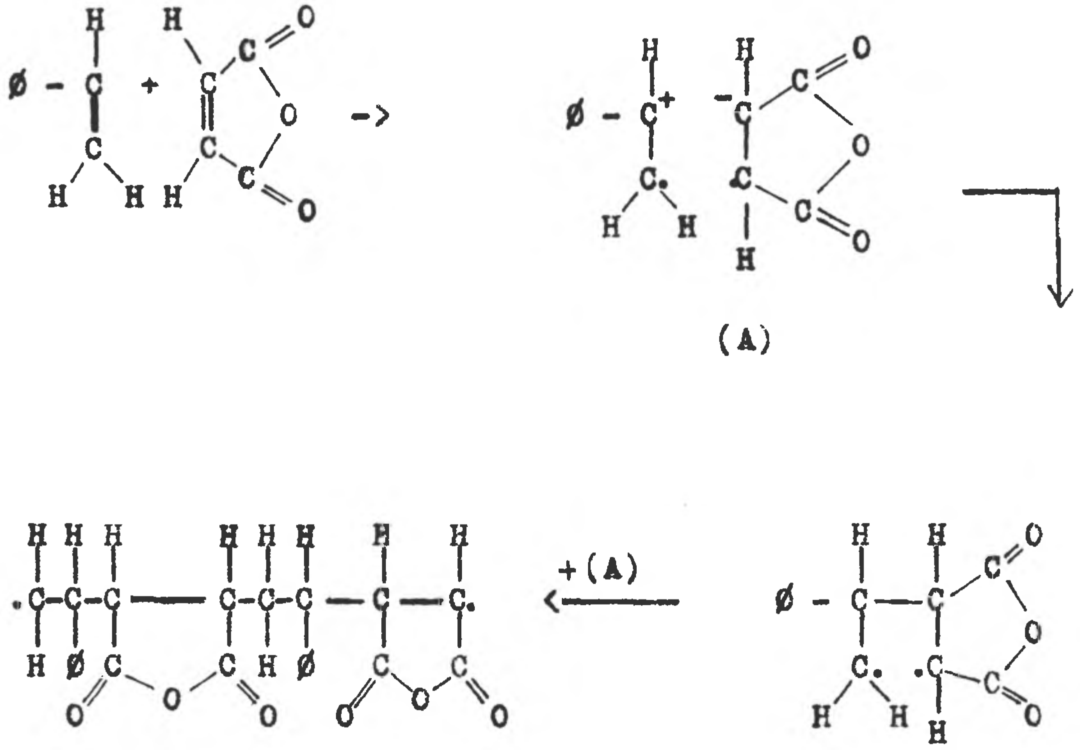
where α is a suitably chosen constant and

$$\eta = G/\alpha+F \; ; \qquad \xi = F/\alpha+F$$

with $G = \frac{X(Y-1)}{Y}$ and $F = \frac{X^2}{Y}$

The X and Y are the mole ratios of the monomers M_1 and M_2 in the feed and the copolymer. η and ξ are variables obtained from the feed and copolymer composition respectively. It was suggested[50] that the linearity of the η versus ξ plot testifies the applicability of the copolymer composition equation and the simple two parameter model implicit in it to the binary system under consideration. Plotting η as a function of ξ (0,1), a straight line is obtained which on extrapolation to $\xi = 0$ and $\xi = 1$ gives $-r_2/\alpha$ and r_1 as the respective intercepts.

In general, the Mayo-Lewis treatment of free radically propagated copolymerization kinetics[31] takes into account only the interactions between the growing polymer radicals and the monomers, ignoring the interactions between the free monomers. If the reacting monomers are polar, carrying pendant electron donating or electron withdrawing groups, the monomer-monomer interactions become highly significant. Thus, the formation of a molecular complex between an electron donor monomer and an electron acceptor monomer has been recognized in free radical copolymerization of styrene and maleic anhydride[57]. The charge-transfer complex formed by one electron transfer from the donor (styrene) to the acceptor (maleic anhydride) undergoes homopolymerization through a di-radical coupling mechanism yielding a strictly alternating copolymer[58-61].



In systems like methyl methacrylate, styrene/allyl compounds or butene isomers, such as isobutylene, 1 or 2-butene, the free radically produced copolymers have greater comonomer content of the latter type than is normally noted, if metal halides like $ZnCl_2$ are present[62,63]. The metal halide increases the electron acceptorability of methyl methacrylate or acrylonitrile as a result of complexation, facilitating the formation of charge-transfer complex between the comonomers[62,63] which can undergo homopolymerization. Similarly, studies on terpolymerization of a monomer pair capable of forming a molecular complex and a third monomer, would show the apparent change in the monomer reactivity ratios with both dilution and the nature of the solvent[64]. In the terpolymerization of β-chloroethyl vinyl ether-maleic anhydride-acrylonitrile, the donor acceptor contents in terpolymer obtained are found to be the same, regardless of the monomer feed, and may be treated as the copolymerisation of acrylonitrile with the charge transfer complex.

The copolymer composition equation, based on the four competitive propagation reactions, was developed initially for free radical chain reactions. It has been extended to carbonium ion propagated cationic copolymerisations[65,66] where the monomers are electron donating relative to the attacking species (e.g. the styrene-β-chlorostyrene-stannic chloride-carbon tetrachloride system). Solvent and catalyst effects are observed. Ionic copolymerisations are required to be carried out at sufficiently low temperatures to arrest side reactions[67]. As predicted by Mayo and Lewis[31], the copolymer composition equation has been decisive in distinguishing between cationic, anionic and free radical propagations (styrene-methyl methacrylate system[68-70]). Amine initiated anionic copolymerization of L-leucine and L-glutamate N-carboxyanhydrides in N,N-dimethyl formamide has also been treated by the binary copolymerisation equation[71].

1.3 Polymerization of Ionizing Monomers in Aqueous Medium

The behaviour of free radicals in aqueous media is of considerable importance for both the biological and physical chemist to justify investigations of these polymerization reactions, despite the experimental difficulties involved[72-74]. It is essentially a free radical process[75] with practically no chain transfer[76,77]. The choice of monomers, for the investigation of polymerization kinetics in water, is restricted to a few unsaturated acids, their derivatives and a few amines due to the solubility limitations of the monomer and the corresponding polymer in water. The kinetic investigation necessitates a preliminary knowledge of the electrochemical properties of both the monomer and the polymer. As compared to unionizable polymer systems, additional factors such as dissociation, specific and non-specific binding of ions, electrostatic and hydrophobic interactions come into play. Polyelectrolyte radicals present during the polymerization of the ionic monomers in aqueous medium and the free radical centres forming a part of the propagating coil are also liable to the influence of their microsurroundings. Thus, a direct relation between the physico-chemical state of the macroradical and its true reactivity can be envisaged.

The polymerization rate of methacrylic acid in ion free aqueous solutions, with hydrogen peroxide as the initiator, has been found to decrease (from an initial value for the propagation rate constant $k_p = 1.94 \times 10^{-4}$ sec.$^{-1}$ at pH 2.41) with increase in the pH of the system[11], attaining a near zero value at pH 5.5. It was reasoned that unionized monomer alone takes part in the polymerization[11].

Investigation of the same monomer, with potassium persulphate as initiator, also showed a decrease in reactivity with increase in pH[12] but polymerisation was observed even at pH 13. The decrease in the rate of polymerisation was attributed to the decrease in the reactivity of methacrylate anion (pKa of methacrylic acid is 4.32) arising from electrostatic charge repulsion between the monomeric anions as well as the ionized growing polymer radical[12]. The effect of pH on the rate of polymerisation of acrylic and methacrylic acids has been studied in detail by Blauer[13,15]. The rate of polymerisation of methacrylic acid was found to drop gradually with increase in pH, reaching a minimum between pH 6 and 7. The minimum observed corresponds to 1/15th of the rate at pH 4.0. Above pH 7.0 the polymerization rate rises slowly and nearly levels off between pH 9 and 12. The rate of polymerization of acrylic acid decreases till pH 7.0 (pKa of acrylic acid is 4.2 and pKa of polyacrylic acid is 6.4) and then rises slowly[14]. Added salts increase the rate of polymerisation of both the acids below pH 10 but decrease the rate between 11 and 12. The increase in rate above pH 7 was attributed to the partial decrease in the rate of termination due to electrostatic repulsion between ionized growing polymer radicals. The system was recently reinvestigated in greater detail[16-19]. It was observed that the presence of different alkali metal ions of varying ionic radii and charge density under similar experimental conditions have differing effects on the rate[16]. Thus, the alkali metal ions vary in their ability to shield electrostatic interactions by the formation of ion pairs with the growing polyelectrolyte radical[78]. The rate of polymerization of acrylic acid in the alkaline range was found to be nearly parallel to that at very low pH while the increase in the rate of polymerization of methacrylic acid was only marginal when sodium hydroxide was used for pH adjustments[19]. When the pH was adjusted with triethylamine the enhancement of rate in the alkaline range was more pronounced for methacrylic acid[18], as the ion pair can be etabilized by the hydrophobic interaction between the ethyl group of triethylamine and the methyl group of the growing poly(methacrylic acid) chain, thereby reducing the electrostatic repulsive interactions. Thus, ion binding to polyelectrolytes is specific[18,19]. If the enhancement in the rate of polymerization at high pH values is due to a decrease in the rate of termination (thereby an increase in the ratio k_p/k_t) as thought of by earlier workers[13-15], then introduction of neutral strong electrolytes into the system should enhance the rate of termination and decrease the overall rate of polymerisation (Table-1). However, the introduction of large concentration of a strong electrolyte was shown to enhance the rate further, indicating that the variation in the rate of polymerization is due to a variation in the rate of propagation with pH. Determination of

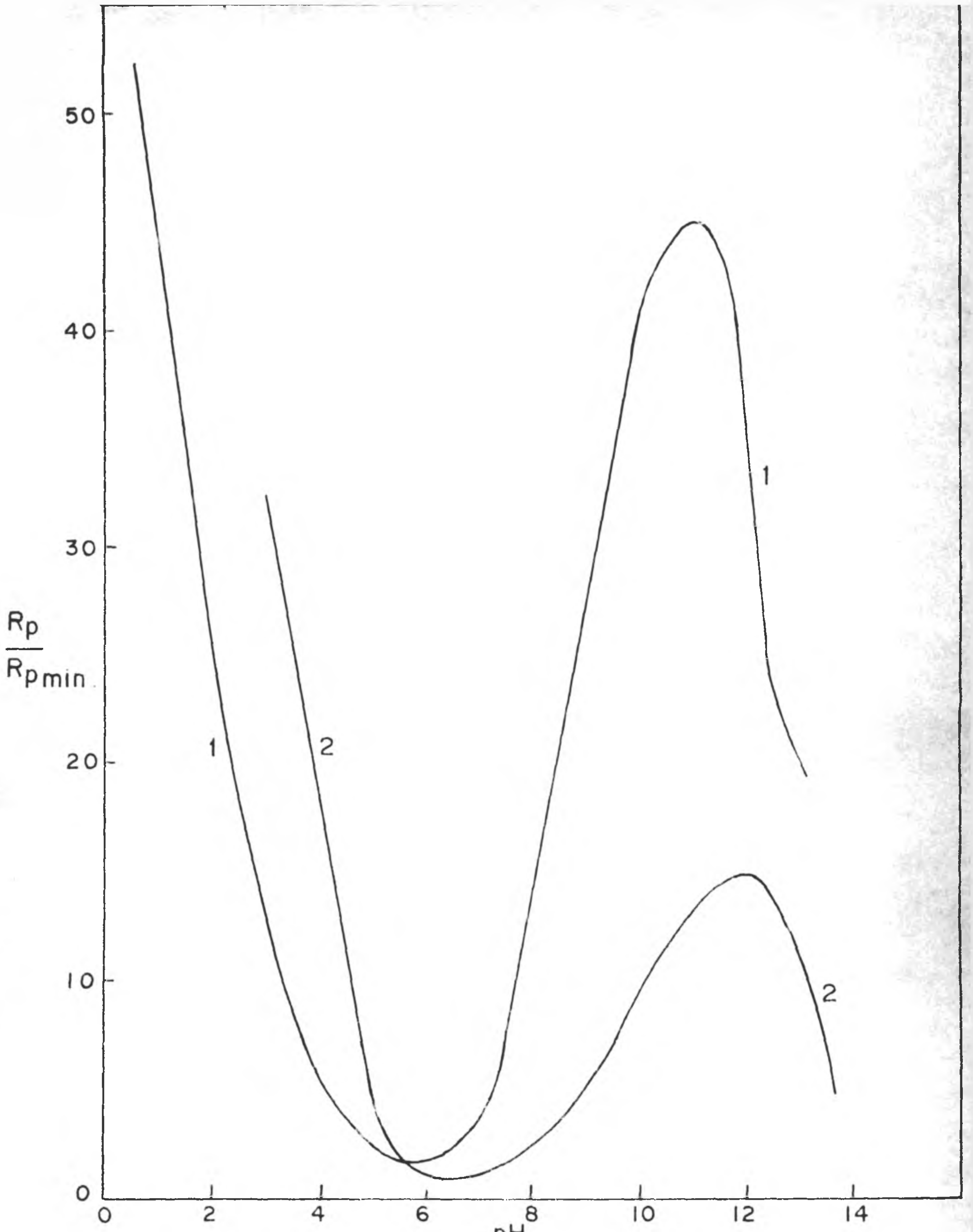


Fig. 1 Relative polymerization rate ($R_p / R_{p\,min}$) versus pH fixed by NaOH for AA (1) and MA (2) polymerization at 60°C.

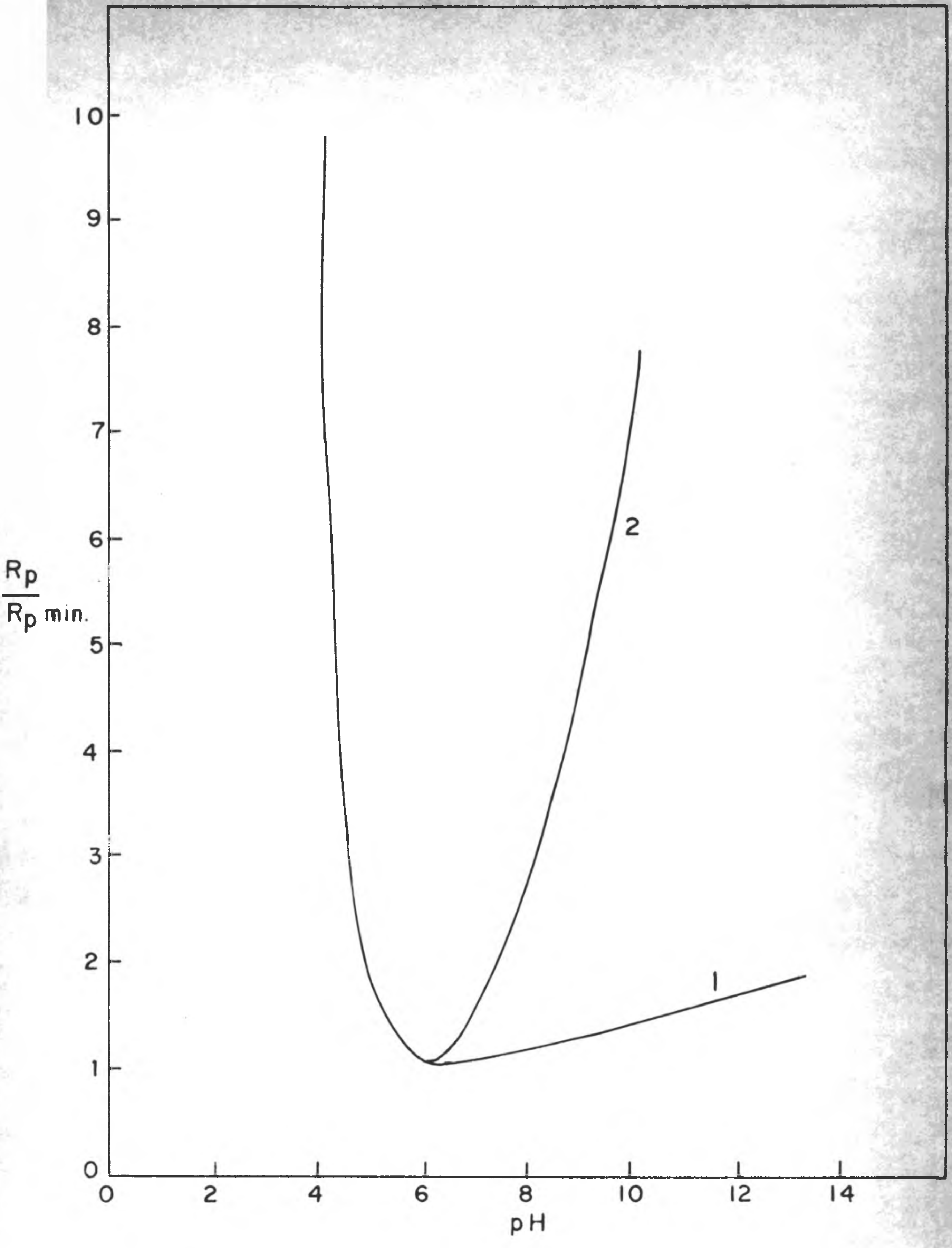


Fig. : 2 Polymerization of AA (1) and MA (2) in aqueous solution of Triethyl amine .

individual rate constants k_p and k_t by rotating sector measurements have shown that k_p varies with pH while k_t is invariant[19] (Table-1). Thus, the ion pairs[16-19] present mainly influence the rate of propagation.

__Table-1:__ Elementary Rate Constants for Polymerisation of Acrylate (AA) and Methacrylate (MA) anions[19]
$[AA] = 1.2$ M $[AIBN] = 8.3 \times 10^{-4}$ M, λ365 nM, 23°C
Aqueous solution, pH adjustment = NaOH

pH	$R_p \times 10^5$ M Sec^{-1}	k_p M^{-1} Sec^{-1}	$k_t \times 10^{-8}$ M^{-1} Sec^{-1}
Ion free, 7.9	0.51	650± 85	2.6±0.27
1.5 M NaCl, 7.9	2.50	3150±140	2.6±0.26
Ion free, 11.0	5.00	6600±925	2.7±0.29
Ion free, 13.6	2.10	2500±380	2.8±0.26
$[MA] = 0.92$ M, $[AIBN] = 2.5 \times 10^{-4}$ M, λ365 nM, 23°C Aqueous solution, pH adjustment = NaOH			
Ion free, 8.6	0.42	670± 80	2.1±0.20
Ion free, 13.6	1.20	1950±160	2.25±0.23

1.4 Copolymerization of Ionic Monomers

Primarily the interest in polyelectrolytes grew from their abnormal conformations and hydrodynamic behaviour in aqueous solution under conditions influencing the ionization of the pendant polar groups[79-82]. Amphoteric polyelectrolytes were studied as synthetic analogues of the more complex biomacromolecules[83]. Interesting features were observed during binary copolymerisations of ionising monomers leading to the preparation of the polyampholytes. Alfrey, Overberger and Pinner[20] observed that the composition of the copolymer system methacrylic acid-diethyl amine ethyl methacrylate depends markedly on the pH of the medium(Table-2).

<u>Table-2:</u> Variation in Reactivity Ratio with pH[20]

pH	Diethyl amino ethyl methacrylate r_1	Methacrylic acid r_2
1.2	0.90±0.23	0.98±0.16
7.2	0.65±0.03	0.08±0.015

Thus, a reversal in the monomer reactivity ratios was observed due to the ionisation of the carboxyl group in methacrylic acid. The system acrylic acid-acrylamide was investigated independently by Bourdais[22] and Smets et al[21] in aqueous and organic medium respectively. The observed values of reactivity ratios are presented in Table-3.

Copolymerisation in aqueous medium was also investigated recently by Kabanov et al[18], for the methacrylic acid-N-vinyl pyrrolidone and methacrylic acid-acrylamide systems

Table-3: Monomer Reactivity Ratios of the System Acrylic acid-Acrylamide

Condition	Acrylic acid r_1	Acrylamide r_2
Low pH[22]	1.43±0.03	0.60±0.02
High pH[22]	0.35±0.03	1.10±0.05
Benzene[21]	1.38	0.36

to perceive whether a parallel exists between the variations in homopolymerization rate and monomer reactivity ratios in binary copolymerisations (with nonionic monomers) with variations in pH. The system methacrylic acid-N-vinyl pyrrolidone was also investigated in DMF by Chapiro et al[134]. Their results are presented in Table-4.

Table-4: Monomer Reactivity Ratios of the Systems[18] Methacrylic acid-N-vinyl Pyrrolidone and Methacrylic acid-Acrylamide

System	Medium	r_1	r_2
MA(1)-NVP(2)[134]	DMF	4.7±0.1	0.07±0.02
MA(1)-NVP(2)	Ion free pH 8.0	0.65±0.02	0.33±0.01
MA(1)-NVP(2)	2M NaCl pH, 8.0	0.30±0.04	0.30±0.03
MA(1)-NVP(2)	Ion free pH, 10.0	1.40±0.02	0.30±0.01
MA(1)-AM(2)	Ion free pH, 8.0	0.25±0.03	0.12±0.02
MA(1)-AM(2)	2M NaCl pH, 8.0	1.36±0.02	0.18±0.01

The system acrylic acid-acrylamide was investigated in the acidic pH range by [illegible] et al[24] and a gradual reversal in the reactivity ratios of both the monomers was observed. Their results are presented in Table-5.

Table-5: Reactivity Ratios of Acrylic acid (r_1) and Acrylamide (r_2) at different pH at 60°C ($K_2S_2O_8$)[24]

pH	r_1	r_2
2.17	1.73±0.21	0.48±0.06
3.77	0.56±0.09	0.56±0.09
4.25	0.45±0.03	0.67±0.04
4.73	0.42±0.02	0.35±0.03
6.25	0.35±0.03	1.32±0.12

These investigations have, in general, been carried out in a narrow pH range to show that monomer reactivity ratios of ionizing monomers are drastically influenced by the reaction medium. The study of reactivity ratios of these systems, over a wide pH range, including the alkaline side would enable a more comprehensive understanding of the monomer reactivities in terms of electrostatic and other secondary interactions between the reacting species.

1.5 Polyelectrolytes

Polyelectrolytes, the macromolecules carrying pendant ionizable groups, undergo ionization in dilute aqueous solutions. The degree of ionization 'α' is determined by the pH of the solution.

For weak polyelectrolytes:

$$\alpha = N/N_T$$

where N_T is the total number of ionisable groups present in the polyelectrolyte and N is the number of ionised groups at a given pH. For a weak polyacid $\alpha \rightarrow 0$ and for a weak polybase $\alpha \rightarrow 1$ at low pH. For polyacids and polybases, variation of pH by the addition of a titrant (base or acid) progressively changes α and the pendant groups of the macromolecule are subjected to repulsive electrostatic charge interactions. In polyampholytes and proteins, repulsive and attractive interactions, short and long range are operative. These are determined by the number and sequence distribution of the different types of ionisable groups. Polyacids and polybases progressively undergo transition to expanded conformations with increased degree of ionization due to the repulsive interactions between the ionized groups. The charged molecules adopt the size and shape governed by the potential energy of the molecule. In many polyelectrolytes the intermolecular electrostatic interactions can largely be suppressed by shielding the charges by the addition in large excess (1 to 2 moles) of a strong electrolyte (NaCl). The conformation and the sise then tends towards that in the nonionizing situation.

The conformational transition which could be from a globule -> random coil -> rigid (or flexible) rod or helix -> coil can be followed by the physico-chemical measurements like viscosity, light scattering, potentiometric titration, etc. In proteins and polypeptides the conformational transition can also be followed by circular dichroism, optical rotatory dispersion and gel permeation chromatography. For synthetic polyelectrolytes like poly (methacrylic acid) the simplest methods of conformational study, namely, potentiometric titration and viscosity are frequently adopted.

1.6 Potentiometric Titration

The potentiometric titration curves of polymeric acids can be described by the generalized Henderson-Hasselbalch equation[79].

$$pH = pK_{app} - n' \log \left[\frac{1-\alpha}{\alpha}\right] \tag{16}$$

where α is the degree of ionization. For monobasic acid $n' = 1$ and $\log \left[\frac{1-\alpha}{\alpha}\right]$ is approximately proportional to α over a wide range of α (0.2 to 0.8) since:

$$\log\left[\frac{1-\alpha}{\alpha}\right] = \frac{2}{2.303}\left[(1-2\alpha)+(1-2\alpha)^3/3 + (1-2\alpha)^5/5 + \ldots\right]$$

$$\simeq \left[1-2\alpha\right] \tag{17}$$

Equation (16) may be transformed to:

$$pH = pK_a - n' + 2n'\alpha \tag{18}$$

The basicity of the acid, n', estimated from the slope of the titration curve at the middle region[84], will be $[dpH/\delta\alpha]/2$. For a monobasic acid the Henderson-Hasselbalch equation follows from the law of mass action. For polymeric acids of DP > 20, the deviation from the titration behaviour of monobasic acids is due to the electrostatic work expended in the removal of proton from the field of the ionised carboxyl groups. The Henderson-Hasselbalch equation modified to account for the additional electrostatic work for the ionization in dilute solutions is given by[85]:

$$pH = pK_a - \log\left[\frac{1-\alpha}{\alpha}\right] + \psi\epsilon/kT \qquad (19)$$

where $\psi\epsilon/kT$ is the electrostatic work term, ψ the electrostatic free energy per unit charge being:

$$\psi = \left(\frac{\delta G_e}{\delta \nu}\right) = \frac{1}{V_\infty}\left(\frac{\delta G_e}{\delta \alpha}\right) \qquad (20)$$

with the degree of ionization. $\alpha = N/N_\infty$, N and N_∞ are the number of charges at a degree of ionization α and the total number of charges and G_e is the Gibbs free energy.

For flexible polyelectrolytes an expression due to Katchalsky[85] describes the electrostatic free energy:

$$pH = pK_o - \log\left[\frac{1-\alpha}{\alpha}\right] + \frac{2\nu\epsilon^2}{DhkT}\left[\log\left(1+\frac{6h}{K\langle h_o^2\rangle}\right) - \frac{0.217\alpha 6h}{K\langle h_o^2\rangle + 6h}\right] \qquad (21)$$

where $\langle h_o^2\rangle$ is the mean square end-to-end distance of the polymer in the uncharged reference state, ϵ is the electronic charge, K is the Debye-Hückel parameter

$[K^2=4\pi I/DKT]$, D,K,T are the dielectric constant, the Boltzmann constant, and the absolute temperature. I, the ionic strength $= \frac{1}{2}\Sigma n_i z_i^2$, where z_i and n_i are the valency and number of the ith ion.

The increase in the electrostatic free energy $F_3(\alpha)$ corresponding to the charging process of the flexible chain polymer is given by another expression used by Wada[86]:

$$F_3(\alpha) = \frac{2e^2}{D}\left[\frac{6}{kh_o} - \left(\frac{8}{3\pi}\right)^{\frac{1}{2}} \frac{h_1}{2}(6/kh_o{}^2)^2\right] \tag{22}$$

where h_o and h_1 are the root mean square end-to-end distance of separation of the coil in the absence and presence of electrostatic interactions, e is the electronic charge.

For rigid rod polyelectrolytes, assuming a cylindrical model with smeared out charge distribution on its surface (α-helix in the case of polypeptides), the electrostatic free energy has been shown to be[87]:

$$F_1(\alpha) = 2\alpha\rho\,(4\pi^2b^2l_o/D)k_o(kb)/kbk_1(kb) \tag{23}$$

where l_o is the segment length, b the radius of the cylinder, k_o, k_1 are the Bessel functions of the second kind, ($\alpha\rho$) the charge density of the helix surface and k the inverse radius of the ion atmosphere. If the rod like model is applicable, the electrostatic potential or the ion distribution around the rod can be calculated by the Poisson-Boltzmann equation:

$$\nabla^2\psi = \frac{-4\pi N_A e}{D\,10^3}\,C_s(e^{-e\psi/kT} - e^{e\psi/kT}) \tag{24}$$

with $\psi(r)$ the electrostatic potential at the position r from the centre of the rod, e the electronic charge, k the Boltzmann constant, C_s the concentration of the uni-univalent electrolyte[88] (moles litre^{-1}).

If the Debye-Hückel approximation is applicable:

$e\psi(r)/kT \ll 1$ and equation (24) reduces to:

$$\nabla^2\psi = k^2\psi \qquad (25)$$

where $k^2 = 8\pi e^2 N_A C_s/10^3 . DKT$ (26)

The parameters pH, the degree of ionisation α, the negative logarithm of the dissociation constant pK_{app} describing the hydrogen ion titration curve are then related by:

$$pK_{app} = pH + \log\left[\frac{1-\alpha}{\alpha}\right] \qquad (27)$$

$$pK_{app} = pK_o + 0.434(e\psi/kT) \qquad (28)$$

where pK_o is the negative logarithm of the intrinsic dissociation constant of the ionizable group in the polyelectrolyte and $(e\psi)$ is the work done by the ionizing proton against the attractive force of charges on the rod.

If the electrostatic potential Z at the surface of the rod or sphere is given as a function of the number of charges of the molecule, the 'G_{el}' (the electrostatic free energy) of the molecule can be calculated by varying the charge of the molecule from zero to that obtained finally.

$$G_{el} = \int_o^Z e\psi\, dz \qquad (29)$$

or $$\frac{G_{el}}{N} = 2.3RT \int_0^{\alpha} (pH + \log\left[\frac{1-\alpha}{\alpha}\right] - pK_o)\, d\alpha \tag{30}$$

where N is the number of ionizable groups in the polyelectrolyte. The equation describing the hydrogen ion titration of polyacids and polybases is, in general, represented as:

$$pH - \log\left[\frac{\alpha}{1-\alpha}\right] = pK_o + \frac{0.434}{\delta\alpha} \tag{31}$$

where α is the degree of ionisation, K_o the intrinsic dissociation constant and G_{el} the electrostatic and conformational energy. At high electrolyte concentrations, the value of the Debye-Hückel parameter K becomes large. Correspondingly, the electrostatic free energy term vanishes and equation (31) reduces to the simple Henderson-Hasselbalch equation:

$$pH = pK_o + \log\left(\frac{\alpha}{1-\alpha}\right) \tag{32}$$

1.7 Titration Behaviour of Synthetic Polyelectrolytes

The synthetic polyelectrolytes, with an essentially carbon backbone, do not exhibit helix-coil conformational transitions unlike proteins and polypeptides. The titration curve of a simple polyelectrolyte like poly(acrylic acid) is essentially featurless, especially at α values below 0.3, implying the absence of any conformational transition. Poly(methacrylic acid) on the other hand, exhibits a conformational transition in the range $0.1 < \alpha < 0.3$. The molecule at a low pH is characterized by a compact globular structure, which then expands to a coil at higher pH values, with a free energy of transition (globule -> coil) of the order of 180-250 cals/mole as determined from the potentiometric titration curves[3,4].

The compact form of the poly(methacrylic acid) is attributed to the hydrophobic interactions arising from the methyl-methyl contacts in aqueous environment[4,92,152,153]. The hydrophobic interactions are entropic in origin (and not energetic) and hence exhibit an increase with a rise in temperature[93,154]. A similar hydrophobic interaction influenced conformational transition is observed in synthetic polypeptides with pendant nonpolar groups. Synthetic polypeptides (of the vinyl type) also generally exhibit a conformational transition from random coil to rigid or flexible rod state at higher degrees of ionization due to the electrostatic repulsive interactions between similarly charged centres with progressive stretching of the coil. This conformational behaviour may be observed from the pH titration curves as well as from the viscosity and light scattering measurements at varied pH.

The influence of hydrophobic interactions in the conformational transition of copolymers of maleic acid-n-alkyl vinyl ethers has been systematically investigated by Strauss[94]. Copolymer of maleic acid-n-butyl vinyl ether exhibits a conformational transition in the region $\alpha = 0.0$ to 0.7 while such a change is unobserveable in copolymers of maleic acid-ethyl vinyl ether. The free energy change ΔG^{o} for the transition from the uncharged compact form to the hypothetical uncharged random coil form estimated from the area bound by the hump of the titration curve for n-butyl vinyl ether-maleic acid copolymer superimposed on the curve obtained for the ethyl vinyl ether-maleic acid copolymer, is of the order of 280 cals/mole of the dibasic acid unit, a value close to that theoretically estimated by Némethy and Scheraga for the formation of hydrophobic interactions of minimum strength[95]. The transition range is broadened to higher values of α with increase in the length of the n-alkyl unit of the vinyl ether. Increase in the number of carbon residues in the side chain leads to an increase in the free energy of transition[96]. Addition of protein denaturants like urea destabilize the hyper-coiled state of hydrophobic polyelectrolytes[97]. This is observable from the decrease in the free energy of stabilisation of the compact structure of n-hexyl vinyl ether-maleic acid copolymer from 1100 cals/mole residue[96] to 830 cals/mole residue in the presence of urea[97].

Further insight into the conformational behaviour of hydrophobic polyelectrolytes is provided by the recent study of styrene-methacrylic acid copolymers[98]. The uncharged polyelectrolyte chains are found to assume a compact globular conformation with the phenyl side chains of styrene making a major contribution. The stability of the globule was found to increase with an increase in the styrene content. Semi-quantitative estimates of the radii (r) of the globule show an increase in r values with increase in α. The conformational transition from globule to coil takes place only after sufficient expansion of the globule. Thus, the globule does not directly participate in the conformational transition[98].

1.8 Conformational Transition by Viscosity

The dilute solution theories of polymer solutions[99] are based on the assumption that the polymer coil is non-draining in the solvent and that segments of a polymer chain have a Gaussian distribution around the centre of the mass. Excluded volume studies of poly(acrylic acid) chains[10,100] show that the coil of ionized polyelectrolytes is not free draining although at high ionic strengths, the expansion factor tends to obey the excluded volume theories for nonionic polymers. The radius of gyration (S) estimates of poly(methacrylic acid) solutions at different concentrations by small angle elastic neutron scattering[101] in the absence of added electrolyte show that (S) remains constant in the polymer concentration range 0.32 eq/litre to 0.10 eq/litre and registers a sharp increase at lower concentrations. Thus, there is a critical concentration for each polyelectrolyte above which the characteristic polyelectrolyte behaviour is not predominant. The $\bar{S}$ of poly(methacrylic acid) was 49A^{o} at the lowest concentration (0.06 eq/litre) when $\alpha = 0.27$ as compared to $\bar{S} = 100A^{o}$ for the fully stretched polyion. The polyelectrolyte segments have a Gaussian distribution at high concentrations, which break down at lower concentrations to a zig-zag conformation with only a few sub-units[101]. The dilute solution behaviour of polyelectrolytes are characterized by large intermolecular interactions reflected in the anamolous values of the second virial coefficient A_2 for the systems: Poly(styrene sulphonates)[102,103], poly (acrylic acid)[10,100] and poly(methacrylic acid)[101].

The conformational changes and the accompanying variations in the hydrodynamic volume of a polyelectrolyte are easily followed by the intrinsic viscosity in aqueous solutions of low electrolyte concentrations. The intrinsic viscosity is proportional to the reciprocal square root of the ionic strength[104] and approaches the value of nonionic polymers at high electrolyte concentrations as the charges on the polyelectrolyte molecules are effectively shielded. At low ionic strength, the viscosity behaviour is represented by[105,106]:

$$\frac{1}{(\eta_{sp}/C)-D} = \frac{1}{A} + \frac{B}{A} C^{\frac{1}{2}} \qquad (33)$$

where A and B are empirical constants and C is the concentration.

At sufficiently high ionic strengths, the well known relationships[99] between the intrinsic viscosity $[\eta]$, the root mean square end-to-end distance $\langle \overline{h^2} \rangle^{\frac{1}{2}}$ and the expansion factor α are applicable to polyelectrolytes:

$$[\eta] = \Phi \langle \overline{h^2} \rangle^{3/2} / M \tag{34}$$

$$[\eta]/[\eta]_\theta = \alpha^3 \tag{35}$$

where Φ is the Flory constant, M the molecular weight $[\eta]_\theta$ the intrinsic viscosity at the θ temperature, and $\alpha^2 = r^2/r_o^2$ with r_o^2 referring to the unperturbed state. However, the Flory constant Φ for polyelectrolytes differs largely from the standard value for nonionic polymers and shows strong dependence on the expansion factor[102] α. The intrinsic viscosity of a given polymer chain which depends on the value of $(\overline{r^2})^{3/2}/M$, increases sharply in the following order with respect to conformation. Globule < random coil < rigid rod. The $[\eta]$, $\overline{r^2}$ and A_2 of poly(styrene sulphonate) and poly(methacrylic acid) in water have been shown to decrease with increase in temperature[103,107]. The $[\eta]$ of poly(methacrylic acid) is nearly independent of ionic strength and is much lower than the value of $[\eta]$ in methanol at 26°C, an organic θ solvent[32]. The later value is 3.5 times higher than that in an aqueous θ solvent (0.002 N HCl at 30°C)[32]. However, $[\eta]$ increases with the degree of ionisation α till $\alpha \geq 0.6$, the increase being greatly marked as the ionic strength is decreased[5]. These features have now been explicitly discussed in terms of the data on unperturbed dimensions of poly(acrylic acid) and poly (methacrylic acid) in aqueous and organic media by viscosity and light scattering[108]. The hydrophobic contractions of polymer coil has been illustrated in the study of a random copolymer of ethyl acrylate and acrylic acid (2:1) whose unperturbed dimensions in an organic θ solvent were 1.3 to 1.4 times those obtained for a fully ionized polymer in an aqueous θ solvent[108]. The compact structure tends to break at higher ionic strengths.

The Stockmayer-Fixman relationships[109]:

$$\frac{\eta}{M^{\frac{1}{2}}} = K_o + 0.51B\,\Phi\,M^{\frac{1}{2}} \tag{36}$$

$$K_o = [\eta]_\theta \,/\, M^{\frac{1}{2}} = \left[\frac{\overline{r_o^2}}{M}\right]^{3/2} \tag{37}$$

where ϕ the Flory constant is $\simeq 2.5\text{x}10^{21}$ dl/g, $\overline{r_o^2}$ is mean square unperturbed end-to-end distance, B is a value which depends on the long range segment interactions, have been applied as such for poly(acrylic acid) by Nagasawa et al[100] and Ptitsyn[110] with the assumption that long range interactions in polyelectrolyte molecules can be considered to be analogous to those in uncharged polymers. The K_o for poly(methacrylic acid) obtained from these relationships show that on increasing α from 0.1 - 0.2 to 0.5 - 0.6 the compact structure of poly (methacrylic acid) disappears and the unperturbed dimensions increase markedly equalizing those found in organic solvents at $\alpha = 0.6$. The long range electrostatic interaction parameter 'B' obtained from the Stockmeyer-Fixman plots has been shown to have only slight dependence on α when $\alpha < 0.2$ for poly(methacrylic acid), unlike in poly(acrylic acid) where the dependence is considerable. This indicates that the long range electrostatic interactions have practically no effect on the dimensions of poly(methacrylic acid) molecules which are compact[5]. To summarise, the dimensions of poly(methacrylic acid) molecules, unperturbed by long range interactions, increase with the degree of ionization, from $\alpha = 0.1 - 0.2$ to $\alpha = 0.5 - 0.6$ and remain constant at lower as well as higher degrees of ionization, suggesting that the cooperative breakdown of the secondary structure of poly(methacrylic acid) produces a cooperative increase in dimensions. In contrast, the long range interaction parameter 'B' for poly(acrylic acid) depends to a large extent on α at low degrees of ionisation.

In addition to the repulsive side chain and contracting hydrophobic interactions, the side chain bulkiness considerably influences the conformational rigidity. An interesting comparison[111] of the three polymers: sodium salts of poly(vinyl sulphate), poly(styrene sulphonate) and poly(3-methacryloyloxy propane-1-sulphonate) for the polymer chain flexibility in terms of the characteristic ratio at infinite ionic strengths, is given by:

$$C_\infty = \langle r_0^2 \rangle / nl^2 = \left[\frac{K_0}{\Phi_0} \right]^{2/3} \frac{M_0}{2\,l^2} \qquad (38)$$

(where $\langle r_0^2 \rangle$ is the mean square unperturbed end-to-end distance, n the number of bonds, l the bond length, K_0 the Mark-Houwink constant at Θ temperature and M_0 the monomer molecular weight) showed that the chain of sodium poly(vinyl sulphonate) is most flexible and sodium poly(3-methacryloyl oxy propane-1-sulphonate) is the most hindered[111]. In sodium poly(styrene sulphonate) and sodium poly(3-methacryloyl oxy propane-1-sulphonate) the hydrophobic interactions and ion hydration around the bulky groups contribute to the rigidity. All the three polyelectrolytes [whose characteristic ratio $C_\infty < 15$] are found to be flexible coils. The bulky groups of the long hydrated side chain of sodium poly(3-methacryloyl oxy propane-1-sulphonate), due to higher side chain mobility, reduce the counter ion screening by the added electrolyte on the coil and remain expanded even in high salt concentrations.

1.9 Present Investigation

In the present work the copolymerization behaviour of four systems, each comprising of an ionisable monomer and a nonionic water soluble monomer, were investigated as a function of the degree of ionization of the ionizing monomer, the ionic strength of the medium ion binding etc. The experimental data was examined in the light of the homopolymerization behaviour of the ionizable monomer in order to understand the monomer reactivity patterns as a function of the pH of the reaction medium.

A study of the effect of folding of poly(methacrylic acid) chain with methacrylic acid sequences randomly interrupted by a single unit of a nonionic hydrophilic segment like N-vinyl pyrrolidone which does not contribute to the hydrophobic interaction and serves only as a diluent to the methyl-methyl contacts show whether long range methyl contacts play any part in bringing about the collapse of the poly(methacrylic acid) chain at low pH. In the present investigation, such random copolymers of methacrylic acid with varying N-vinyl pyrrolidone contents were prepared and their hydrogen ion titration behaviour and viscosity were studied, especially at lower degrees of ionization, to understand the collapsed structure of poly (methacrylic acid) chain.

CHAPTER-II

TREATMENT OF DATA

2. TREATMENT OF DATA

2.1 Copolymerization

The copolymerization reactions are characterized by the monomer reactivity ratios of the reacting monomers. Reviews on the various procedures available for their evaluation have been presented in literature[46,47]. A few well known procedures are reviewed in the introductory chapter of this Thesis.

Reliable solution for the monomer reactivity ratios r_1 and r_2 in binary copolymerization of monomers M_1 and M_2 are obtained by the nonlinear least square procedure[41] or the 'YBR' method[45] for low conversion data. Mayo and Lewis integrated equation[45,46], however, yields the best solution for r_1 and r_2 for both low and high conversion data.

The experimental data in the present work were treated by (i) the differential form of the copolymerization procedure using the 'YBR' method, and (ii) the Mayo-Lewis integrated equation. The r_1 and r_2 values obtained by the integrated equation were accepted as the more reliable values for discussion.

The applicability of the recently proposed equation by Kelen and Tüdös[49] was tested for our copolymerization systems[148] involving conversion less than 60%.

2.1.1 The YBR Method[45]

The 'YBR' equation, which in effect is a symmetrical form of the Fineman-Ross type equation, is derived as follows. The differential form of the copolymer composition equation:

$$\frac{dM_1}{dM_2} = \frac{[M_1]}{[M_2]} \quad \frac{r_1[M_1] + [M_2]}{r_2[M_2] + [M_1]} \qquad (2)$$

may be expressed as:

$$K = \frac{r_1[M_1] + [M_2]}{r_2[M_2] + [M_1]} \qquad (39)$$

$$\text{where } K = \frac{dM_1}{dM_2}\,\frac{[M_2]}{[M_1]} \simeq \frac{m_1}{m_2}\,\frac{[M_2]}{[M_1]}$$

where $\frac{dM_1}{dM_2}$ and $\frac{m_1}{m_2}$ are the monomer mole ratios in the incremental copolymer formed and $[M_1]$ and $[M_2]$ the monomer concentrations in the feed. Equation (2) becomes:

$$Kr_2[M_2] + K[M_1] = r_1[M_1] + [M_2] \qquad (39a)$$

Dividing by $[M_2]$,

$$Kr_2 + KF = r_1F+1 \quad \text{or}$$

$$KF-1 = r_1F-Kr_2 \quad \text{where } F = [M_1] / [M_2]$$

Dividing by K yields:

$$F - \frac{1}{K} = \frac{F}{K}\,r_1 - r_2 \qquad (40)$$

Division of equation (39a) by F yields:

$$\frac{1}{F} - K = \frac{K}{F} r_2 - r_1 \tag{41}$$

Equations (40) and (41) which are essentially the Fineman and Ross equations (11) and (12), give different values of r_1 and r_2 due to disymmetry with respect to r_1 and r_2. Equation (40) is best suited for evaluation when $F >> 1$ and equation (41) is best suited when $F << 1$. The equations are interconvertible by multiplying equation (40) by $-K/F$ and equation (41) by $-F/K$. A symmetric equation with respect to r_1 and r_2 can thus be arrived at by multiplying equation (40) by $\sqrt{K/F}$ and equation (41) by $\sqrt{F/K}$.

$$\sqrt{KF} - 1/\sqrt{KF} = r_1 \sqrt{F/K} - r_2 \sqrt{K/F} \tag{42}$$

Substituting f/F for K in equation (42) and rearranging, we get,

$$\frac{F}{f^{\frac{1}{2}}} r_1 - \frac{f^{\frac{1}{2}}}{F} r_2 = f^{\frac{1}{2}} - 1/f^{\frac{1}{2}} \tag{13}$$

This linearization known as the YBR method is symmetrical with respect to r_1 and r_2.

Solution for r_1 and r_2 is obtained in the following manner. Equation (42) on multiplication by $\sqrt{F/K}$ and $\sqrt{K/F}$ gives,

$$r_1 F/K - r_2 = F - 1/K \tag{40}$$

$$r_2 K/F - r_1 = \frac{1}{F} - K \tag{41}$$

Equations (40) and (41) on summation to N data points become:

$$r_1A_1 - r_2N = C_1 \tag{43}$$

$$-r_1N + r_2A_2 = C_2 \tag{44}$$

where $$A_1 = \sum_{i=1}^{N} F_i/K_i \tag{45}$$

$$A_2 = \sum_{i=1}^{N} K_i/F_i \tag{46}$$

$$C_1 = \sum_{i=1}^{N} \left(F_i - 1/K_i\right) \tag{47}$$

$$C_2 = \sum_{i=1}^{N} -\left(K_i - 1/F_i\right) \tag{48}$$

and N is the number of experiments.

Equation (43) and (44) can be resolved for r_1 and r_2. Multiplication of equation (43) by N and equation (44) by A_1, followed by adding and rearranging,

$$r_1A_1N - r_2N^2 = C_1N \tag{49}$$

$$-r_1A_1N + r_2A_1A_2 = C_2A_1 \tag{50}$$

$$r_2(A_1A_2 - N^2) = A_1C_2 + NC_1 \tag{51}$$

$$r_2 = \frac{A_1C_2 + NC_1}{A_1A_2 - N^2} \tag{52}$$

Similarly,

$$r_1 = \frac{C_1A_2 + C_2N}{A_1A_2 - N^2} \tag{53}$$

The method of least squares can be applied to evaluate the mean square error in the determination of the monomer reactivity ratios, by substituting in equation (13) the r_1 and r_2 values obtained from equations (52) and (53).

$$\Lambda_l^2 = \sum_{i=1}^{N} \Lambda_i^2 \Big/ N-2 \qquad (54)$$

where $\Lambda_i^2 = \left(r_1 \sqrt{F_i/K_i} - r_2 \sqrt{\frac{K_i}{F_i}} - \sqrt{K_iF_i} + 1/\sqrt{K_iF_i}\right)^2 \qquad (55)$

Thus, the expression for mean square error in the determination of r_1 and r_2 is:

$$\Lambda_{r_1}^2 = \frac{\Lambda^2 A_2}{A_1A_2 - N^2} \qquad (56)$$

$$\Lambda_{r_2}^2 = \frac{\Lambda^2 A_1}{A_1A_2 - N^2} \qquad (57)$$

The exact values of r_1 and r_2 are then:

$$r_1 = \frac{A_2C_1 + NC_2}{A_1A_2 - N^2} \pm \sqrt{\frac{\Lambda^2 A_2}{A_1A_2 - N^2}} \qquad (58)$$

$$r_2 = \frac{A_1C_2 + NC_1}{A_1A_2 - N^2} \pm \sqrt{\frac{\Lambda^2 A_1}{A_1A_2 - N^2}} \qquad (59)$$

Thus, the method gives very balanced average parameters in spite of any stray experimental error in a set of data.

Though the method is suited theoretically for experiments carried to very low conversions (<5%), it has been found to give fairly accurate values even at conversions as high as 20%[46]. The range of applicability of this equation increases to higher conversions (>25%) if the average monomer feed values as defined by Joshi[46] are used for computation.

The average feed values are defined:

$$\mathrm{MFC} = \mathrm{WFC}\ \frac{M_2^o\, b + a\,(1-M_2^o\,)}{m_2\, b + a\,(1-m_2\,)} \tag{60}$$

$$\bar{M}_2 = \frac{2M_2^o - \mathrm{MFC}\ (M_2^o + m_2)}{2(1-\mathrm{MFC})} \tag{61}$$

where MFC and WFC are the mole fraction and weight fraction conversions respectively, a and b are the molecular weights of monomers, and M_2^o, $\bar{M}_2$ and m_2 are the mole fractions of the monomer 2 in the initial feed, its average mole fraction in the feed and its average mole fraction in the copolymer respectively.

2.1.2 Integrated Equation

Experiments carried out to low conversions suffer from many inaccuracies[55]. Copolymerizations could alternatively be carried out to high conversions and the integrated copolymer composition equation[31] used to compute

r_1 and r_2. The Mayo and Lewis integrated equation[31] is resolved by Joshi's procedure[46]. This procedure involves a preliminary determination of r_1 and r_2 by the YBR differential method[45] using average monomer feed values. The values of r_1 and r_2 arbitrarily represent a point on the hypothetical r_2 versus r_1 plot of Mayo and Lewis differential equation[31] which is the same as the best point Of intersection of the several lines representing r_2 versus r_1. Using this best point, the coordinates of the point of intersection of the normal to the ith line are found. The new coordinates of the point of intersection to a line on the Mayo-Lewis plots are designated $(r_1)_i$ and $(r_2)_i$. By narrowly altering the values of $(r_1)_i$ and $(r_2)_i$ around the best point by appropriate magnitudes with the help of an auxiliary constant, $Z = 0.1$, three values of P

$$\left[P = \frac{1-r_1}{1-r_2}\right]$$

are obtained. Using these three values of P, the Mayo-Lewis integrated equation[31] is solved and the appropriate portion of the integrated curves in the significant region are obtained on r_2 versus r_1 plot. The portion of each integral curve representing the points obtained from the three values of P is approximated as the root mean square straight lines and their slopes ($m = F^2/f$) and intercepts $\left[C = F\left(\frac{1}{f} - 1\right)\right]$ are computed. These new slopes (m) and intercept (C) are treated in the same manner as in the differential YBR procedure and the final values of r_1 and r_2 with their standard deviations are obtained.

2.2 Conformational Studies

2.2.1 Potentiometric Titration

Zimm and Rice[89] have shown that ΔG^o_{hel} values can be obtained from the potentiometric titration data of ionisable random coil polypeptides for the transformation

$$\text{(uncharged coil)} \rightleftharpoons \text{(uncharged helix)}$$

This is based on the equation,

$$pH = pK_o + \log \left[\frac{\alpha}{1-\alpha}\right] + \Delta pk(\alpha) \tag{62}$$

the complete change in free energy upon ionisation of the macromolecule (based on one mole of the monomer unit) is given by:

$$G_{ion} = 2.303\ RT \int_0^1 \left[pH-\log\left(\frac{\alpha}{1-\alpha}\right)\right] d\alpha \tag{63}$$

The term G_{ion} includes the free energy change due to the conformational transition. If the change in conformation takes place over a narrow range of pH, then the free energy term for ionization can be separated by graphical extrapolation of the part of the titration curve at large α to $\alpha = 0$. Subtraction of the free energy of ionization from the total free energy yields the free energy of conformational transition.

$$\Delta G_{\text{conf.Transition}} = G_{(\text{TOTAL})} - G_{\text{Ionization}} \qquad (64)$$

[TOTAL = conformational change + ionization]

$$G_{\text{conf}} = 2.303RT\left[\int_0^1\left[pH_\alpha - \log\left(\frac{\alpha}{1-\alpha}\right)\right]d\alpha - \int_0^1\left[pH_{\alpha_2} - \log\left(\frac{\alpha_2}{1-\alpha_2}\right)\right]d\alpha_2\right] \qquad (65)$$

where α_2 refers to ionisation without conformational transition and α to the situation involving both ionisation and conformational transition. Thus,

$$G_{\text{conformation}} = 2.303RT\int_0^1\left[pH_\alpha - pH_{\alpha_2}\right]\, d\alpha \qquad (66)$$

The method of Nagasawa and Holtzer^{90} assumes equilibrium between the undissociated forms of the helix and the coil.

$$h_o \rightleftharpoons C_o \qquad (67)$$

with the standard free energy change of the reaction

$$\Delta G^o = -RT\ l_n\left[C_co/C_{oh}\right] \qquad (68)$$

involving charge independent factors. The concentration of the helix as coil of any charge was computed from the theory of protolytic equilibrium and the individual curves of the helix and the coil. The total free energy change of conformational transition was derived as:

$$\Delta G = \Delta G_o + \int_{pH_o}^{pH} \frac{\delta(\Delta G)}{\delta(pH)}\ d(pH)$$

$$= \Delta G_o - 2.303\ RT\int_{pH_o}^{pH} \Delta\alpha\ d(pH) \qquad (69)$$

where $\Delta\alpha = \alpha_1 - \alpha_2$, the difference between the degrees of ionisation of the two conformations at the given pH and pH_o is the nature of pH for which $\Delta\alpha = 0$ (or in other words to very small α). ΔG_o, the free energy of conformational transition is given by:

$$\Delta G_o = 2.303\ RT \int_{pH_o}^{pH_m} \Delta\alpha\ (dpH) \qquad (70)$$

where pH_m is the mid point of the conformational transition. The conformational free energy estimates by the methods of Zimm and Rice[89] and Nagasawa and Holtzer[90] are shown to be theoretically equivalent[90]. The potentiometric titration curve (pH titration curves) have been shown to be independent of the polymer concentration[90] (in the dilute solution range) and the molecular weight of the samples[3,91].

The negative free energy of conformational transition per mole of the titratable carboxyls ($-\Delta F^o/N$) of the uncharged compact form to the hypothetically uncharged expanded form is estimated by the equation:

$$\frac{-\Delta F^o}{N} = 2.303\ RT \oint pK_{app}\ d\alpha = 2.303\ RTA \qquad (71)$$

2.2.2 Intrinsic Viscosity

Fuoss and Strauss observed that the sharp rise in the reduced viscosity η_{sp}/C of polyelectrolytes solutions in ion free water with dilution could be represented by the empirical expression[131,132]:

$$\eta_{sp}/C = \frac{A}{1+BC^{\frac{1}{2}}} + D \tag{72}$$

where A and B are empirical constants, (A+D) is the limiting value of η_{sp}/C as the concentration C approaches zero and B is dependent on the dielectric constant of the medium[133] and molecular weight[106]. The D term has been interpreted as a measure of the hydrodynamic volume of the uncharged polymer coil and serves primarily as an adjustable parameter to give a linear plot. The equation can be rearranged as:

$$1/[\eta_{sp}/C - D] = \frac{1}{A} + BC^{\frac{1}{2}}/A \tag{33}$$

A plot of $1/(\eta_{sp}/C-D)$ versus $C^{\frac{1}{2}}$ gives the value of $\frac{1}{A}$ at infinite dilution. D is not always negligible but may be disregarded for low molecular weight polyelectrolytes[151] and the value of A is determined from the extrapolation of C/η_{sp} vs. $C^{\frac{1}{2}}$ plot to $C^{\frac{1}{2}} = 0$ and is taken as $[\eta]$.

CHAPTER-III

EXPERIMENTAL

3. EXPERIMENTAL

3.1 Copolymerization Studies

3.1.1 Reagents and Chemicals

Potassium peroxydisulphate/sodium sulphite and potassium peroxydisulphate/sodium hydrosulphite were used as the redox initiator pairs for the aqueous solution copolymerization studies. Standard sodium hydroxide and hydrochloric acid solutions were used for adjusting the pH during copolymerizations. Sodium chloride was used as the electrolyte. Hydroquinone was used for terminating copolymerisations. Potassium sulphate, mercuric oxide, selenium and sulphuric acid were used as catalysts and NaOH 48% w/v, $Na_2S_2O_3$ 44% w/v as digestion mixture in semimicro Kjeldahl nitrogen estimation for the characterization of the copolymers. Boric acid as 4% aqueous solution was used to absorb the evolved ammonia. Potassium dichromate, sodium thiosulphate, potassium bromate, potassium bromide, potassium iodide, starch (0.1%) were used for the monomer purity determinations. These reagents and chemicals were of analytical reagent grade and were used without further purification.

3.1.2 Monomer Purification

The monomers - acrylic acid, methacrylic acid and N-vinyl pyrrolidone- were all of commercial grade carrying suitable inhibitors. The monomers were freed from inhibitors by distillation under reduced pressure over a blanket of purified nitrogen. In each case the middle fraction boiling at constant temperature [acrylic acid 48.5°C (15 torr)[112], methacrylic acid 60°C (12 torr)[112] and N-vinyl pyrrolidone 96°C (14 torr)[112]] were used, provided a purity of >99.5% was attained. The monomer purity was checked by gas chromatography and bromide/bromate mixture (bromine addition method[113]). Acrylamide used in the copolymerization studies was also of commercial grade. The monomer was purified by recrystallization twice from chloroform followed by recrystallisation once from benzene: ethylacetate (7:3) mixture. The purity was determined by melting point (84°C)[112] and bromide/bromate method[113].

3.1.3 Solvents

Acetone, benzene, ethyl acetate, chloroform, dioxane, dimethyl formamide, ethanol and methanol were all commercial grade and purified by standard procedures[114] and were distilled prior to use. Water used in the copolymerization studies was doubly distilled over alkaline potassium permanganate and was ion free.

3.1.4 Apparatus

3.1.4.1 Constant Temperature Bath

The copolymerization experiments were carried out in a constant temperature 'thermostat' water bath maintained at $30 \pm 0.05^{\circ}$C by a 'toluene regulator' and an electronic relay.

3.1.4.2 Purified Nitrogen

Nitrogen used for the distillation of monomers and in copolymerisation studies was of a high purity grade. It was freed from traces of oxygen by passing through Fieser's solution[115] (alkaline sodium hydrosulphite solution containing small amount of sodium anthroquinone β-sulphonate). Sulphurous impurities were removed by bubbling through 10% lead acetate solution and moisture was eliminated by bubbling through 98% sulphuric acid. Nitrogen for copolymerisation experiments was saturated with water vapour by bubbling through ion free water before admitting into the reaction vessels.

3.1.5 Polymerization Procedure

The copolymerisations were carried under nitrogen atmosphere at fixed pH values in specially designed cylindrical flat bottomed corning reaction vessels (7.5 cm length and 3.5 cm diameter) fitted with a B-34 F joint. The total reaction volume was adjusted exactly to 20 ml for the systems acrylic acid (AA)- N-vinyl pyrrolidone (NVP) (I) and methacrylic acid (MA)- N-vinyl pyrrolidone (NVP) (II) and to 10 ml for the systems acrylic acid (AA)-acrylamide (AM) (III) and methacrylic acid (MA)-acrylamide (AM) (IV). The total monomer concentration was kept around 1 mole/litre.

For each pH, the monomer molar feed ratios were varied in the range 9:1, 7:3, 1:1, 3:7 and 1:9. The redox pair $K_2S_2O_8/Na_2SO_3$ was used for the systems AA-NVP(I) and MA-NVP (II). The systems AA-AM (III) and MA-AM (IV) were initiated by the redox pair $K_2S_2O_8$-$Na_2S_2O_4$.

Ion free water (5 ml) was taken in the reaction vessels and the two monomers under investigation were accurately weighed into the vessels in the required mole ratios. The pH was varied by addition of exactly known volume of standardised sodium hydroxide solution ($\approx$ 2N) and the pH readings were recorded by a L 1-10 model Elico pH meter with an accuracy of ±0.05 pH unit. The glass and calomel electrodes were standardised with buffers of known pH (4.00, 7.00 and 9.18). The electrodes were washed with small amounts of deionised water and the washings were added to the monomer feed. The pH of the solutions were again checked for any possible drift. The reaction vessels were then thermostated and the contents flushed with nitrogen for about 15 minutes. The freshly prepared initiators in oxygen and ion free water were then introduced, first the persulphate followed by the reducing agent (Na_2SO_3, $Na_2S_2O_4$). The initiator concentrations were in the range 2.5×10^{-3} to 5×10^{-4} moles/litre. The nitrogen bubbling was then stopped. Nitrogen bubbling during polymerisations has been shown to retard the rate[15]. The polymerization under nitrogen atmosphere has a rate parallel to that in sealed ampules after elaborate freeze-thawing[15]. Though the initiator was effective in the entire pH range, only $K_2S_2O_8$ may be operating in the alkaline range[57,116,117].

3.1.6 Isolation of Polymers

The polymerizations were stopped after a predetermined time interval (1 to 5 hours) by the addition of hydroquinone, at twice the initiator concentration, in ion free water. The pH of the system was then brought to zero by the gradual addition of 30% HCl. Water was then pumped out from the reaction vessels under reduced pressure (10^{-2} torr) at 30^{o} . To facilitate the quick removal of water, acetone was added frequently. The copolymers were precipitated from the concentrated solutions (<5 ml) by the addition of acetone (250-300 ml). Hydroquinone added to terminate the polymerisation completely dissolved in acetone and the sodium ions added during the pH adjustment, in the form of NaCl, were completely precipitaed by acetone along with the copolymer. The solids were redissolved in ion free water and reprecipitated with acetone. The dissolutions-precipitations were repeated twice. The solids were quantitatively collected by filtration, dried 'in vacuo' at $60^{o}C$ to constant weight. The weight of the copolymer obtained in each case was corrected for by subtracting the weight of sodium chloride formed. The weight of sodium chloride was computed from the known amount of Na^+ ions introduced during the pH adjustment. Blank runs with the monomer mixtures showed no copolymerization during the isolation procedure and the sodium chloride formed was found to be equivalent to the amount of Na^+ introduced. Acetone:water mixture in the ratio (95:5) was found to precipitate the electrolytes completely even in the presence of polyelectrolytes which are good solubilizing agents. No homopolymerization occurs since all the copolymerizations were terminated very much prior to the depletion of either of the monomers. The copolymers were characterised by their nitrogen content, estimated by the semimicro Kjeldahl method[118-119]. The procedure gave a systematic error of -15.1% for poly(N-vinyl pyrrolidone) [as found by us by blank estimation of pure poly(N-vinyl pyrrolidone) and by others[120,121]], in the nitrogen estimation and this error was corrected for the copolymers containing N-vinyl pyrrolidone.

3.1.7 Nitrogen Estimation : Semimicro Kjeldahl Procedure

The solids quantitatively collected and dried to a constant weight were weighed accurately into Kjeldahl digestion flasks. For each 100 mg weight of the sample exactly 1.5 gm of finely ground catalyst mixture consisting of 30:2:1 ratio by weight of potassium sulphate, mercuric oxide and selenium was used. Exactly 5 ml of AR sulphuric acid was added for each 1.5 gm of the catalyst mixture. The sample was digested in a chamber maintained around 400 °C, avoiding boiling, till a clear pale yellow solution resulted. The contents were cooled and transferred quantitatively to a micro Kjeldahl set up, 20 ml of 48% w/v sodium hydroxide solution and 4 ml of 44% w/v sodium thiosulphate solution were then added and the contents were steam distilled under pressure. The ammonia liberated was absorbed in 4% boric acid solution. The solution was then titrated against 0.01 N HCl using a few drops of a mixed indicator of methyl red and bromocresol green (1:5 ratio of 0.1% w/v solutions of MR and BCG in 95:5 alcohol:water mixture). The end point was indicated by the change in colour from green to red.

3.1.8 Systems Investigated

3.1.8.1 Acrylic acid-N-vinyl Pyrrolidone[122]

The copolymerizations were carried out at $30 \pm 0.05^\circ$C at pHs 4,5,7,8 and 9 in ion free water and at pH 6.5 in the presence of 1 molar sodium chloride. The total volume was kept at 20 ml and the monomer concentration at 1 M. At each pH the molar monomer feed ratios were varied in the range 9:1, 7:3, 1:1, 3:7 and 1:9. The redox system $K_2S_2O_8/Na_2SO_3$ was used in the concentration range 5×10^{-4} M at low pH to 2.5×10^{-3} M at high pH. The polymerisation time ranged from 3 to 5 hours. The experimental observations are presented in Tables 6-11.

3.1.8.2 Methacrylic acid-N-vinyl Pyrrolidone[123,124]

The copolymerization behaviour was investigated at the pHs 2,3,4,5,6,7,8,9 and 10 in ion free water and at pHs 3,7 and 10 in the presence of 1 molar sodium chloride. At each pH the molar monomer feed ratios were varied in the range 9:1, 7:3, 1:1, 3:7 and 1:9. The temperature was maintained at 30±0.05°C. The redox system $K_2S_2O_8$/Na_2SO_3 in the concentration range $5x10^{-4}$ moles/litre at low pH to $2.5x10^{-3}$ moles/litre at high pH, was used for initiating the copolymerizations. The total monomer concentrations were kept at 1 molar and the volume at 20 ml. The copolymerization time varied between 1 and 3 hours. The observations are presented in Tables 12-23.

3.1.8.3 Acrylic acid-Acrylamide[125]

The copolymerisations were carried in nitrogen atmosphere at 30±0.05°C at the pH values 2,4,6,8 and 9 in ion free water and at pHs 4 and 6 in the presence of 1 molar sodium chloride. The total monomer concentration was kept around 1 molar and the volume exactly at 10 ml. At each pH the molar monomer feed ratios were varied as 9:1, 7:3, 1:1, 3:7 and 1:9. The redox system $K_2S_2O_8$/$Na_2S_2O_4$ at the constant concentration of $2.5x10^{-3}$ moles/litre was used to initiate the copolymerization. The copolymerization time ranged from 1 to 3 hours. The experimental results are presented in Tables 24-31.

3.1.8.4 Methacrylic acid-Acrylamide[125]

The copolymerisations were carried under nitrogen atmosphere at 30±0.05°C at arrested pHs 4,5,6,8,9 and 10 in ion free water and at pHs 4 and 10 in the presence of 1 molar sodium chloride solution. At each pH the molar monomer feed ratios were varied as 9:1, 7:3, 1:1, 3:7 and 1:9. The total monomer concentration was approximately 1 molar and the volume was exactly 10 ml. The redox pair, $K_2S_2O_8/Na_2S_2O_4$ at a constant concentration of 2.5×10^{-3} molar, was used to initiate the copolymerization. The copolymerization time varied from 1 to 3 hours. The experimental details are presented in Tables 32-40.

3.2 Conformational Studies

3.2.1 Introduction

The copolymers of methacrylic acid and N-vinyl pyrrolidone, a nonionic hydrophilic monomer, were synthesised by redox initiated aqueous solution copolymerization of methacrylic acid and N-vinyl pyrrolidone at 30±0.05°C in the absence of metal ions. The N-vinyl pyrrolidone content varied from 2.23 to 35.91 mole percent in the copolymer. The side chain ionization induced conformational transition was studied by potentiometric titration and viscosity.

3.2.2 Synthesis of Methacrylic acid (MA)-N-Vinyl Pyrrolidone (NVP) Copolymers

The purified monomers, methacrylic acid and N-vinyl pyrrolidone were copolymerized at 30±0.05°C by the redox system $K_2S_2O_8/Na_2SO_3$ in ion free water at pH 3 as described in Section 3.1.3.1 . The monomer reactivity ratios of the system at pH 3 as determined earlier[123,124] is $r_{MA} = 8.3$ and $r_{NVP} = 0$. Proper feed ratios of the monomers were chosen to arrive at copolymers of the desired composition. The total monomer and initiator concentrations were maintained around 1 mole/litre and 2.5×10^{-3} moles/litre respectively. The copolymerizations were stopped after sufficient conversion range (5 to 10%) by the addition of hydroquinone (5×10^{-3} moles/litre) and the copolymers were precipitated by the addition of an excess of 1:1 acetone: ethylacetate mixture. The copolymers were further purified by precipitation of their solutions in ethanol with the same non-solvent mixture (acetone, ethylacetate 1:1), dried at 40°C under vacuum (10^{-2} torr) to a constant weight and were characterized by their nitrogen content estimated by the semi micro Kjeldahl procedure[117], as described for the copolymers in Section 3.1.7
The samples were stored under anhydrous conditions in vacuum desiccators. It follows from the monomer reactivity ratios[123,124] [$r_{MA} = 8.3$ and $r_{NVP} = 0$] that the distribution of the N-vinyl pyrrolidone units in the

poly(methacrylic acid) chain is random. In the methacrylic acid rich copolymers long sequences of methacrylic acid will be interrupted by a single unit of N-vinyl pyrrolidone. At higher N-vinyl pyrrolidone contents e.g. 30%, the N-vinyl pyrrolidone length will still be of one segment interposed between diads of methacrylic acid. The $r_{NVP}=0$ and hence a N-vinyl pyrrolidone unit cannot add on to another unit of the same kind in the polymer chain. The monomer feed copolymer composition data are presented in Table-41.

3.2.3 Potentiometric Titration

Potentiometric titrations were carried out in ion free water, in 0.10 molar NaCl solution. The copolymer solutions were prepared by weighing accurately the dry copolymers into ion free water or 0.10 molar NaCl solutions and adding calculated amount of sodium hydroxide solution till exact neutralization i.e. the degree of ionization is equal to 1. The copolymer concentration was kept around $(3-5)\times10^{-2}$ equivalents of the titratable groups per litre. The experiments were conducted under nitrogen blanket at $30\pm0.05^{\circ}C$ with 0.5 molar hydrochloric acid solution keeping the electrolyte concentration constant. Small increments of hydrochloric acid were added and the corresponding pH were recorded with a El-10 model Elico pH meter accurate to 0.05 pH unit (standardised with buffers of known pH).

Titrations were carried to $\alpha = 0$. Blank titrations were carried out and the corrections, found to be negligible in the experimental pH range, were not applied. Precipitation occurred below pH 3.5 for systems richer in NVP.

The degree of ionisation α when the sodium salt is titrated by the acid is given by:

$$\alpha = 1 - \left[\text{Volume of HCl added to titrate at a given pH} \middle| \text{Total volume of HCl required for titration to } \alpha = 0 \right]$$

The apparent pH (pK_{app}) for different values of α were computed from the equation[79]:

$$pK_{app} = pH + \log \left[\frac{1-\alpha}{\alpha}\right]$$

The intrinsic pK (pK_c) values were obtained by extrapolation of pK_{app} versus $\alpha^{1/3}$ plots to $\alpha = 0$ as suggested by Arnold[126]. The titration data from high α (random coil region) in the pK versus α plot were extrapolated to pK_0 by curved extrapolation[3,90,127,128]. The free energy of conformational transition per mole of the titratable carboxyls ($-\Delta F^o/N$) of the uncharged expanded form was estimated by the Zimm and Rice procedure[89].

$$\frac{-\Delta F^o}{N} = 2.303RT \oint pK_{app}\, d\alpha = 2.303\ RTA.$$

where A is the area enclosed by the loop formed by the experimental titration curve, the extrapolated curve and the pK_o on the ordinate. The pK_{app} vs. $\alpha^{1/3}$ plots for a representative copolymer in ion free water and 1 molar sodium chloride solution are shown in Figs. (3) and (4). The pH and pK_{app} vs. α plots in ion free water and 1 molar sodium chloride solution are shown in Figs. 5 to 17.

3.2.4 Viscosity Measurements

The intrinsic viscosities were determined from the viscosity measurements in the copolymer concentration range 0.05 to 0.5 gm/dl in 0.10 molar sodium chloride solution using Ubbelhode type suspended level viscometers at 30±0.05°C. The shear rate correction[129]

$$\Big[\ \text{shear rate} = rhgd/2l\eta_r\eta_o$$

where η_o and η_r are the solvent viscosity and relative viscosity of the solution $\Big]$ was not found to be appreciable under the experimental conditions (capillary radius 0.026 cm, length 12 cm, efflux time for 0.10 molar sodium chloride solution = 170 secs.) even for extended molecules and hence was not applied. Polymer solutions at α = 0.1, 0.2, 0.3 and 0.85 were prepared in 0.10 molar sodium chloride solution and the diluting solvent was maintained at the same pH as the polymer solution. The Fuoss plot (c/η_{sp} vs. $C^{\frac{1}{2}}$) and Huggins plot (η_{sp}/C vs. C) are shown in Figs.18-31. The Huggins plot was used for α = 0.1.

The Fuoss-Strauss equation[130-133]:

$$\eta_{sp}/C = (A/1 + BC^{\frac{1}{2}})$$

was used for the determination of $[\eta]$ at higher values of α. C/η_{sp} was plotted against $C^{\frac{1}{2}}$ and the intercept $1/[C/\eta_{sp}]_{c \to 0}$ was taken as $[\eta]$.

Table-6: Acrylic acid (M_1) N-vinyl Pyrrolidone (M_2)
Monomer feed Copolymer Composition and Conversion Data

Water pH = 4.0
Temperature = $30 \pm 0.05^\circ$C
Initiator = $K_2S_2O_8$ 5×10^{-4} M, Na_2SO_3 5×10^{-4} M
Monomers ≃ 1 M
Total volume = 20 ml
Polymerization time = 3 hrs.
AA = 72.06
NVP = 111.15

Monomer feed		Mole fraction of M_2 in the feed	Mole fraction of M_2 in the copolymer	Weight of copolymer	Weight fraction conversion
AA(M_1) gm	NVP(M_2) gm	M_2	m_2	gm	
1.7110	0.2759	0.0947	0.0163	1.4009	0.7051
1.1703	0.8003	0.3072	0.1065	0.2754	0.1398
0.7895	1.1946	0.4957	0.3306	0.5418	0.2860
0.3989	1.7023	0.7347	0.5043	0.8850	0.4212
0.1137	2.0058	0.9196	0.6471	0.3307	0.1560

Differential YBR[1,2] $r_1 = 5.39 \pm 1.72$ $r_2 = 0.072 \pm 0.128$

Integrated Mayo Lewis $r_1 = 5.26 \pm 1.51$ $r_2 = 0.078 \pm 0.108$

Table-7: Acrylic acid (M_1) N-vinyl Pyrrolidone (M_2)
Monomer feed Copolymer Composition and Conversion Data

Water pH = 5.0
Temperature = 30±0.05°C
Initiator = $K_2S_2O_8$ $5x10^{-4}$ M
Na_2SO_3 $5x10^{-4}$ M
Monomers ≃ 1 M

Total volume = 20 ml
Polymerization time = 3 hrs.
AA = 72.06
NVP = 111.15

Monomer feed		Mole fraction of M_2 in the feed	Mole fraction of M_2 in the copolymer	Weight of copolymer	Weight fraction conversion
AA(M_1) gm	NVP(M_2) gm	M_2	m_2	gm	
1.6834	0.3454	0.1174	0.0882	1.1429	0.5633
1.1661	0.7833	0.3035	0.2833	1.2995	0.6666
0.7460	1.2572	0.5226	0.3211	0.9551	0.4768
0.3673	1.6303	0.7423	0.6755	0.5058	0.2532
0.1534	2.0483	0.8966	0.7900	0.3903	0.1773

Differential YBR $r_1 = 1.36 \pm 0.30$ $r_2 = 0.30 \pm 0.12$

Integrated Mayo-Lewis $r_1 = 1.32 \pm 0.29$ $r_2 = 0.31 \pm 0.17$

Table-8: Acrylic acid (M_1) N-vinyl Pyrrolidone (M_2)
Monomer feed Copolymer Composition and Conversion Data

Water pH = 7.0
Temperature = 30±0.05°C
Initiator = $K_2S_2O_8$ 2.5x10^{-3} M
Na_2SO_3 2.5x10^{-3} M
Monomers ≃ 1 M
Total volume = 20 ml
Polymerization time = 4 hrs.
AA = 72.06
NVP = 111.15

Monomer feed		Mole fraction of M_2 in the feed	Mole fraction of M_2 in the copolymer	Weight of copolymer	Weight fraction conversion
AA(M_1) gm	NVP(M_2) gm	M_2	m_2	gm	
1.7702	0.3153	0.1035	0.0181	0.7541	0.3616
1.1963	0.8444	0.3140	0.0432	0.8093	0.3966
0.8222	1.1716	0.4803	0.1151	0.9970	0.5001
0.4381	1.5450	0.6602	0.2211	0.7162	0.3505
0.1281	1.9022	0.9059	0.3293	0.2136	0.1052

Differential YBR r_1= 8.58±0.52 r_2 = -0.035±0.017
Integrated Mayo-Lewis r_1= 8.12±0.43 r_2 = 0.019±0.017

Table-9: Acrylic acid (M_1) N-vinyl Pyrrolidone (M_2)
Monomer feed Copolymer Composition and Conversion Data

Water pH = 8.0
Temperature = 30±0.05°C
Initiator = $K_2S_2O_8$ 2.5×10^{-3} M
Na_2SO_3 2.5×10^{-3} M
Monomers ≃ 1 M

Total volume = 20 ml
Polymerization time = 5 hrs.
AA = 72.06
NVP = 111.15

Monomer feed		Mole fraction of M_2 in the feed	Mole fraction of M_2 in the copolymer	Weight of copolymer	Weight fraction conversion
AA(M_1) gm	NVP(M_2) gm	M_2	m_2	gm	
1.8104	0.2236	0.0742	0.0158	1.3006	0.6394
1.1536	0.8055	0.3169	0.1248	1.2838	0.6553
0.7902	1.0554	0.4702	0.2405	0.9051	0.4904
0.4264	1.7375	0.7302	0.4268	0.9157	0.4232
0.1246	1.8398	0.9075	0.7350	0.4559	0.2321

Differential YBR $r_1 = 8.94 \pm 0.44$ $r_2 = 0.19 \pm 0.034$

Integrated Mayo-Lewis $r_1 = 6.66 \pm 0.63$ $r_2 = -0.084 \pm 0.016$

Table-10: Acrylic acid (M_1) N-vinyl Pyrrolidone (M_2)
Monomer feed Copolymer Composition and Conversion Data

Water pH = 9.0
Temperature = $30 \pm 0.05\,^{\circ}C$
Initiator = $K_2S_2O_8$ 2.5×10^{-3} M
Na_2SO_3 2.5×10^{-3} M
Monomers ≃ 1 M

Total volume = 20 ml
Polymerization time = 5 hrs.
AA = 72.06
NVP = 111.15

Monomer feed		Mole fraction of M_2 in the feed	Mole fraction of M_2 in the copolymer	Weight of copolymer	Weight fraction conversion
AA(M_1) gm	NVP(M_2) gm	M_2	m_2	gm	
1.7596	0.2170	0.0740	0.0178	1.2957	0.6555
1.2080	0.7658	0.2919	0.0441	1.0395	0.5266
0.6262	1.1382	0.5414	0.2492	0.7648	0.4335
0.5207	1.6673	0.6752	0.3964	0.3620	0.4397
0.1762	1.8564	0.8724	0.4225	0.3263	0.1605

Differential YBR $r_1 = 8.43 \pm 0.43$ $r_2 = 0.014 \pm 0.02$

Integrated Mayo-Lewis $r_1 = 7.22 \pm 0.37$ $r_2 = 0.010 \pm 0.019$

Table-11: Acrylic acid (M_1) N-vinyl Pyrrolidone (M_2)
Monomer feed Copolymer Composition and Conversion Data

1 M NaCl pH = 6.5
Temperature = 30±0.05°C
Initiator = $K_2S_2O_8$ 2.5×10^{-3} M
Na_2SO_3 2.5×10^{-3} M
Monomers ≃ 1 M

Total volume = 20 ml
Polymerization time = 3 hrs.
AA = 72.06
NVP = 111.15

Monomer feed		Mole fraction of M_2 in the feed	Mole fraction of M_2 in the copolymer	Weight of copolymer	Weight fraction conversion
AA(M_1) gm	NVP(M_2) gm	M_2	m_2	gm	
1.7116	0.2762	0.0947	0.0257	0.9564	0.4812
1.1316	0.8709	0.3332	0.0299	0.8597	0.4293
0.7255	1.1332	0.5048	0.0670	0.5752	0.3095
0.4443	1.5967	0.7002	0.0938	0.4072	0.1995
0.1991	2.2068	0.8780	0.0980	0.2097	0.0872

Differential YBR $r_1 = 6.29 \pm 0.68$ $r_2 = -0.088 \pm 0.017$
Integrated Mayo-Lewis $r_1 = 5.87 \pm 0.63$ $r_2 = -0.077 \pm 0.020$

Table-12: Methacrylic acid (M_1) N-vinyl Pyrrolidone (M_2)
Monomer feed Copolymer Composition and Conversion Data

Water pH = 2.0
Temperature = 30±0.05°C
Initiator = $K_2S_2O_8$ 5×10^{-4} M
Na_2SO_3 5×10^{-4} M
Monomers ≃ 1 M

Total volume = 20 ml
Polymerisation time = 3 hrs
MA = 86.09
NVP = 111.15

Monomer feed		Mole fraction of M_2 in the feed	Mole fraction of M_2 in the copolymer	Weight of copolymer	Weight fraction conversion
MA(M_1) gm	NVP(M_2) gm	M_2	m_2	gm	
1.6518	0.2351	0.0993	0.0239	0.3186	0.4868
1.2895	0.7591	0.3132	0.0547	0.5885	0.2873
0.9433	1.1778	0.4916	0.1061	0.3254	0.1534
0.5638	1.7517	0.7064	0.1545	0.3090	0.1335
0.1736	2.2200	0.9083	0.3886	0.1181	0.0433

Differential YBR $r_1 = 6.87 \pm 0.39$ $r_2 = -0.035 \pm 0.025$

Integrated Mayo-Lewis $r_1 = 6.49 \pm 0.42$ $r_2 = -0.038 \pm 0.028$

Table-13: **Methacrylic acid (M_1) N-vinyl Pyrrolidone (M_2)**
Monomer feed Copolymer Composition and Conversion Data

Water pH	= 3.0	Total volume	= 20 ml
Temperature	= 30±0.05°C	Polymerization time	= 3 hrs.
Initiator	= $K_2S_2O_8$ 1×10^{-3} M	MA	= 86.09
	Na_2SO_3 1×10^{-3} M	NVP	= 111.15
Monomers	$\simeq$ 1 M		

Monomer feed		Mole fraction of M_2 in the feed	Mole fraction of M_2 in the copolymer	Weight of copolymer	Weight fraction conversion
MA(M_1) gm	NVP(M_2) gm	M_2	m_2	gm	
1.7134	0.3532	0.1577	0.0322	1.1110	0.5376
1.3648	0.7060	0.2861	0.0552	0.7636	0.3716
0.9023	1.2242	0.5124	0.1413	0.6156	0.2895
0.4854	1.6877	0.7292	0.2449	0.4469	0.2057
0.1272	2.1723	0.0703	0.3704	0.1390	0.0604

Differential YBR $r_1 = 8.62\pm0.17$ $r_2 = -0.059\pm0.005$

Integrated Mayo-Lewis $r_1 = 8.34\pm0.014$ $r_2 = -0.006\pm0.003$

Table-14: Methacrylic acid (M_1) N-vinyl Pyrrolidone (M_2)
Monomer feed Copolymer Composition and Conversion Data

Water pH = 4.0
Temperature = $30\pm0.05^{\circ}C$
Initiator = $K_2S_2O_8$ 2.5×10^{-3} M
Na_2SO_3 2.5×10^{-3} M
Monomers ≈ 1 M

Total volume = 20 ml
Polymerization time = 3 hrs.
MA = 86.09
NVP = 111.15

Monomer feed		Mole fraction of M_2 in the feed	Mole fraction of M_2 in the copolymer	Weight of copolymer	Weight fraction conversion
MA(M_1) gm	NVP(M_2) gm	M_2	m_2	gm	
1.7539	0.2565	0.1018	0.0379	0.2474	0.1231
1.2226	0.7722	0.3285	0.1354	0.1177	0.0590
0.9634	1.2094	0.4931	0.1077	0.2537	0.1168
0.5144	1.6716	0.6157	0.2450	0.2073	0.0948
0.1724	2.1892	0.9077	0.3433	0.2010	0.0851

Differential YBR $r_1 = 2.99\pm0.18$ $r_2 = -0.035\pm0.016$

Integrated Mayo-Lewis $r_1 = 2.99\pm0.018$ $r_2 = -0.032\pm0.015$

Table-15: **Methacrylic acid (M_1) N-vinyl Pyrrolidone (M_2)**
Monomer feed Copolymer Composition and Conversion Data

Water pH = 5.0
Temperature = 30±0.05°C
Initiator = $K_2S_2O_8$ 2.5×10^{-3} M
Na_2SO_3 2.5×10^{-3} M
Monomers ≃ 1 M

Total volume = 20 ml
Polymerization time = 3 hrs.
MA = 86.09
NVP = 111.15

Monomer feed		Mole fraction of M_2 in the feed	Mole fraction of M_2 in the copolymer	Weight of copolymer	Weight fraction conversion
MA(M_1) gm	NVP(M_2) gm	M_2	m_2	gm	
1.7414	0.1997	0.0816	0.0285	1.3711	0.7064
1.2990	0.7715	0.3151	0.1086	1.0633	0.5135
0.9523	1.1965	0.4932	0.1633	0.3984	0.1854
0.5940	1.7219	0.6919	0.3044	0.4396	0.1898
0.1984	2.3386	0.9013	0.5920	0.4465	0.1760

Differential YBP $r_1 = 5.79\pm1.11$ $r_2 = 0.073\pm0.106$

Integrated Mayo-Lewis $r_1 = 4.90\pm0.91$ $r_2 = 0.052\pm0.086$

Table-16: Methacrylic acid (M_1) N-vinyl Pyrrolidone (M_2)
Monomer feed copolymer Composition and Conversion Data

Water pH = 6.0
Temperature = $30 \pm 0.05^\circ C$
Initiator = $K_2S_2O_8$ 2.5×10^{-3} M
Na_2SO_3 2.5×10^{-3} M
Monomers ≃ 1 M

Total volume = 20 ml
Polymerization time = 3 hrs.
MA = 86.09
NVP = 111.15

Monomer feed		Mole fraction of M_2 in the feed	Mole fraction of M_2 in the copolymer	Weight of copolymer	Weight fraction conversion
MA(M_1) gm	NVP(M_2) gm	M_2	m_2	gm	
1.7065	0.3600	0.1404	0.0518	1.2637	0.6115
1.1549	0.8210	0.3551	0.1207	0.6058	0.3066
0.9021	1.2187	0.5113	0.2115	0.5572	0.2627
0.5201	1.6929	0.7160	0.3429	0.3324	0.1050
0.1604	2.2067	0.9142	0.2993	0.1131	0.0478

Differential YBR $r_1 = 4.33 \pm 0.17$ $r_2 = -0.026 \pm 0.009$

Integrated Mayo-Lewis $r_1 = 4.00 \pm 0.102$ $r_2 = -0.027 \pm 0.006$

Table-17: **Methacrylic acid (M_1) N-vinyl Pyrrolidone (M_2)**
Monomer feed Copolymer Composition and Conversion Data

Water pH	= 7.0	**Total volume**	= 20 ml
Temperature	= $30 \pm 0.05^{\circ}C$	**Polymerization time**	= 3 hrs.
Initiator	= $K_2S_2O_8$ 2.5×10^{-3} M	**MA**	= 86.09
	Na_2SO_3 2.5×10^{-3} M	**NVP**	= 111.15
Monomers	$\simeq$ 1 M		

Monomer feed		**Mole fraction of M_2 in the feed**	**Mole fraction of M_2 in the copolymer**	**Weight of copolymer**	**Weight fraction conversion**
MA(M_1) **gm**	**NVP(M_2)** **gm**	M_2	m_2	**gm**	
1.7435	0.2324	0.0936	0.0329	0.8615	0.4360
1.3162	0.7109	0.2950	0.0821	0.3727	0.1839
0.9217	1.3410	0.5298	0.2256	0.2400	0.1061
0.5655	1.6691	0.6957	0.4308	0.0874	0.0391
0.1476	2.3266	0.9243	0.7871	0.1426	0.0576

Differential	YBR	$r_1 = 4.17 \pm 0.28$	$r_2 = 0.291 \pm 0.05$
Integrated Mayo-Lewis		$r_1 = 4.03 \pm 0.29$	$r_2 = 0.28 \pm 0.062$

Table-18: Methacrylic acid (M_1) N-vinyl Pyrrolidone (M_2)
Monomer feed Copolymer Composition and Conversion Data

Water pH = 8.0
Temperature = 30±0.05°C
Initiator = $K_2S_2O_8$ 2.5×10^{-3} M
Na_2SO_3 2.5×10^{-3} M
Monomers ≃ 1 M

Total volume = 20 ml
Polymerization time= 4 hrs.
MA = 86.09
NVP = 111.15

Monomer feed		Mole fraction of M_2 in the feed	Mole fraction of M_2 in the copolymer	Weight of copolymer	Weight fraction conversion
MA(M_1) gm	NVP(M_2) gm	M_2	m_2	gm	
1.7100	0.2347	0.0961	0.0887	0.5506	0.2831
1.2060	0.6423	0.2920	0.0577	0.3059	0.1655
0.9230	1.2200	0.5043	0.0871	0.2133	0.0993
0.5585	1.6335	0.6938	0.5509	0.1266	0.0578
0.1575	2.3725	0.9210	0.5001	0.4331	0.1712

Differential YBF $r_1 = 1.23 \pm 0.52$ $r_2 = -0.011 \pm 0.047$
Integrated Mayo-Lewis $r_1 = 0.92 \pm 0.29$ $r_2 = 0.67 \pm 0.19$

Table-19: Methacrylic acid (M_1) N-vinyl Pyrrolidone (M_2)
Monomer feed Copolymer Composition and Conversion Data

Water pH = 9.0
Temperature = 30±0.05°C
Initiator = $K_2S_2O_8$ 2.5x10^{-3} M
Na_2SO_3 2.5x10^{-3} M
Monomers ≃ 1 M

Total volume = 20 ml
Polymerization time= 5 hrs.
MA = 86.09
NVP = 111.15

Monomer feed		Mole fraction of M_2 in the feed	Mole fraction of M_2 in the copolymer	Weight of copolymer	Weight fraction conversion
MA(M_1) gm	NVP(M_2) gm	M_2	m_2	gm	
1.6572	0.2120	0.0902	0.0456	0.2699	0.1444
1.3017	0.7325	0.3035	0.0868	0.3392	0.1668
0.8857	1.0890	0.4878	0.2315	0.3967	0.2003
0.5594	1.5378	0.6304	0.2864	0.2432	0.1160
0.1437	2.3406	0.9237	0.6543	0.3351	0.1346

Differential YBR $r_1 = 2.33 \pm 0.39$ $r_2 = 0.039 \pm 0.065$

Integrated Mayo-Lewis $r_1 = 2.33 \pm 0.38$ $r_2 = 0.037 \pm 0.062$

Table-20: Methacrylic acid (M_1) N-vinyl Pyrrolidone (M_2)
Monomer feed Copolymer Composition and Conversion Data

Water pH = 10.0
Temperature = 30±0.05°C
Initiator = $K_2S_2O_8$ 2.5×10^{-3} M
Na_2SO_3 2.5×10^{-3} M
Monomers ≃ 1 M

Total volume = 20 ml
Polymerization time= 5 hrs.
MA = 86.09
NVP = 111.15

Monomer feed		Mole fraction of M_2 in the feed	Mole fraction of M_2 in the copolymer	Weight of copolymer	Weight fraction conversion
MA(M_1) gm	NVP(M_2) gm	M_2	m_2	gm	
1.8014	0.2820	0.1081	0.0364	0.4103	0.1369
1.3153	0.7700	0.3120	0.1037	0.4692	0.2250
0.9276	1.1993	0.5005	0.1595	0.3277	0.1541
0.6229	1.3440	0.6256	0.1043	0.1186	0.0602
0.1225	2.0995	0.9299	0.6194	0.2028	0.0913

Differential YBR $r_1 = 3.59 \pm 0.23$ $r_2 = -0.313 \pm 0.036$

Integrated Mayo-Lewis $r_1 = 3.58 \pm 0.23$ $r_2 = -0.031 \pm 0.035$

Table-21: Methacrylic acid (M_1) N-vinyl Pyrrolidone (M_2)
Monomer feed Copolymer Composition and Conversion Data

1 M NaCl pH = 3.0
Temperature = 30$\pm$0.05°C
Initiator = $K_2S_2O_8$ 2.5x10^{-3} M
Na_2SO_3 2.5x10^{-3} M
Monomers ≃ 1 M

Total volume = 20 ml
Polymerization time= 4 hrs.
MA = 86.09
NVP = 111.15

Monomer feed		Mole fraction of M_2 in the feed	Mole fraction of M_2 in the copolymer	Weight of copolymer	Weight fraction conversion
MA(M_1) gm	NVP(M_2) gm	M_2	m_2	gm	
1.5966	0.3395	0.1414	0.0382	0.6343	0.3276
1.1997	0.7350	0.3218	0.0961	0.5126	0.2650
0.9050	1.2010	0.5069	0.2501	0.2787	0.1323
0.5899	1.5860	0.6756	0.3103	0.1415	0.0650

Differential YBP $r_1 = 5.01\pm0.42$ $r_2 = 0.28\pm0.12$
Integrated Mayo-Lewis $r_1 = 4.90\pm0.40$ $r_2 = 0.27\pm0.12$

Table-22: **Methacrylic acid (M_1) N-vinyl Pyrrolidone (M_2)**
Monomer feed Copolymer Composition and Conversion Data

1 M NaCl pH = 7.0
Temperature = 30±0.05°C
Initiator = $K_2S_2O_8$ 2.5×10^{-3} M
Na_2SO_3 2.5×10^{-3} M
Monomers ≃ 1 M

Total volume = 20 ml
Polymerization time= 5 hrs.
MA = 86.09
NVP = 111.15

Monomer feed		Mole fraction of M_2 in the feed	Mole fraction of M_2 in the copolymer	Weight of copolymer	Weight fraction conversion
MA(M_1) gm	NVP(M_2) gm	M_2	m_2	gm	
1.7307	0.2905	0.1151	0.0330	0.4197	0.2076
1.3309	0.6368	0.2702	0.0607	0.3336	0.1695
0.8282	1.1592	0.5202	0.0593	0.6191	0.3115
0.4552	1.5930	0.7305	0.2199	0.1859	0.0908
0.1436	2.1260	0.9198	0.7183	0.2811	0.1239

Differential YBR $r_1 = 4.42\pm0.38$ $r_2 = -0.084\pm0.042$

Integrated Mayo-Lewis $r_1 = 4.44\pm0.39$ $r_2 = -0.059\pm0.044$

Table-23: **Methacrylic acid (M_1) N-vinyl Pyrrolidone (M_2)**

Moncmer feed Copolymer Composition and Conversion Data

1 M NaCl pH = 10.0

Temperature = 30±0.05°C

Initiator = $K_2S_2O_8$ 2.5x10^{-3} M

Na_2SO_3 2.5x10^{-3} M

Monomers ≃ 1 M

Total volume = 20 ml

Polymerization time = 5 hrs.

MA = 86.09

NVP = 111.15

Monomer feed		Mole fraction of M_2 in the feed	Mole fraction of M_2 in the copolymer	Weight of copolymer	Weight fraction conversion
MA(M_1) gm	NVP(M_2) gm	M_2	m_2	gm	
1.6236	0.3404	0.1397	0.0382	0.2744	0.1397
1.4305	0.7106	0.2778	0.0732	0.5027	0.2348
0.9520	1.1120	0.4750	0.1553	0.3097	0.1500
0.5126	1.6994	0.7197	0.1675	0.2681	0.1212
0.1782	2.1513	0.9034	0.4721	0.1004	0.0431

Differential YBR $r_1 = 4.45 \pm 0.20$ $r_2 = -0.031 \pm 0.02$

Integrated Mayo-Lewis $r_1 = 4.43 \pm 0.19$ $r_2 = -0.030 \pm 0.019$

Table-24: Acrylic acid (M_1) Acrylamide (M_2)
Monomer feed Copolymer Composition and Conversion Data

Water pH = 2.0
Temperature = 30±0.05°C
Initiator = $K_2S_2O_8$ 2.5×10^{-3} M
$Na_2S_2O_4$ 2.5×10^{-3} M
Monomers ≃ 1 M

Total volume = 10 ml
Polymerization time = 3 hrs.
AA = 72.06
AM = 71.08

Monomer feed		Mole fraction of M_2 in the feed	Mole fraction of M_2 in the copolymer	Weight of copolymer	Weight fraction conversion
AA(M_1) gm	AM(M_2) gm	M_2	m_2	gm	
0.6115	0.4385	0.4209	0.2970	0.3023	0.2879
0.3701	0.3526	0.4913	0.4659	0.5107	0.7067
0.2685	0.4935	0.6508	0.5512	0.4648	0.6100

Differential YBR $r_1 = 0.93 \pm 0.79$ $r_2 = 0.23 \pm 0.33$
Integrated Mayo-Lewis $r_1 = 0.92 \pm 0.82$ $r_2 = 0.25 \pm 0.36$

Table-25: Acrylic acid (M_1) Acrylamide (M_2)
Monomer feed Copolymer Composition and Conversion Data

Water pH	= 4.0	Total volume	= 10 ml
Temperature	= 30±0.05°C	Polymerization time	= 3 hrs
Initiator	= $K_2S_2O_8$ 2.5x10^{-3} M	AA	= 72.06
	$Na_2S_2O_4$ 2.5x10^{-3} M	AM	= 71.08
Monomers	≃ 1 M		

Monomer feed		Mole fraction of M_2 in the feed	Mole fraction of M_2 in the copolymer	Weight of copolymer	Weight fraction conversion
AA(M_1) gm	AM(M_2) gm	M_2	m_2	gm	
0.5184	0.2198	0.3006	0.3816	0.3827	0.5184
0.3890	0.3263	0.4596	0.5147	0.4532	0.6336
0.3940	1.0015	0.7204	0.8095	0.1599	0.1146
0.3240	0.7285	0.6951	0.6683	0.2569	0.2441

Differential YBR r_1 = 0.30±0.06 r_2 = 0.56±0.09

Integrated Mayo-Lewis r_1 = 0.32±0.046 r_2 = 0.57±0.067

Table-26: Acrylic acid (M_1) Acrylamide (M_2)
Monomer feed Copolymer Composition and Conversion Data

Water pH = 6.0
Temperature = 30±0.05°C
Initiator = $K_2S_2O_8$ 2.5x10^{-3} M
$Na_2S_2O_4$ 2.5x10^{-3} M
Monomers ≃ 1 M

Total volume = 10 ml
Polymerization time = 3 hrs
AA = 72.06
AM = 71.08

Monomer feed		Mole fraction of M_2 in the feed	Mole fraction of M_2 in the copolymer	Weight of copolymer	Weight fraction conversion
AA(M_1) gm	AM(M_2) gm	M_2	m_2	gm	
0.6010	0.1273	0.1768	0.3037	0.2490	0.3419
0.4921	0.1817	0.2723	0.2880	0.3177	0.4715
0.3152	0.4013	0.5635	0.5861	0.5537	0.7728
0.4110	0.7085	0.6361	0.7276	0.4646	0.4150

Differential YBR r_1 = 0.34±0.20 r_2 = 0.89±0.64

Integrated Mayo-Lewis r_1 = 0.34±0.20 r_2 = 0.85±0.62

Table-27: Acrylic acid (M_1) Acrylamide (M_2)
Monomer feed Copolymer Composition and Conversion Data

Water pH = 8.0
Temperature = 30±0.05°C
Initiator = $K_2S_2O_8$ 2.5×10^{-3} M
$Na_2S_2O_4$ 2.5×10^{-3} M
Monomers ≃ 1 M

Total volume = 10 ml
Polymerization time = 3 hrs.
AA = 72.06
AM = 71.08

Monomer feed		Mole fraction of M_2 in the feed	Mole fraction of M_2 in the copolymer	Weight of copolymer	Weight fraction conversion
AA(M_1) gm	AM(M_2) gm	M_2	m_2	gm	
0.6298	0.1662	0.2111	0.2311	0.3183	0.3999
0.5474	0.2331	0.3015	0.2990	0.3145	0.4029
0.2182	0.4525	0.6777	0.5118	0.2701	0.3505
0.0890	0.8075	0.9019	0.6814	0.4012	0.4475

Differential	YBR	$r_1 = 0.63 \pm 0.005$	$r_2 = 0.12 \pm 0.005$
Integrated	Mayo-Lewis	$r_1 = 0.63 \pm 0.004$	$r_2 = 0.12 \pm 0.004$

Table-28: Acrylic acid (M_1) Acrylamide (M_2)
Monomer feed Copolymer Composition and Conversion Data

Water pH	= 9.0	Total volume	= 10 ml.
Temperature	= 30$\pm$0.05°C	Polymerization time	= 3 hrs.
Initiator	= $K_2S_2O_8$ 2.5x10^{-3} M	AA	= 72.06
	$Na_2S_2O_4$ 2.5x10^{-3} M	AM	= 71.08
Monomers	$\simeq$ 1 M		

Monomer feed		Mole fraction of M_2 in the feed	Mole fraction of M_2 in the copolymer	Weight of copolymer	Weight fraction conversion
AA(M_1) gm	AM(M_2) gm	M_2	m_2	gm	
0.6330	0.2145	0.2557	0.4165	0.2557	0.2127
0.5185	0.2095	0.2906	0.3674	0.2906	0.3512
0.4810	0.4800	0.5029	0.6183	0.5029	0.4573
0.4111	0.5865	0.5912	0.6417	0.5912	0.1298
0.3052	0.7585	0.7159	0.7550	0.7512	0.1033

Differential YBR $r_1 = 0.30\pm0.10$ $r_2 = 0.95\pm0.21$

Integrated Mayo-Lewis $r_1 = 0.30\pm0.10$ $r_2 = 0.95\pm0.20$

Table-23: Acrylic acid (M_1) Acrylamide (M_2)
Monomer feed Copolymer Composition and Conversion Data

1 M NaCl pH = 2.0
Temperature = 30±0.05°C
Initiator = $K_2S_2O_8$ 2.5×10^{-3} M
$Na_2S_2O_4$ 2.5×10^{-3} M
Monomers ≃ 1 M

Total volume = 10 ml
Polymerization time = 3 hrs.
AA = 72.06
AM = 71.08

Monomer feed		Mole fraction of M_2 in the feed	Mole fraction of M_2 in the copolymer	Weight of copolymer	Weight fraction conversion
AA(M_1)	AM(M_2)				
gm	gm	M_2	m_2	gm	
0.5878	0.4122	0.4155	0.3611	0.2969	0.2969
0.4796	0.4940	0.5108	0.4214	0.3217	0.3304
0.3880	0.6139	0.6160	0.4784	0.4076	0.4068
0.2713	0.6975	0.7227	0.6341	0.1948	0.2011

Differential YBR $r_1 = 0.93 \pm 0.39$ $r_2 = 0.33 \pm 0.17$

Integrated Mayo-Lewis $r_1 = 0.94 \pm 0.38$ $r_2 = 0.34 \pm 0.16$

Table-30: Acrylic acid (M_1) Acrylamide (M_2)
Monomer feed Copolymer Composition and Conversion Data

1 M NaCl pH = 4.0
Temperature = 30$\pm$0.05^{o}C
Initiator = $K_2S_2O_8$ 2.5x10^{-3} M
$Na_2S_2O_4$ 2.5x10^{-3} M
Monomers $\simeq$ 1 M

Total volume = 10 ml
Polymerization time= 3 hrs.
AA = 72.06
AM = 71.08

Monomer feed		Mole fraction of M_2 in the feed	Mole fraction of M_2 in the copolymer	Weight of copolymer	Weight fraction conversion
AA(M_1) gm	AM(M_2) gm	M_2	m_2	gm	
0.7820	0.4727	0.3800	0.3039	0.0578	0.0461
0.5849	0.3932	0.4053	0.4216	0.1365	0.1396
0.5121	0.4791	0.4867	0.4582	0.2682	0.2706
0.4563	0.6040	0.5730	0.5625	0.5054	0.4767

Differential	YBR	r_1 = 0.91$\pm$0.24	r_2 = 0.67$\pm$0.13
Integrated	Mayo-Lewis	r_1 = 0.92$\pm$0.25	r_2 = 0.68$\pm$0.13

Table-31: Acrylic acid (M_1) Acrylamide (M_2)
Monomer feed Copolymer Composition and Conversion Data

1 M NaCl pH = 6.0
Temperature = 30±0.05°C
Initiator = $K_2S_2O_8$ 2.5×10^{-3} M
$Na_2S_2O_4$ 2.5×10^{-3} M
Monomers ≃ 1 M

Total volume = 10 ml
Polymerization time = 3 hrs.
AA = 72.06
AM = 71.08

Monomer feed		Mole fraction of M_2 in the feed	Mole fraction of M_2 in the copolymer	Weight of copolymer	Weight fraction conversion
AA(M_1) gm	AM(M_2) gm	M_2	m_2	gm	
0.8074	0.2947	0.2701	0.4084	0.3083	0.2797
0.5744	0.4623	0.4493	0.4926	0.7088	0.6837
0.4756	0.5094	0.5206	0.6177	0.4458	0.4526

Differential	YBR	$r_1 = 0.29 \pm 0.19$	$r_2 = 0.93 \pm 0.57$
Integrated	Mayo-Lewis	$r_1 = 0.28 \pm 0.20$	$r_2 = 0.86 \pm 0.59$

Table-32: Methacrylic acid (M_1) Acrylamide (M_2)
Monomer feed Copolymer Composition and Conversion Data

Water pH = 4.0
Temperature = 30±0.05°C
Initiator = $K_2S_2O_8$ 2.5x10^{-3} M
$Na_2S_2O_4$ 2.5x10^{-3} M
Monomers ≃ 1 M

Total volume = 10 ml
Polymerization time= 1 hr.
MA = 86.09
AM = 71.08

Monomer feed		Mole fraction of M_2 in the feed	Mole fraction of M_2 in the copolymer	Weight of copolymer	Weight fraction conversion
MA(M_1) gm	AM(M_2) gm	M_2	m_2	gm	
0.7510	0.1648	0.2100	0.0360	0.2406	0.2627
0.6285	0.2211	0.2988	0.1432	0.1534	0.1806
0.4800	0.3401	0.4618	0.1394	0.1612	0.1966
0.2315	0.6067	0.7604	0.4521	0.0839	0.1001
0.1235	0.7313	0.8776	0.6812	0.0600	0.0702

Differential YBR r_1 = 2.84±0.47 r_2 = 0.20±0.07

Integrated Mayo-Lewis r_1 = 2.81±0.44 r_2 = 0.20±0.07

Table-33: Methacrylic acid (M_1) Acrylamide (M_2)
Monomer feed Copolymer Composition and Conversion Data

Water pH = 5.0
Temperature = 30±0.05°C
Initiator = $K_2S_2O_8$ $2.5x10^{-3}$ M
$Na_2S_2O_4$ $2.5x10^{-3}$ M
Monomers ≃ 1 M

Total volume = 10 ml
Polymerization time = 1 hr.
MA = 86.09
AM = 71.08

Monomer feed		Mole fraction of M_2 in the feed	Mole fraction of M_2 in the copolymer	Weight of copolymer	Weight fraction conversion
MA(M_1) gm	AM(M_2) gm	M_2	m_2	gm	
0.7380	0.0765	0.1115	0.0692	0.1475	0.1811
0.6738	0.2514	0.3112	0.1541	0.1560	0.1686
0.5297	0.3174	0.4205	0.1803	0.1041	0.1229
0.2745	0.7227	0.7612	0.5367	0.0986	0.0989
0.0339	0.8050	0.9121	0.8233	0.1003	0.1116

Differential YBF $r_1 = 1.95 \pm 0.35$ $r_2 = 0.30 \pm 0.13$
Integrated Mayo-Lewis $r_1 = 1.94 \pm 0.35$ $r_2 = 0.30 \pm 0.12$

Table-34: Methacrylic acid (M_1) Acrylamide (M_2)

Monomer feed Copolyme r Composition and Conversion Data

Water pH = 6.0
Temperature = 30±0.05°C
Initiator = $K_2S_2O_8$ $2.5x10^{-3}$ M
$Na_2S_2O_4$ $2.5x10^{-}$ M
Monomers - 1 M

Total volume = 10 ml
Polymerization time = 1 hr.
MA = 86.09
AM = 71.08

Monomer feed		Mole fraction of M_2 in the feed	Mole fraction of M_2 in the copolymer	Weight of copolymer	Weight fraction conversion
MA(M_1) gm	AM(M_2) gm	M_2	m_2	gm	
0.6228	0.2972	0.3663	0.4329	0.1176	0.1278
0.4802	0.4500	0.5316	0.5982	0.1536	0.1716
0.2560	0.6118	0.7432	0.7070	0.1583	0.1824
0.1347	0.7469	0.8704	0.8853	0.2175	0.2467

Differential YBR $r_1 = 0.19 \pm 0.08$ $r_2 = 0.55 \pm 0.08$

Integrated Mayo-Lewis $r_1 = 0.19 \pm 0.08$ $r_2 = 0.55 \pm 0.08$

Table-35: Methacrylic acid (M_1) Acrylamide (M_2)
Monomer feed Copolymer Composition and Conversion Data

Water pH = 8.0
Temperature = $30 \pm 0.05^{\circ}C$
Initiator = $K_2S_2O_8$ 2.5×10^{-3} M
$Na_2S_2O_4$ 2.5×10^{-3} M
Monomers $\simeq$ 1 M

Total volume = 10 ml
Polymerization time = 1 hr.
MA = 86.09
AM = 71.08

Monomer feed		Mole fraction of M_2 in the feed	Mole fraction of M_2 in the copolymer	Weight of copolymer	Weight fraction conversion
MA(M_1) gm	AM(M_2) gm	M_2	m_2	gm	
0.6020	0.2104	0.2974	0.4013	0.1810	0.2228
0.2525	0.4819	0.6380	0.6622	0.0631	0.0859
0.1358	0.6139	0.8456	0.8013	0.2935	0.3915

Differential YBR $r_1 = 0.32 \pm 0.002$ $r_2 = 0.53 \pm 0.001$
Integrated Mayo-Lewis $r_1 = 0.32 \pm 0.004$ $r_2 = 0.53 \pm 0.003$

Table-36: Methacrylic acid (M_1) Acrylamide (M_2)
Monomer feed Copolymer Composition and Conversion Data

Water pH = 9.0
Temperature = 30±0.05°C
Initiator = $K_2S_2O_8$ 2.5×10^{-3} M
$Na_2S_2O_4$ 2.5×10^{-3} M
Monomers ≃ 1 M

Total volume = 10 ml
Polymerization time = 1 hr.
MA = 86.09
AM = 71.08

Monomer feed		Mole fraction of M_2 in the feed	Mole fraction of M_2 in the copolymer	Weight of copolymer	Weight fraction conversion
MA(M_1) gm	AM(M_2) gm	M_2	m_2	gm	
0.7601	0.0970	0.1339	0.2252	0.2279	0.2659
0.6296	0.2117	0.2894	0.3971	0.2064	0.2453
0.3251	0.4360	0.6190	0.6654	0.1548	0.2034
0.3251	0.5520	0.6728	0.6296	0.1192	0.1359
0.1193	0.7665	0.8861	0.8416	0.1158	0.1307

Differential YBR $r_1 = 0.34 \pm 0.05$ $r_2 = 0.57 \pm 0.06$
Integrated Mayo-Lewis $r_1 = 0.34 \pm 0.05$ $r_2 = 0.58 \pm 0.06$

Table-37: Methacrylic acid (M_1) Acrylamide (M_2)

Monomer feed Copolymer Composition and Conversion Data

Water pH = 10.0
Temperature = 30±0.05°C
Initiator = $K_2S_2O_8$ 2.5×10^{-3} M
$Na_2S_2O_4$ 2.5×10^{-3} M
Monomers ≃ 1 M

Total volume = 10 ml
Polymerization time= 1 hr.
MA = 86.09
AM = 71.08

Monomer feed		Mole fraction of M_2 in the feed	Mole fraction of M_2 in the copolymer	Weight of copolymer	Weight fraction conversion
MA(M_1) gm	AM(M_2) gm	M_2	m_2	gm	
0.7238	0.1483	0.1988	0.2729	0.4755	0.5452
0.5942	0.2440	0.3322	0.3955	0.3526	0.4207
0.4470	0.3470	0.4846	0.4576	0.3568	0.4494
0.2686	0.4640	0.6766	0.6217	0.0403	0.0550
0.1162	0.6865	0.8774	0.8358	0.2468	0.3075

Differential YBR r_1 = 0.38±0.06 r_2 = 0.51±0.06
Integrated Mayo-Lewis r_1 = 0.39±0.06 r_2 = 0.51±0.06

Table-38: Methacrylic acid (M_1) Acrylamide (M_2)
Monomer feed Copolymer Composition and Conversion Data

1 M NaCl pH = 4.0
Temperature = 30$\pm$0.05°C
Initiator = $K_2S_2O_8$ 2.5x10^{-3} M
$Na_2S_2O_4$ 2.5x10^{-3} M
Monomers $\simeq$ 1 M

Total volume = 10 ml
Polymerization time = 1 hr.
MA = 86.09
AM = 71.08

Monomer feed		Mole fraction of M_2 in the feed	Mole fraction of M_2 in the copolymer	Weight of copolymer	Weight fraction conversion
MA(M_1) gm	AM(M_2) gm	M_2	m_2	gm	
0.8118	0.1165	0.1481	0.0904	0.4617	0.4974
0.6138	0.2467	0.3253	0.1469	0.4345	0.5014
0.4520	0.4410	0.5416	0.4066	0.0631	0.0707
0.2703	0.5250	0.7017	0.6170	0.0748	0.0941
0.1603	0.7007	0.8411	0.6559	0.1122	0.1303

Differential YBR $r_1 = 1.84\pm0.48$ $r_2 = 0.35\pm0.17$

Integrated Mayo-Lewis $r_1 = 1.79\pm0.45$ $r_2 = 0.35\pm0.16$

Table-39: Methacrylic acid (M_1) Acrylamide (M_2)
Monomer feed Copolymer Composition and Conversion Data

1 M NaCl pH = 6.0
Temperature = 30±0.05°C
Initiator = $K_2S_2O_8$ 2.5×10^{-3} M
$Na_2S_2O_4$ 2.5×10^{-3} M
Monomers ≃ 1 M

Total volume = 10 ml
Polymerization time = 1 hr.
MA = 86.09
AM = 71.08

Monomer feed		Mole fraction of M_2 in the feed	Mole fraction of M_2 in the copolymer	Weight of copolymer	Weight fraction conversion
MA(M_1) gm	AM(M_2) gm	M_2	m_2	gm	
0.7630	0.0943	0.1302	0.2842	0.1302	0.3014
0.6596	0.1942	0.2628	0.3558	0.2628	0.2495
0.4477	0.3790	0.5063	0.5593	0.5063	0.2118
0.3047	0.6019	0.7053	0.6930	0.7053	0.2181
0.1400	0.6565	0.8503	0.8528	0.8503	0.2570

Differential YBR $r_1 = 0.22 \pm 0.06$ $r_2 = 0.76 \pm 0.13$
Integrated Mayo-Lewis $r_1 = 0.21 \pm 0.06$ $r_2 = 0.75 \pm 0.13$

Table-40: Methacrylic acid (M_1) Acrylamide (M_2)
Monomer feed Copolymer Composition and Conversion Data

1 M NaCl pH = 10.0
Temperature = 30±0.05°C
Initiator = $K_2S_2O_8$ 2.5×10^{-3} M
$Na_2S_2O_4$ 2.5×10^{-3} M
Monomers ≃ 1 M

Total volume = 10 ml
Polymerization time = 1 hr.
MA = 86.09
AM = 71.08

Monomer feed		Mole fraction of M_2 in the feed	Mole fraction of M_2 in the copolymer	Weight of copolymer	Weight fraction conversion
MA(M_1) gm	AM(M_2) gm	M_2	m_2	gm	
0.7223	0.2580	0.3020	0.3371	0.3541	0.3612
0.5774	0.2088	0.3046	0.3224	0.4988	0.6344
0.4053	0.3552	0.5149	0.4328	0.3446	0.4531
0.3259	0.6030	0.6914	0.6150	0.5020	0.5404
0.0811	0.7382	0.9168	0.8359	0.3585	0.4376

Differential YBR $r_1 = 0.52 \pm 0.07$ $r_2 = 0.24 \pm 0.02$
Integrated Mayo-Lewis $r_1 = 0.51 \pm 0.07$ $r_2 = 0.22 \pm 0.02$

Table-41: Composition of Methacrylic acid N-vinyl Pyrrolidone Copolymers

Water pH = 3.0

Temperature = 30±0.05°C

Initiator = $K_2S_2O_8$ 2.5×10^{-3} M

Na_2SO_3 2.5×10^{-3} M

Polymer sample	Average monomer feed (moles x 10)		Weight percent conversion	Copolymer composition (moles x 10)		Mole percent
	MA	NVP		MA	NVP	NVP
Poly(methacrylic acid)	0.15		9.8	-	-	-
Copoly(MA-NVP) I	1.089	0.8045	10.7	11.28	0.2574	2.23
Copoly(MA-NVP) II	1.456	0.4386	21.6	10.94	0.5238	4.52
Copoly(MA-NVP) III	1.131	0.8240	7.6	10.23	1.076	9.51
Copoly(MA-NVP) IV	1.539	0.4340	9.3	9.426	1.696	15.24
Copoly(MA-NVP) V	0.5144	1.3450	6.1	7.909	2.872	26.62
Copoly(MA-NVP) VI	0.6340	1.0490	25.0	6.831	3.706	35.92

POTENTIOMETRIC TITRATION

Determination of pK_o . Arnold's Method

pK_{app} versus $\alpha^{1/3}$

Fig.3. (MA-NVP) Copolymer, 2.23 mole % NVP in ion free water

Fig.4. Poly(methacrylic acid) in 0.10 M sodium chloride solution.

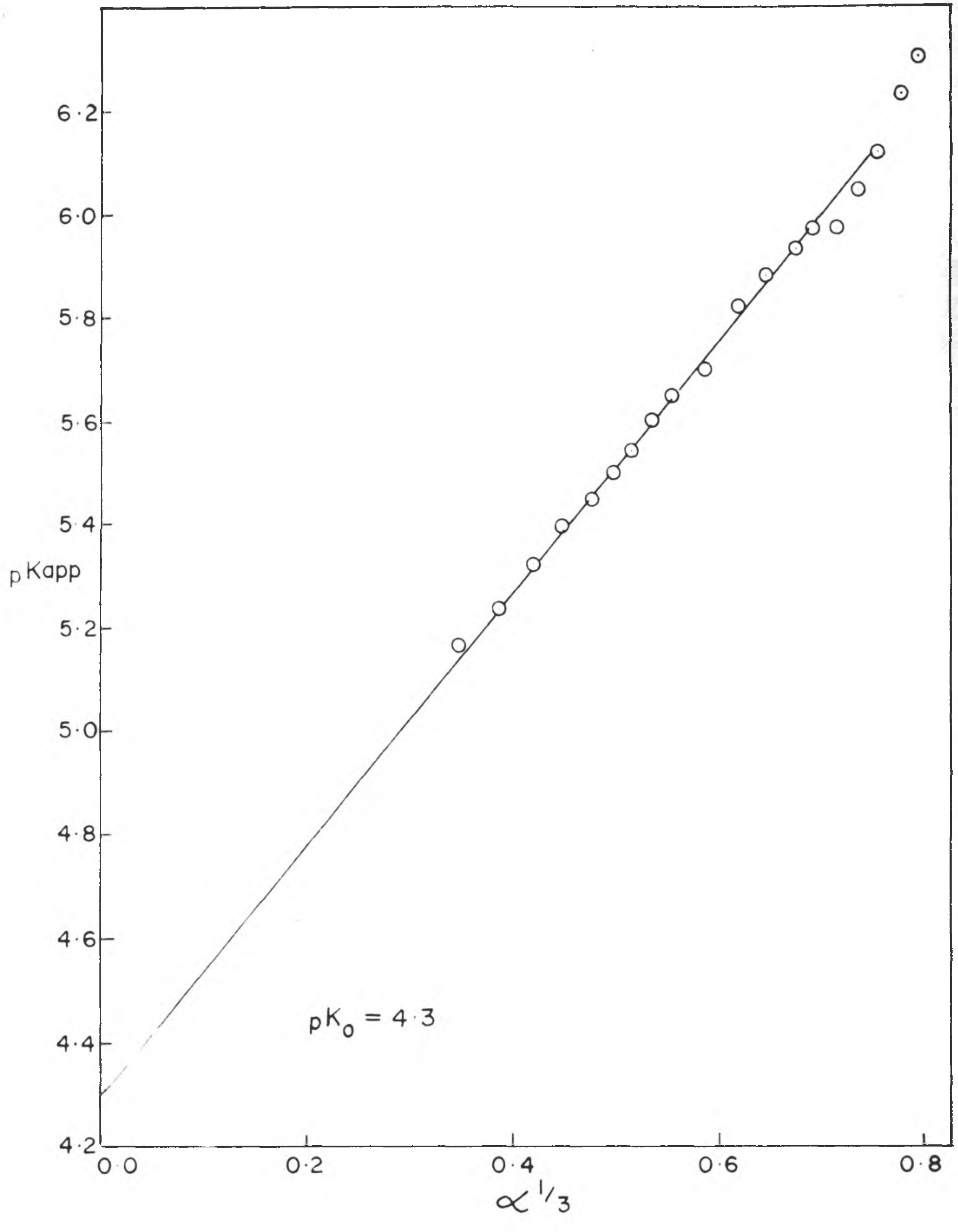


Fig. 3 Determination of pK_0 Arnold's method

pKapp Vs $\alpha^{1/3}$ of (MA-NVP) copolymer (2·23 mole % NVP) in ion free water.

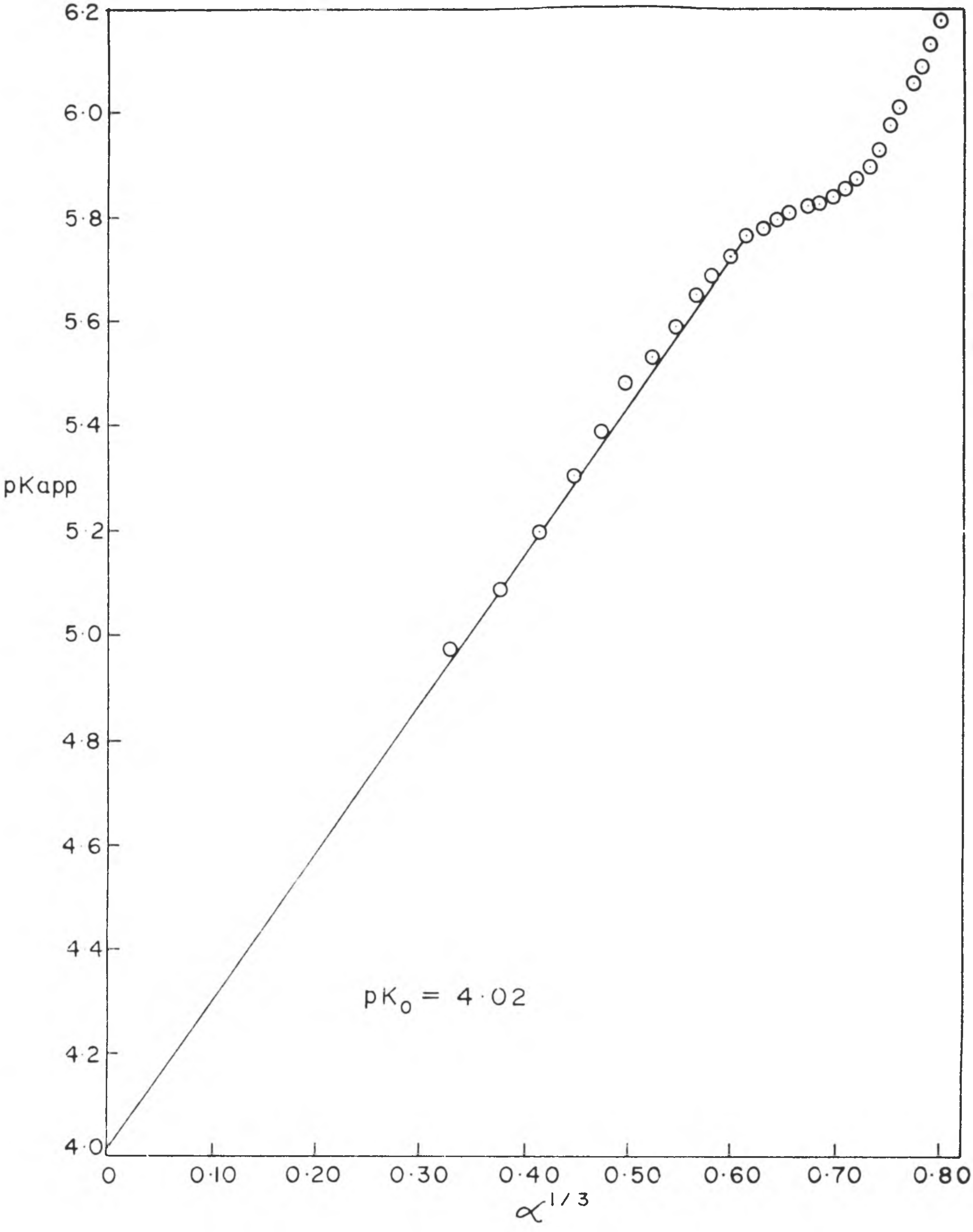


Fig. 4 Determination of pK_0. pKapp Vs. $\alpha^{1/3}$ plot of poly (methacrylic acid) in 0·10 M NaCl solution. Arnold's method.

POTENTIOMETRIC TITRATION CURVES

in ion free water pK_{app} vs. α

Fig. 5	0 mole % NVP	Fig.6	2.23 mole % NVP
Fig.7	4.52 mole % NVP	Fig.8	9.51 mole % NVP
Fig.9	15.24 mole % NVP	Fig.10	35.92 mole % NVP

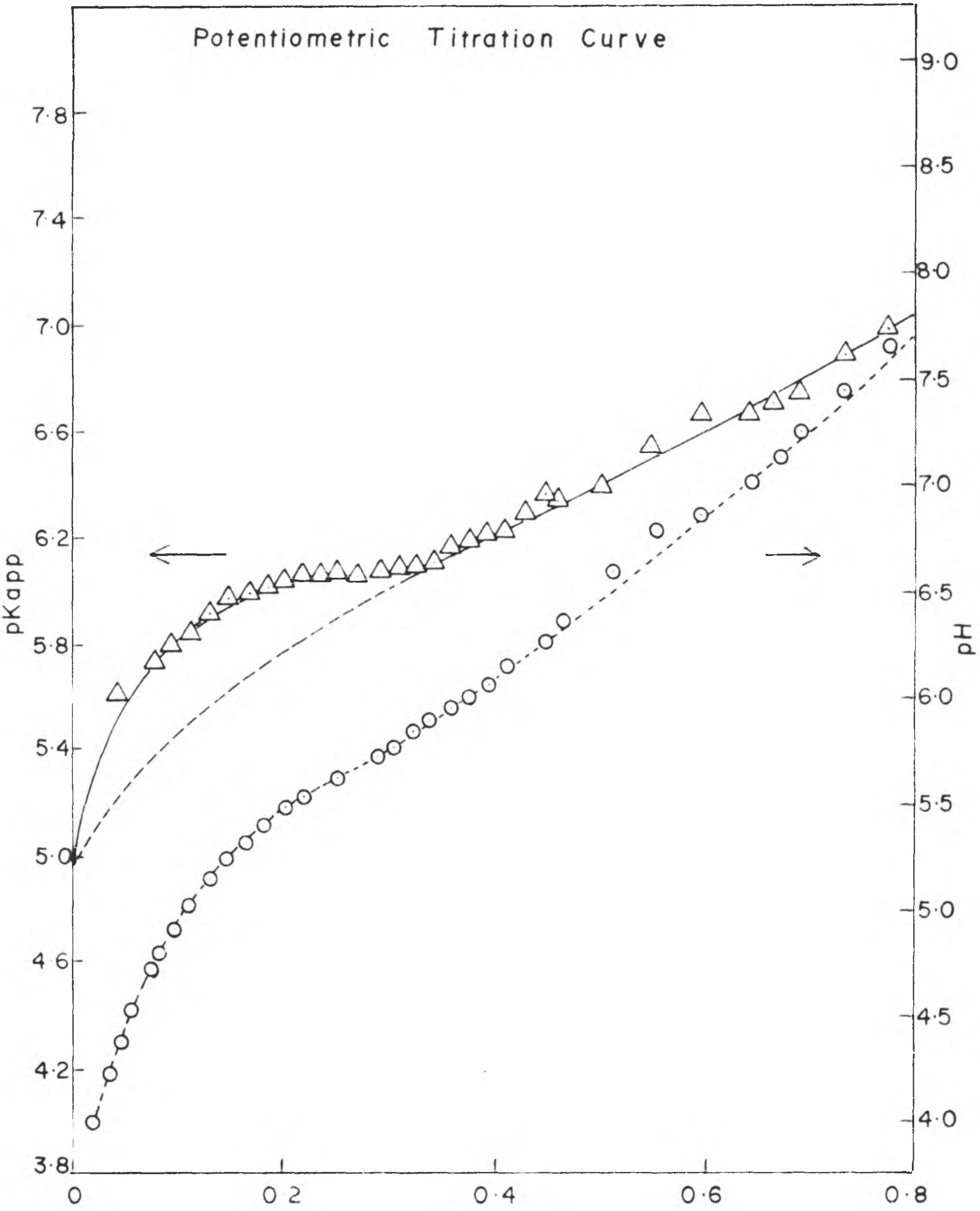


Fig 5 pH, pKa Vs α plots of poly (methacrylic acid) in ion free water

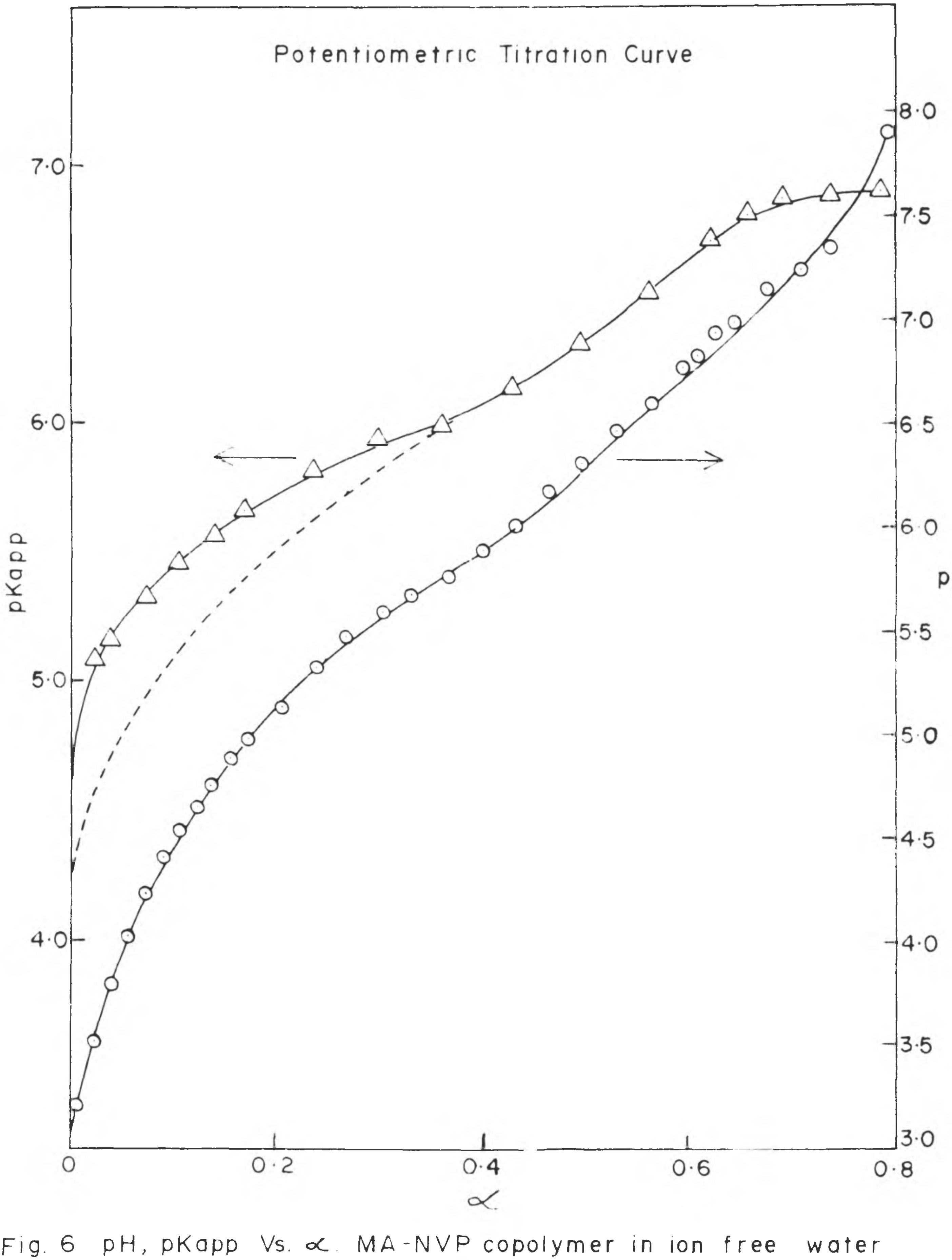


Fig. 6 pH, pKapp Vs. ∝ MA-NVP copolymer in ion free water (2·23 mole % NVP)

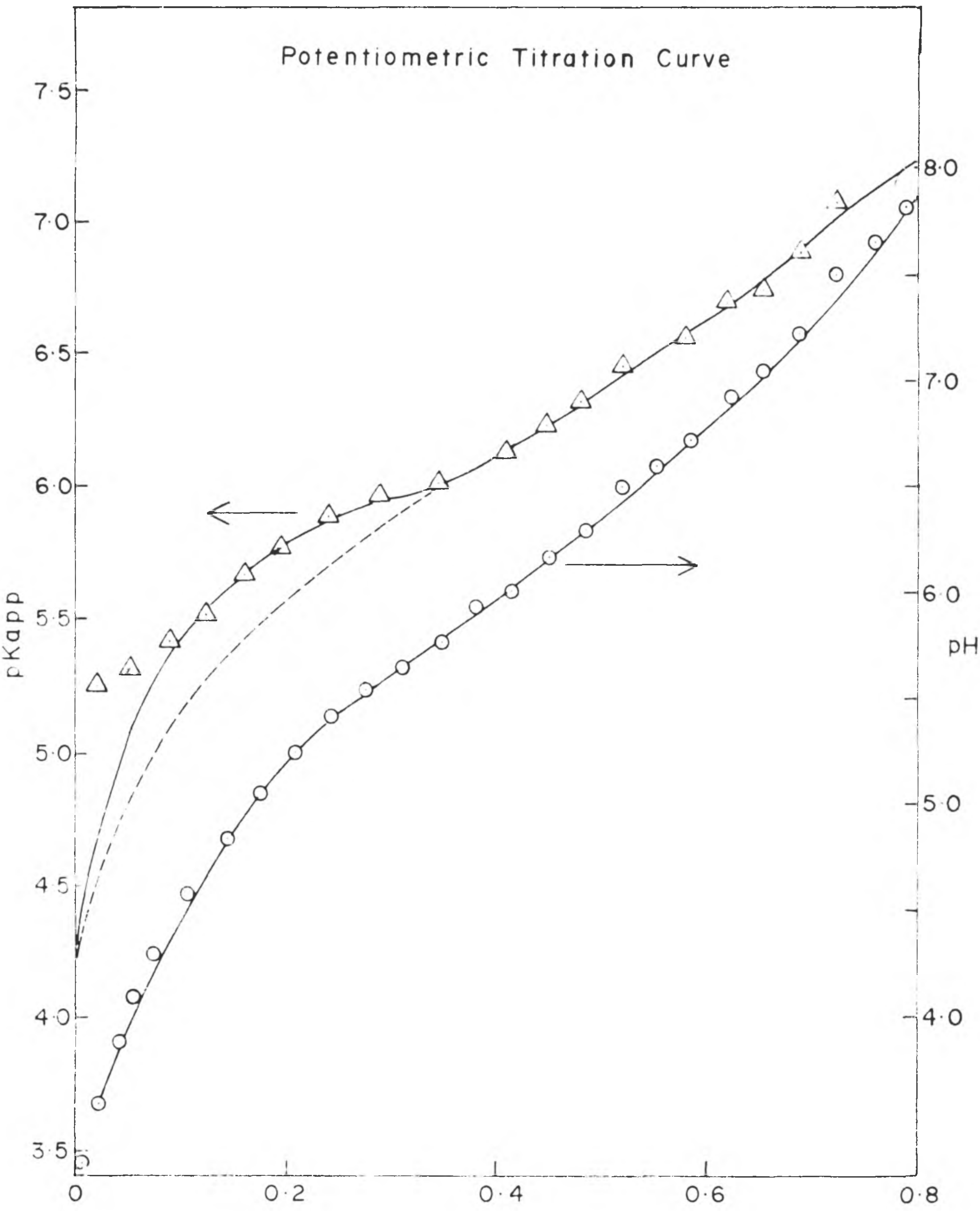


Fig. 7 pH, pKapp Vs. ∝. (MA-NVP) copolymer in ion free water (4·52 mole % NVP)

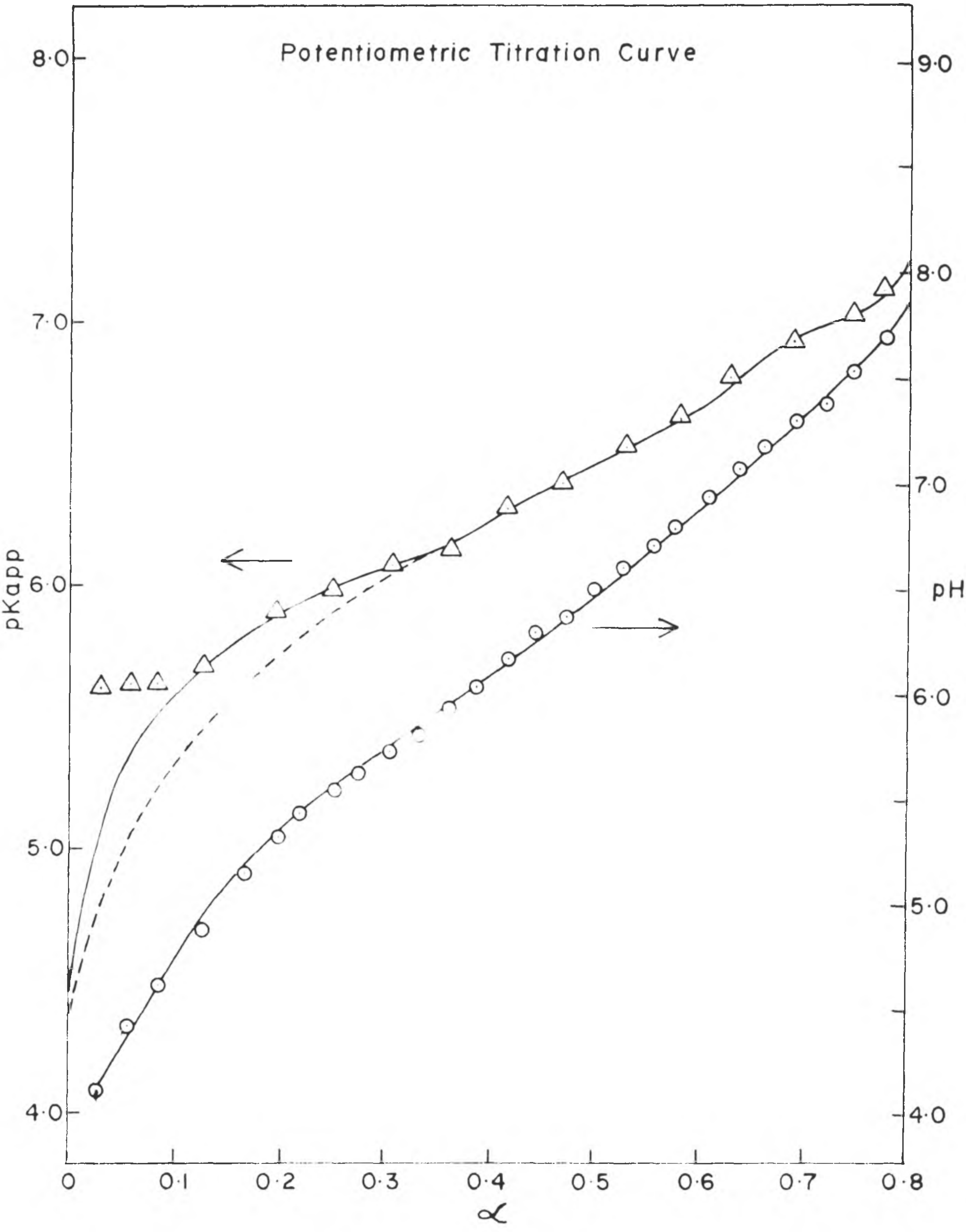


Fig. 8 pH, pKapp Vs ∝. (MA-NVP) copolymer in ion free water
(9·51 mole % NVP)

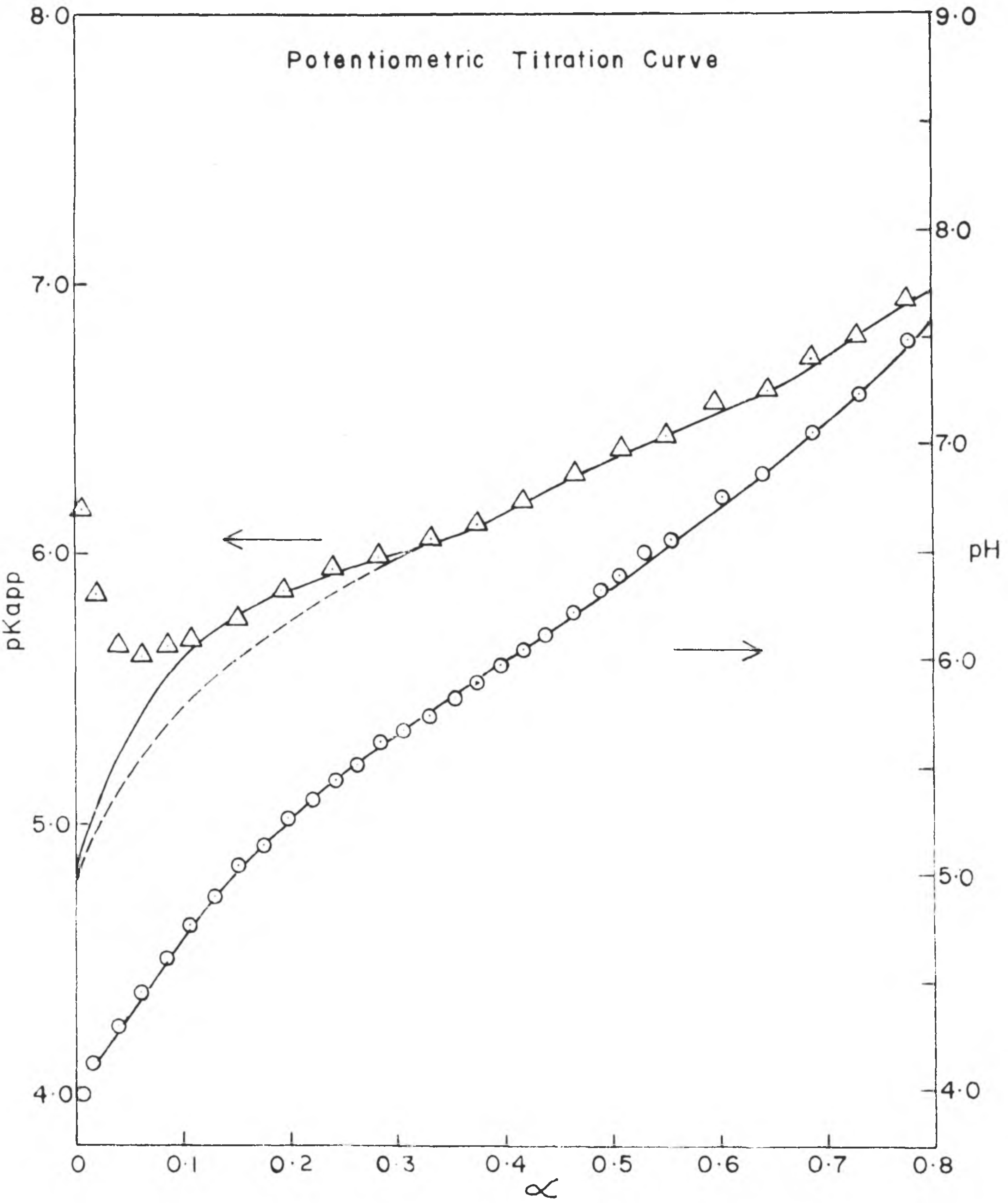


Fig. 9 pH, pKapp Vs. α. (MA-NVP) copolymer in ion free water (15·24 mole % NVP)

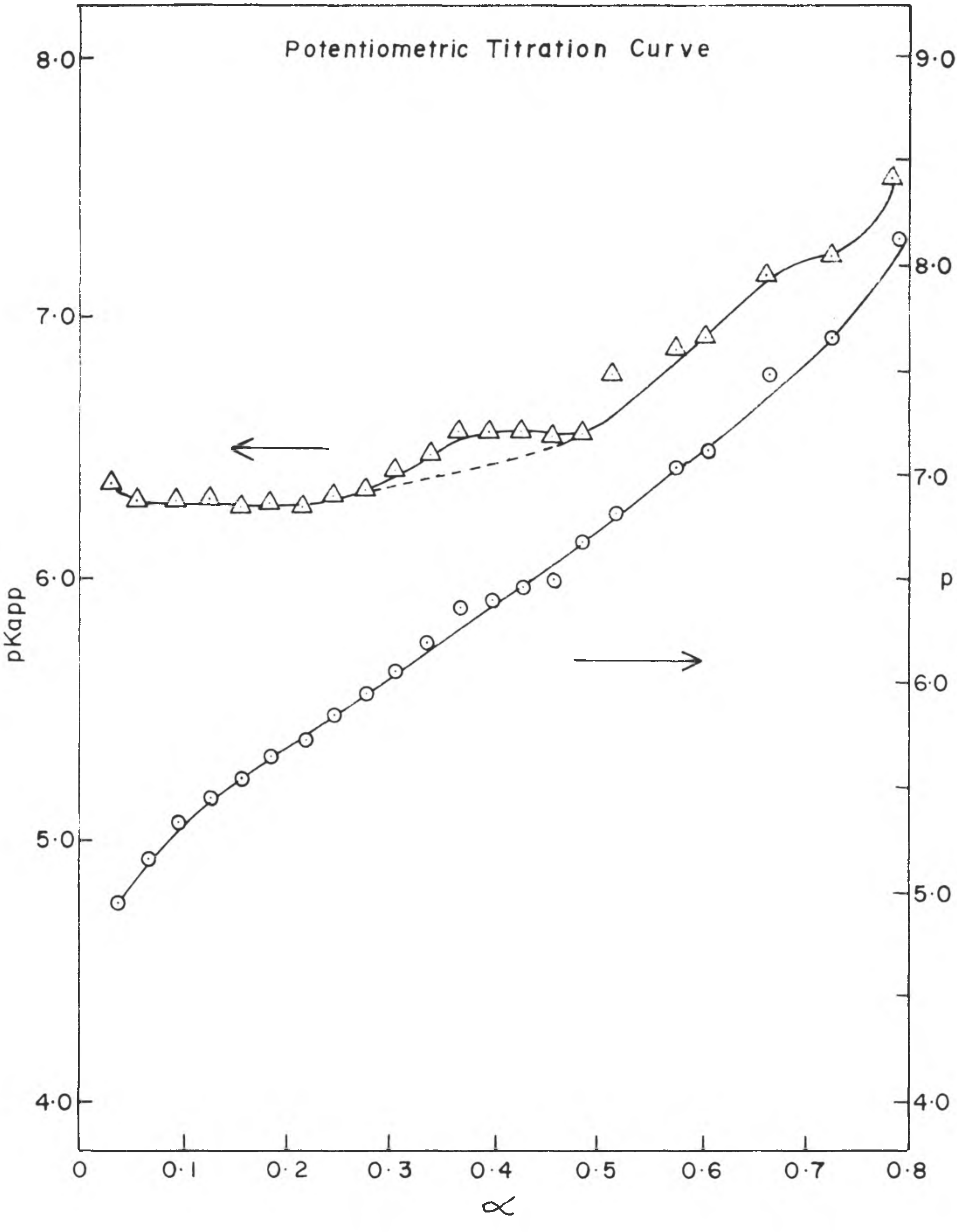


Fig. 10 pH, pKapp Vs ∝, (MA-NVP) copolymer in ion free water (35·92 mole % NVP)

POTENTIOMETRIC TITRATION CURVES

in 0.10 molar sodium chloride solution

pK_{app} vs. α

Fig.11	0 mole % NVP
Fig.12	2.23 mole % NVP
Fig.13	4.52 mole % NVP
Fig.14	9.51 mole % NVP
Fig.15	15.24 mole % NVP
Fig.16	26.62 mole % NVP
Fig.17	35.92 mole % NVP

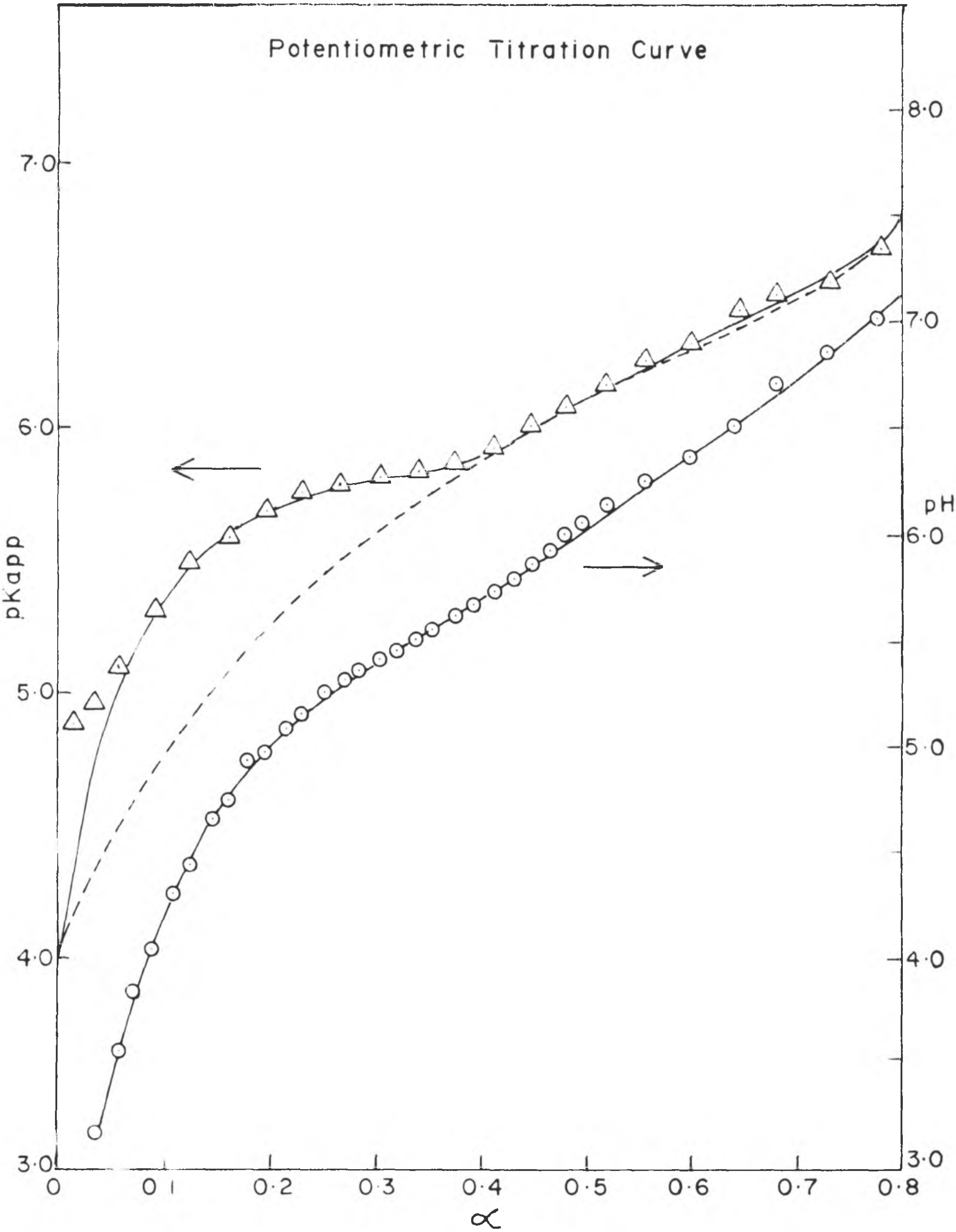


Fig 11 pH, pKapp Vs. α. Poly (methacrylic acid) in 0·10 M NaCl solution.

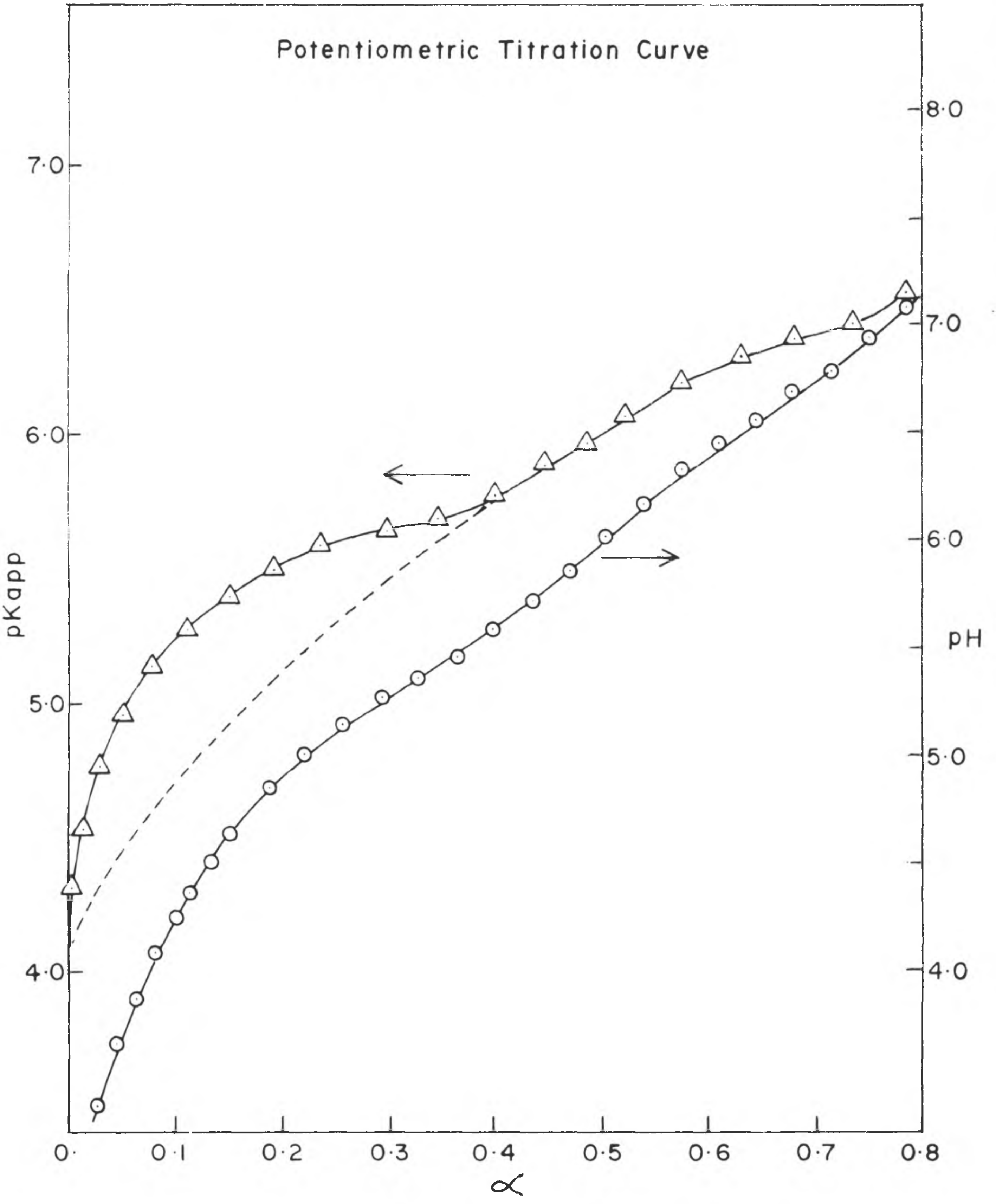


Fig. 12 pH pKapp Vs α. (MA-NVP) copolymer in 0·10M NaCl solution (2·23 mole % NVP)

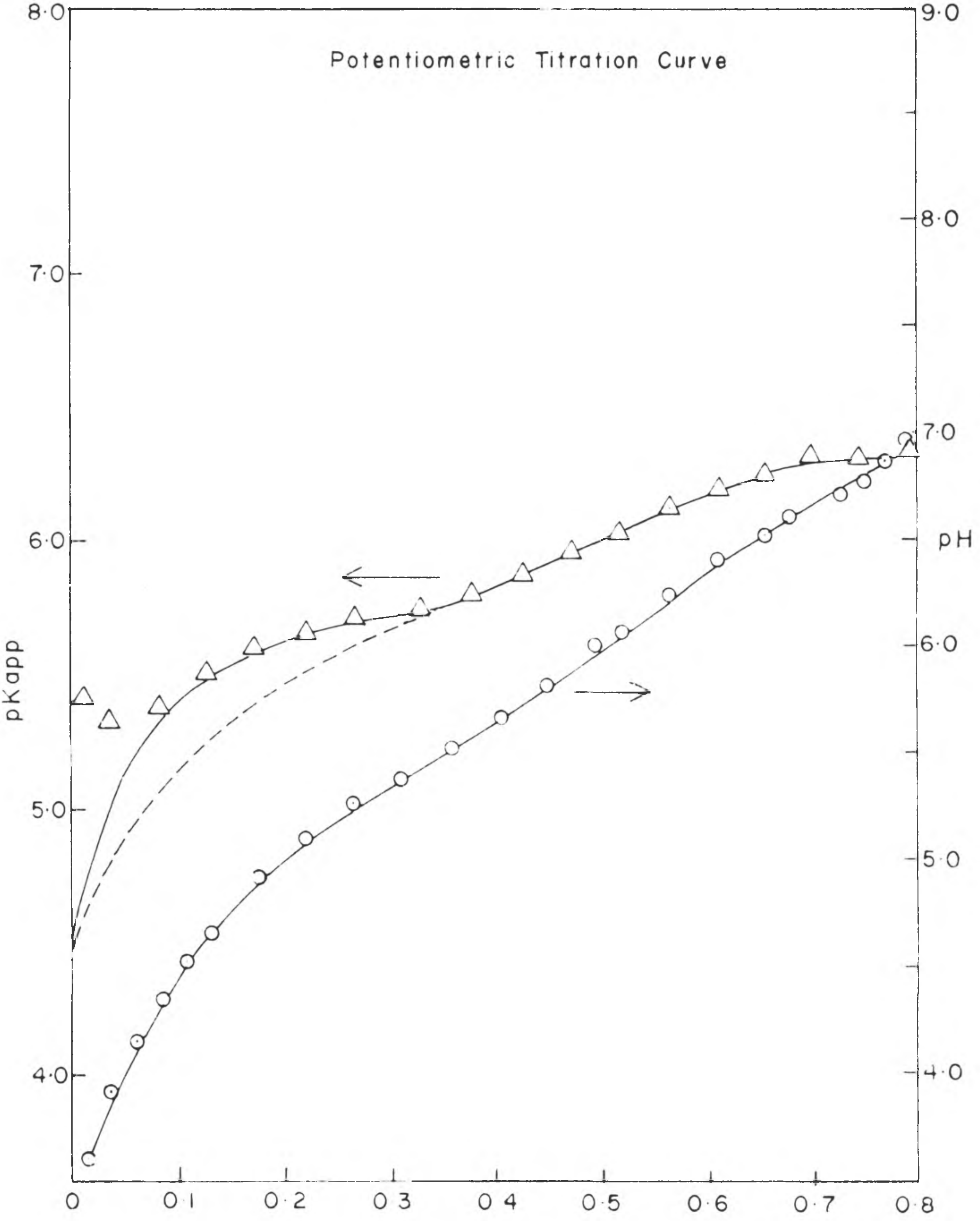


Fig. 13 pH, pKapp Vs ∝ (MA-NVP) copolymer in 0·10M NaCl solution (4·52 mole % NVP)

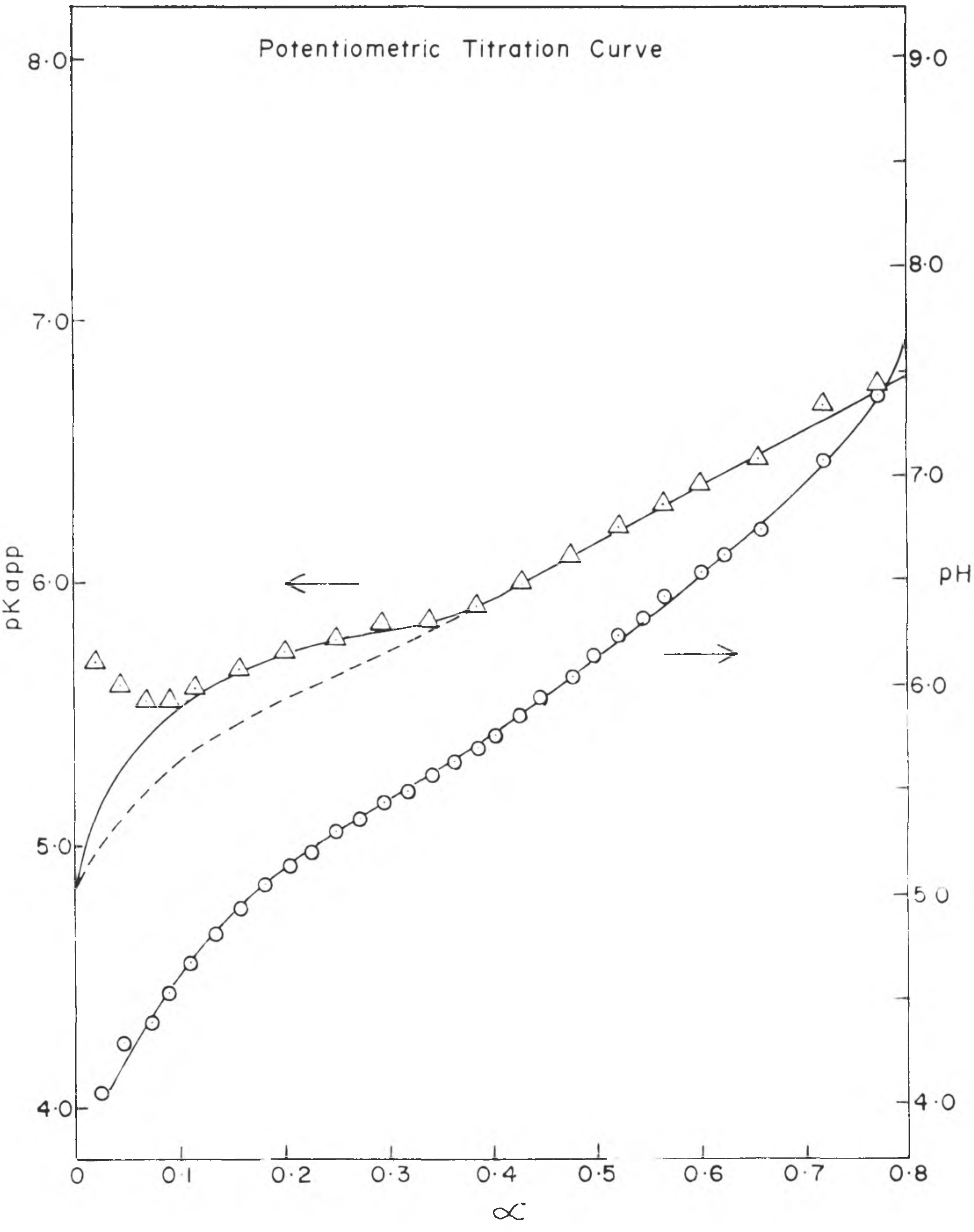


Fig 14 pH, pKapp Vs. ∝ . (MA-NVP) copolymer in 0·10M NaCl soln. (9·51 mole % NVP)

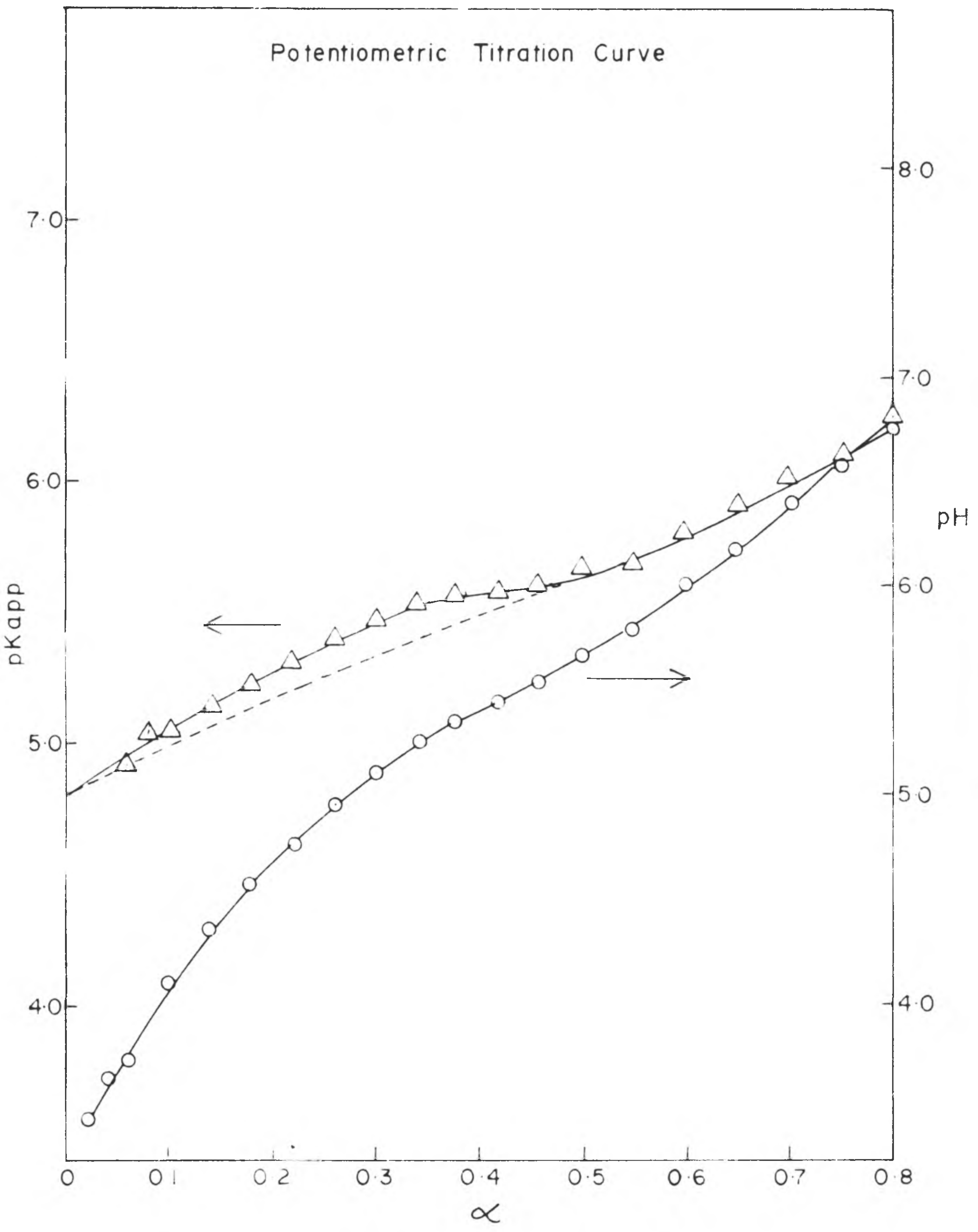


Fig 15 pH, pKapp Vs. α. (MA-NVP) copolymer in 0·10M NaCl solution
(15·24 mole % NVP)

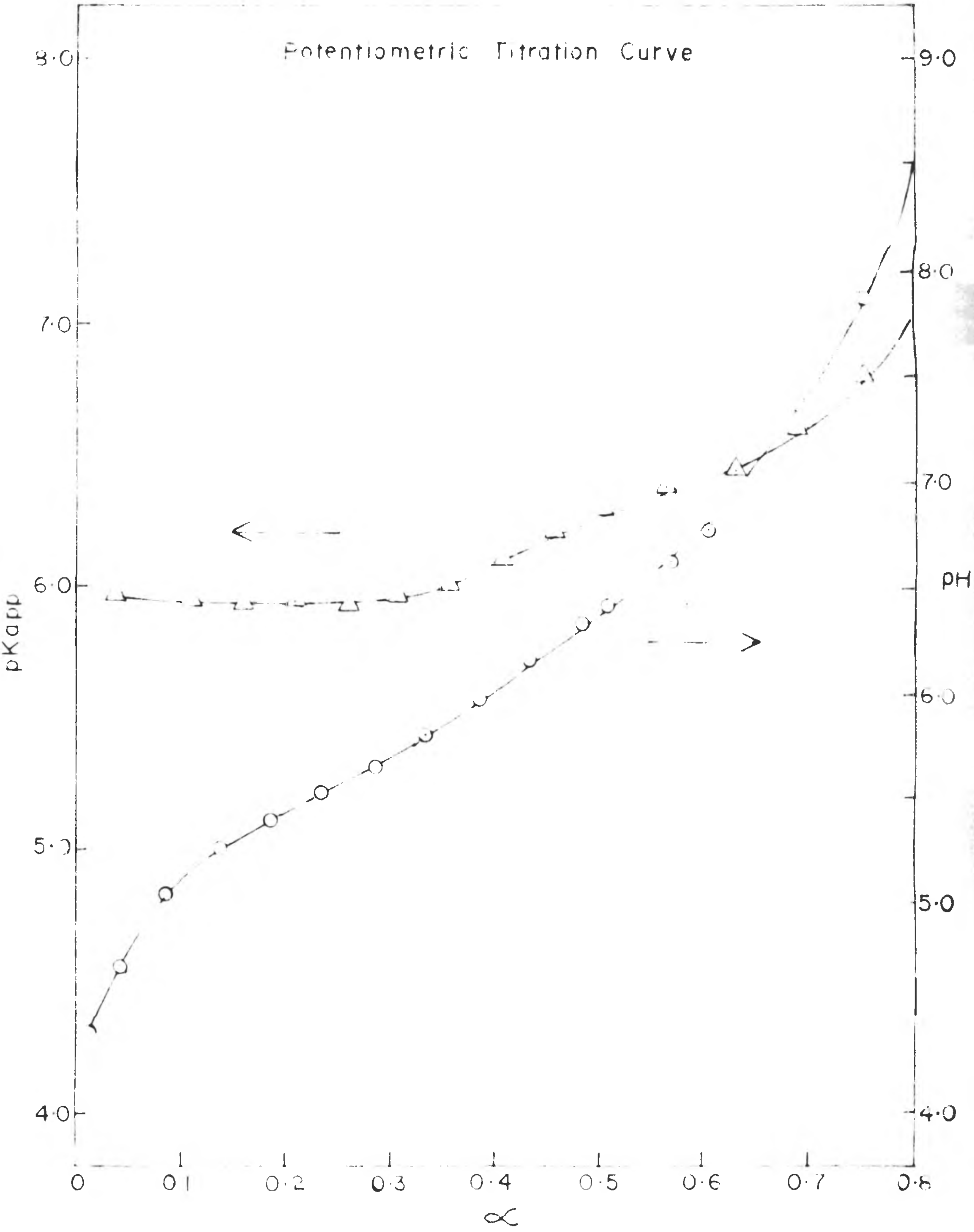


Fig 16 pH, pKapp Vs ∝ (MA-NVP)copolymer in 0·10M NaCl solution (26·62 mole % NVP)

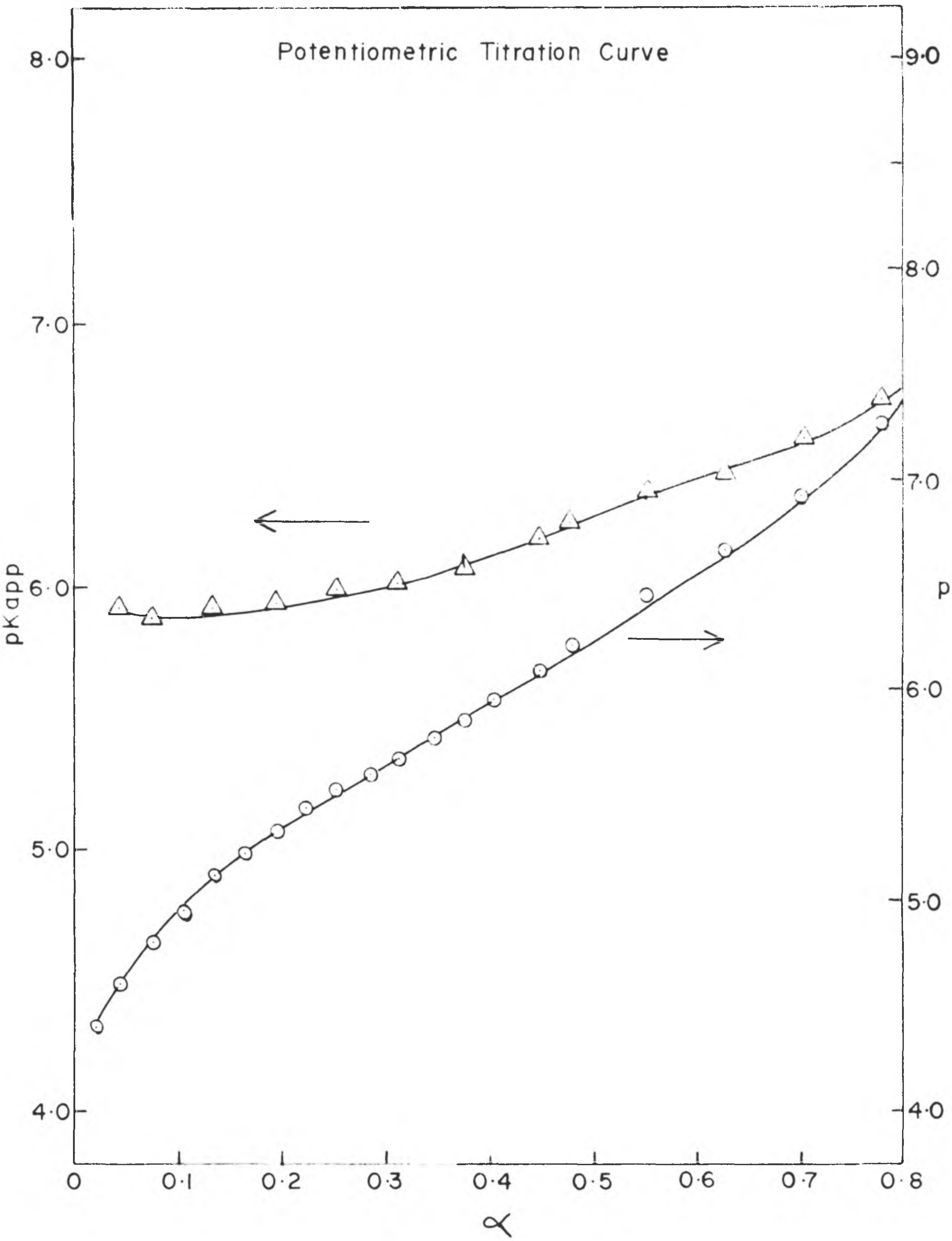


Fig. 17 pH, pKapp Vs ∝.(MA-NVP) copolymer in 0·10 M NaCl solution (35 92 mole % NVP)

HUGGINS PLOT IN o.10 M NaCl SOLUTION

Fig. 18	0 mole % NVP
Fig. 19	2.23 mole % NVP
Fig. 20	4.52 mole % NVP
Fig. 21	9.51 mole % NVP
Fig. 22	15.24 mole % NVP
Fig. 23	26.62 mole % NVP
Fig. 24	35.92 mole % NVP

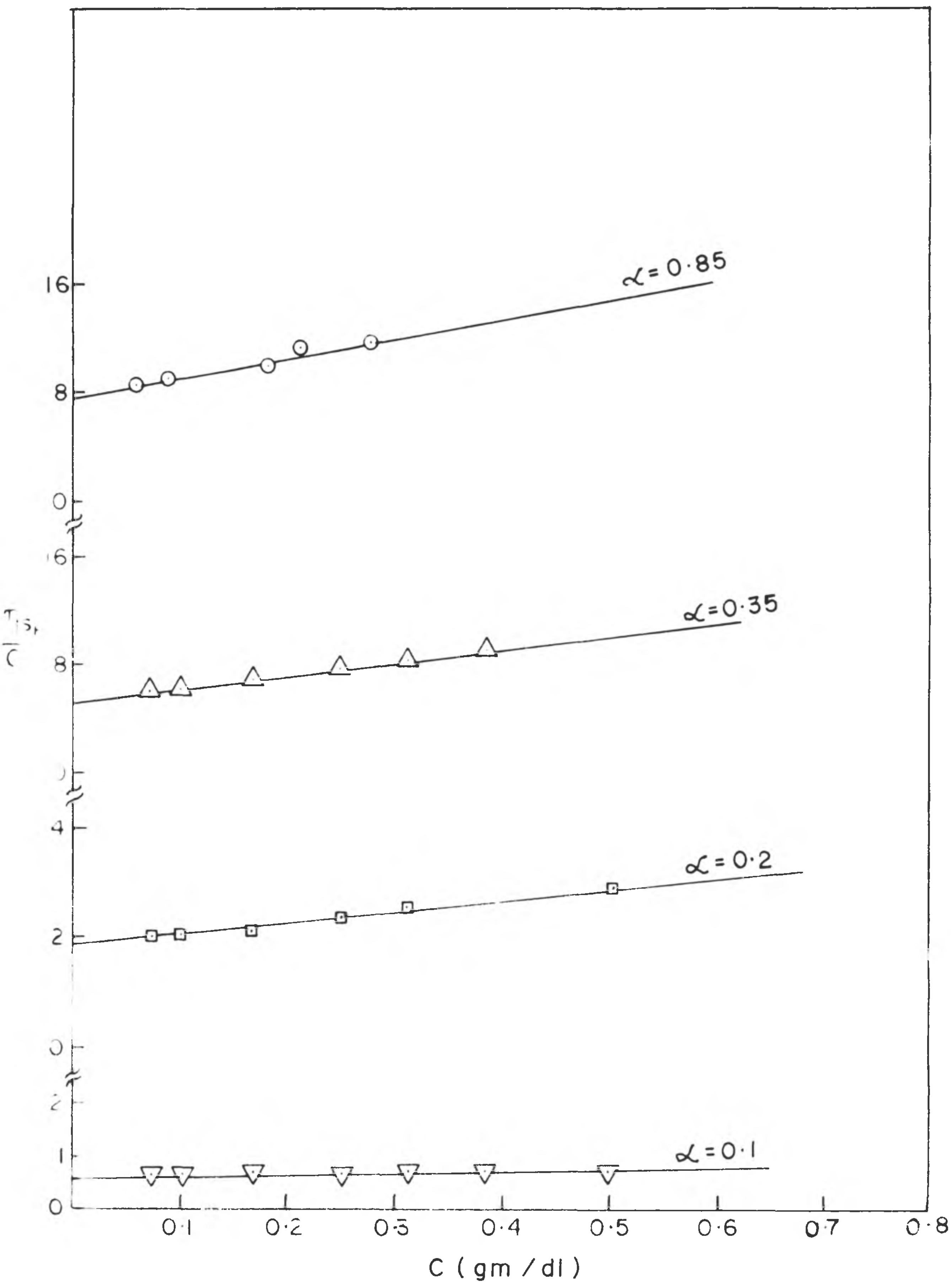


Fig. 18 Huggin's plot of poly (methacrylic acid) in 0·10 M NaCl solution

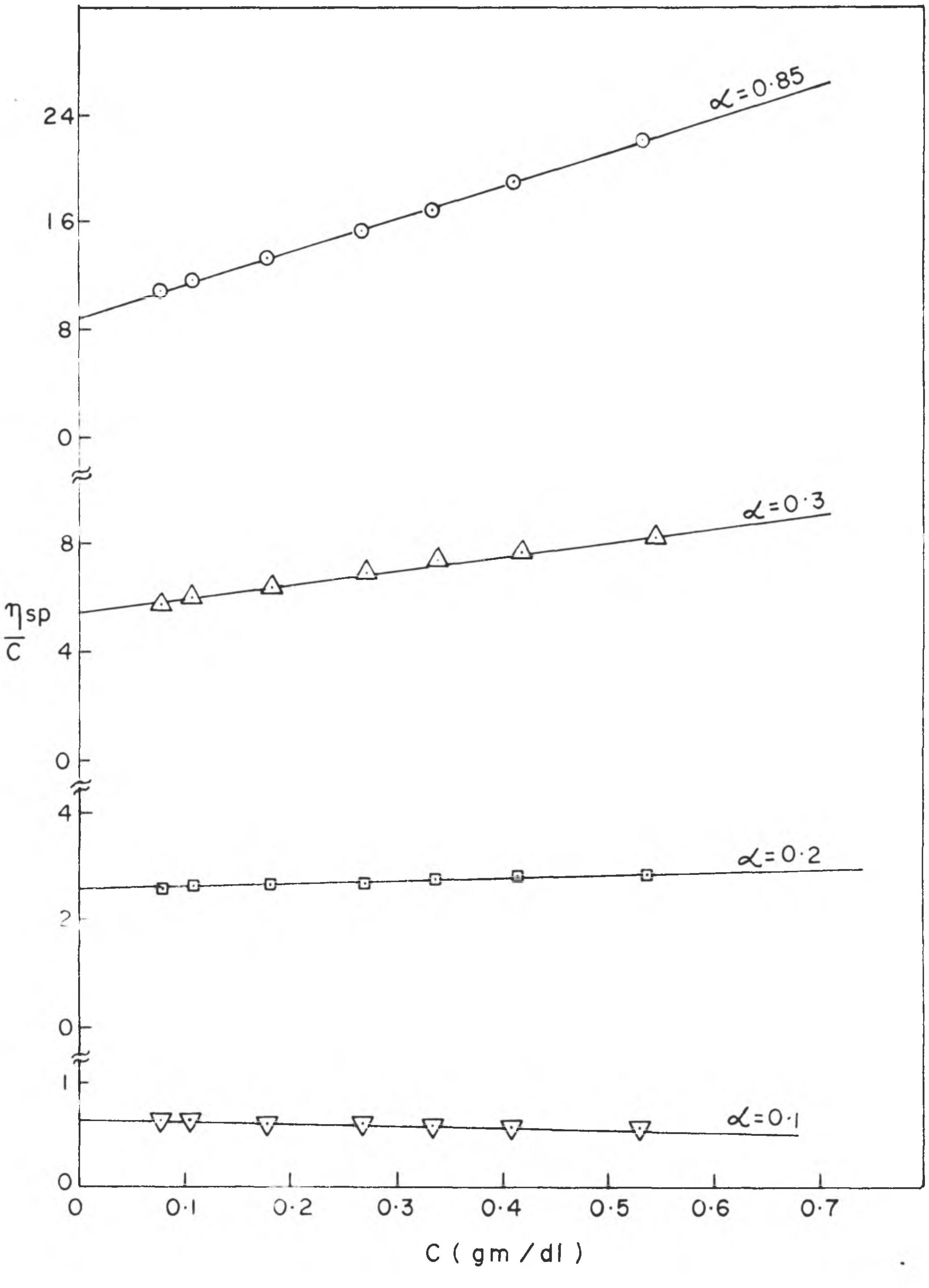


Fig 19 Huggin's plot of (MA-NVP)copolymer in 0·10M NaCl solution (2·23 mole % NVP)

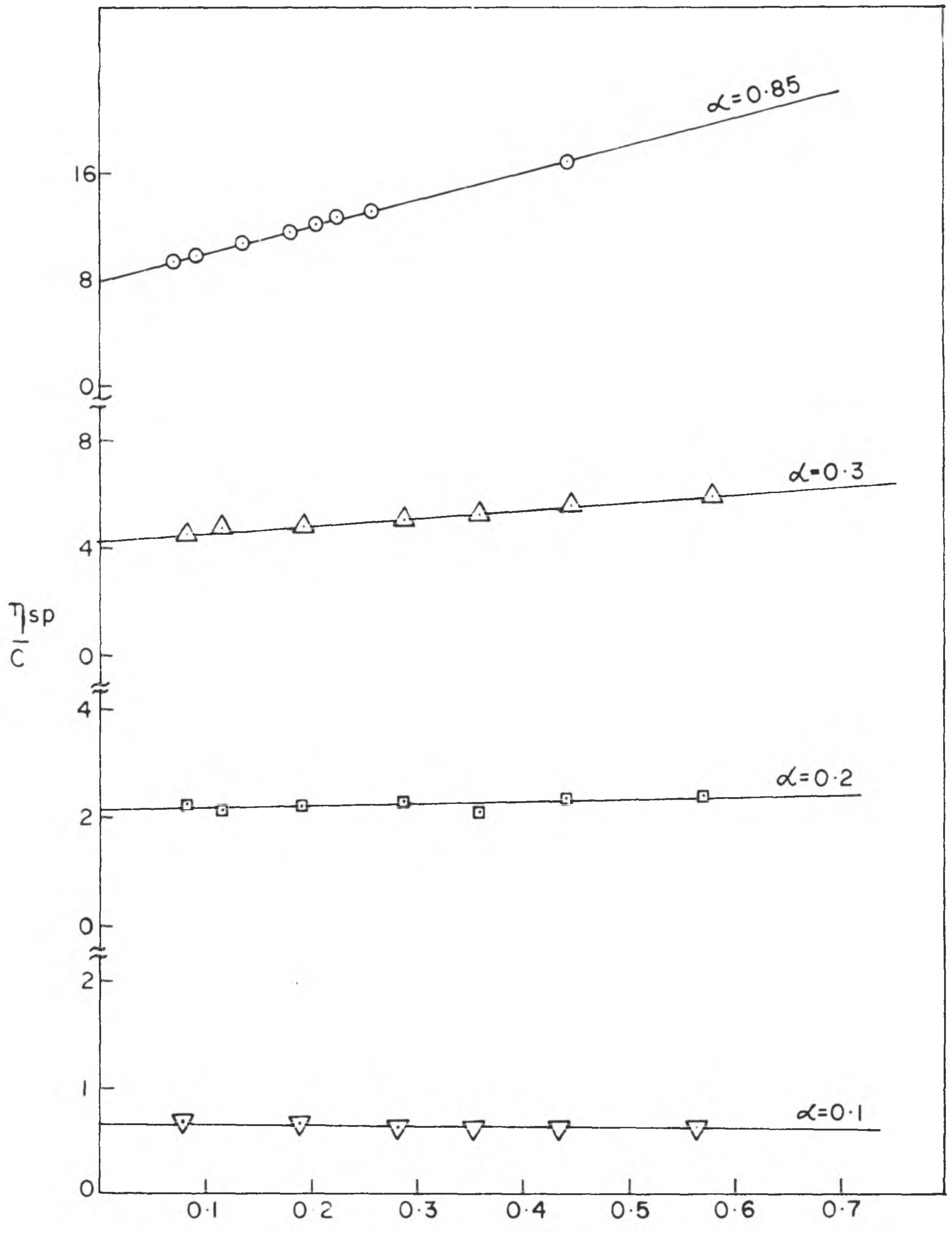


Fig. 20 Huggin's plot of (MA-NVP) copolymer in 0·10M NaCl solution (4·52 mole % NVP)

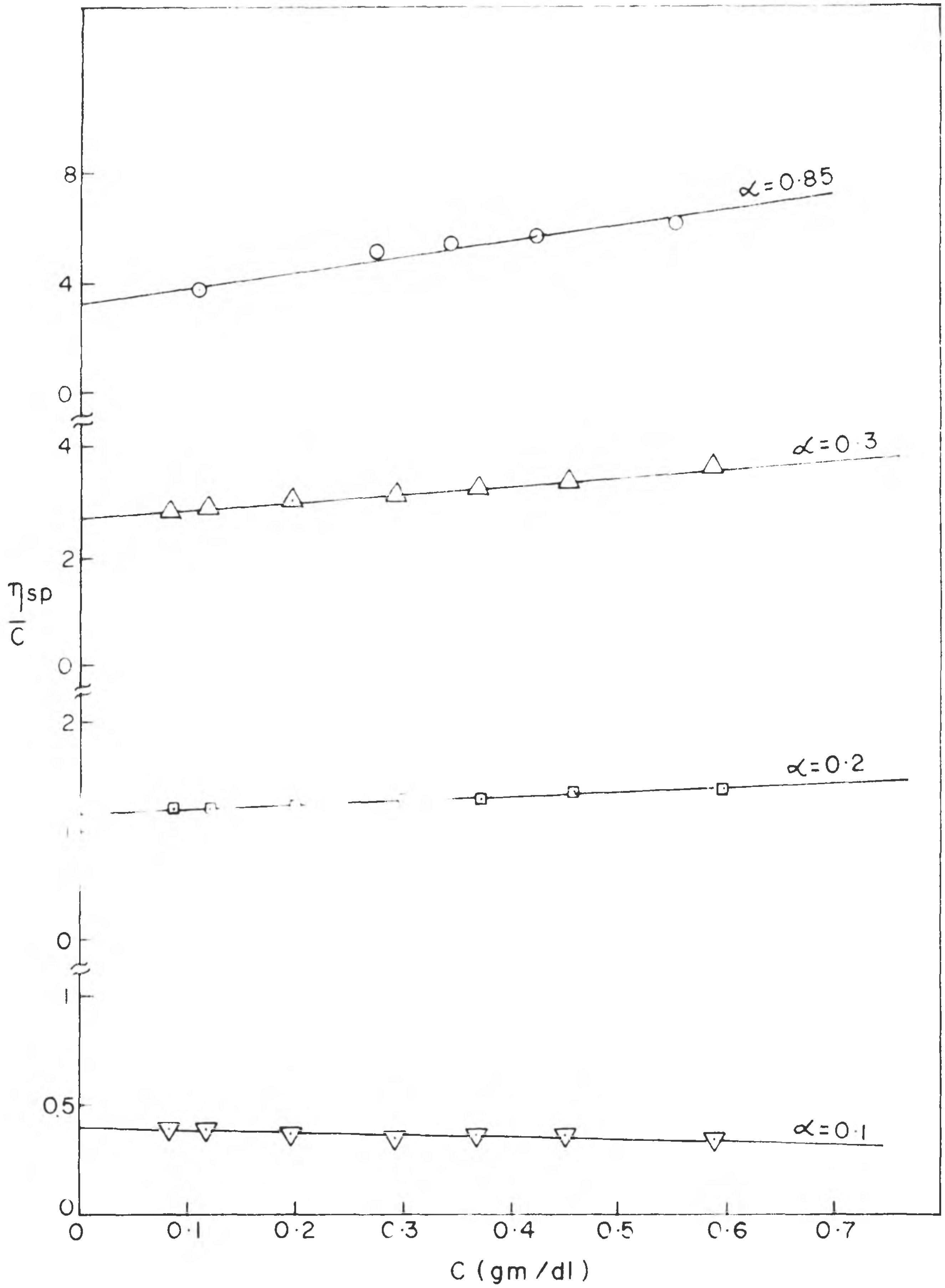


Fig. 21 Huggin's plot of (MA-NVP) copolymer in 0·10M NaCl solution (9·51 mole % NVP)

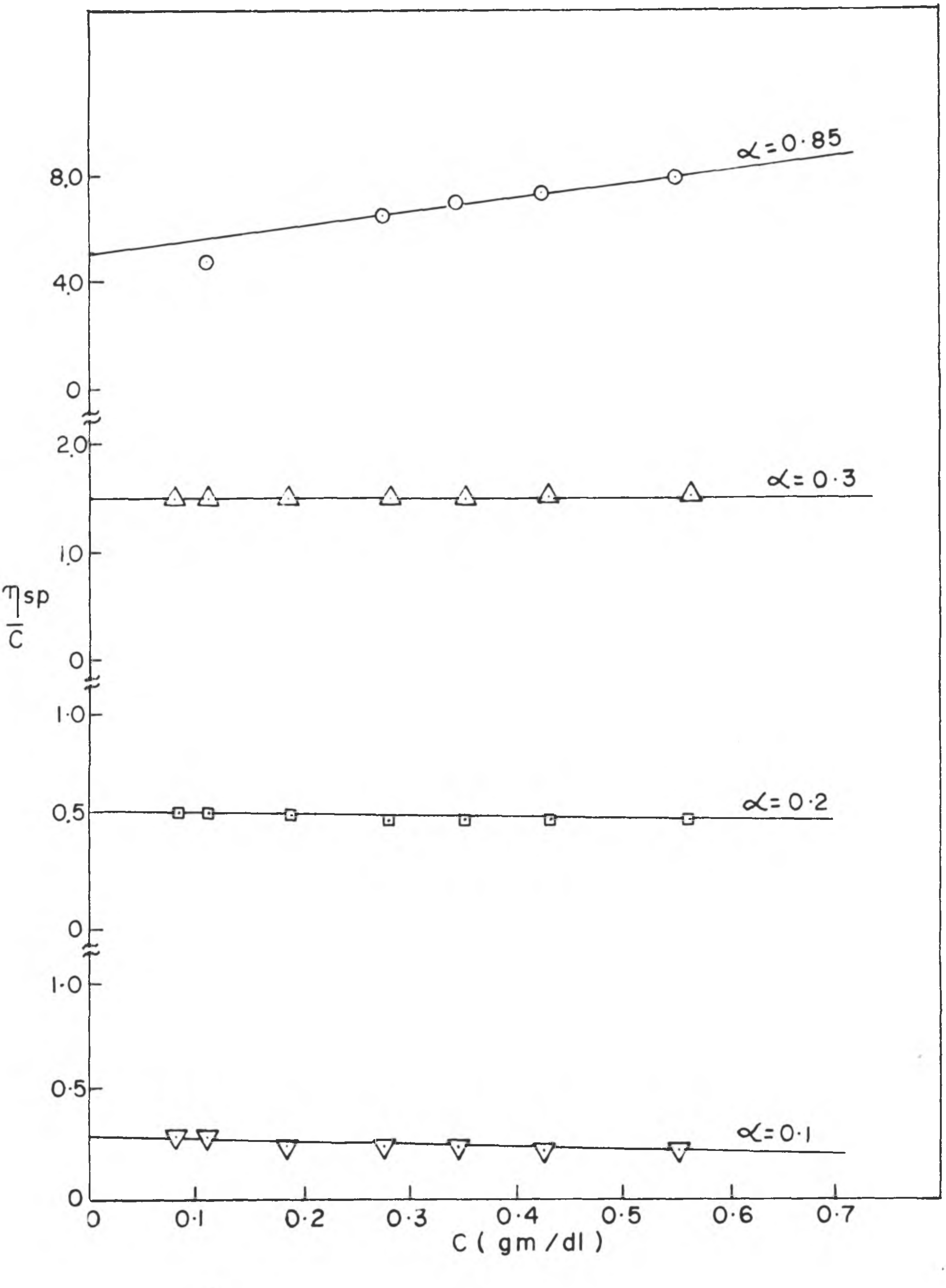


Fig. 22 Huggin's plot of (MA-NVP) copolymer in 0·10 M NaCl solution (15·24 mole % NVP)

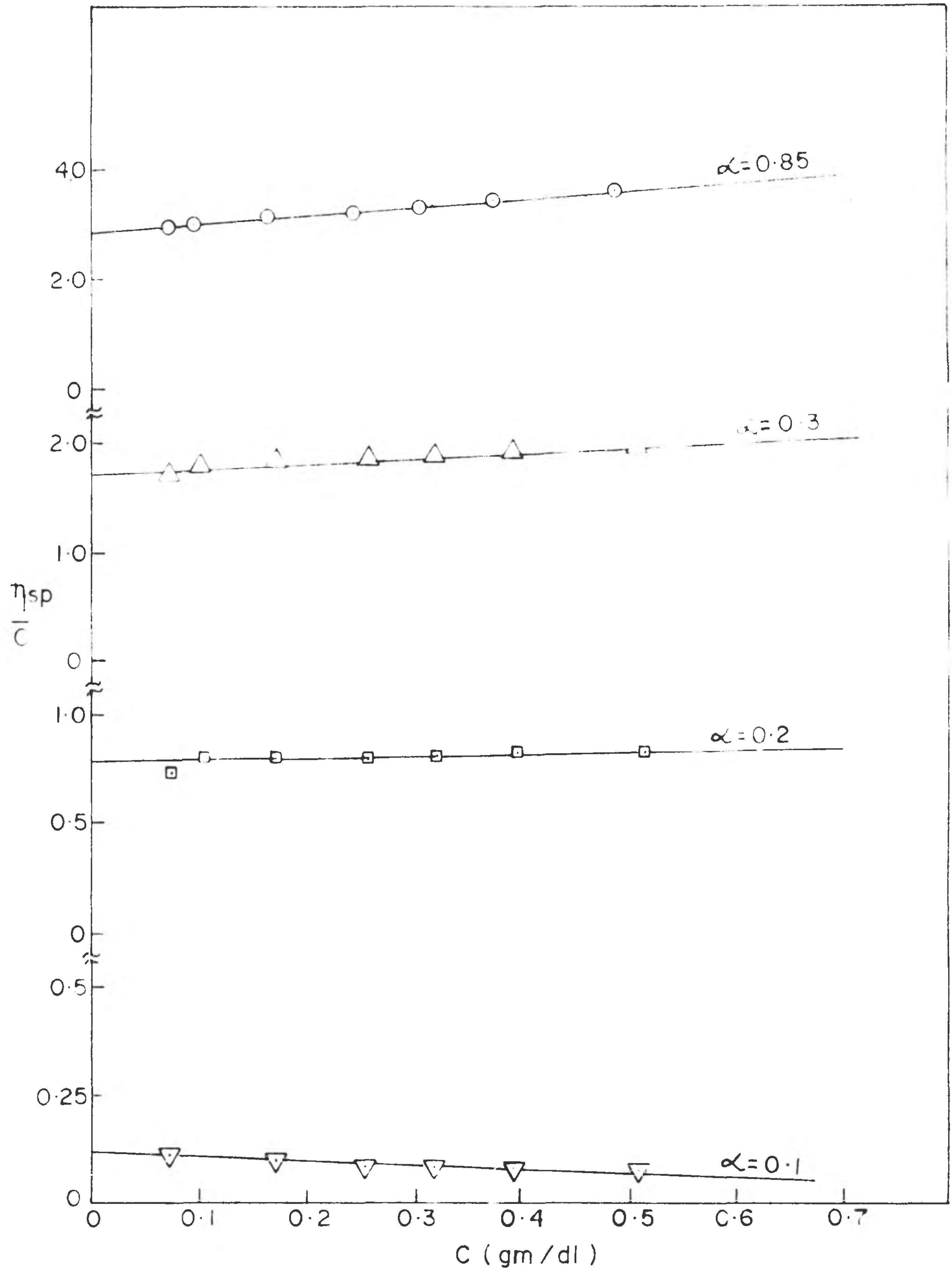


Fig 23 Huggin's plot of (MA-NVP) copolymer in 0·10 M NaCl solution (26·62 mole % NVP)

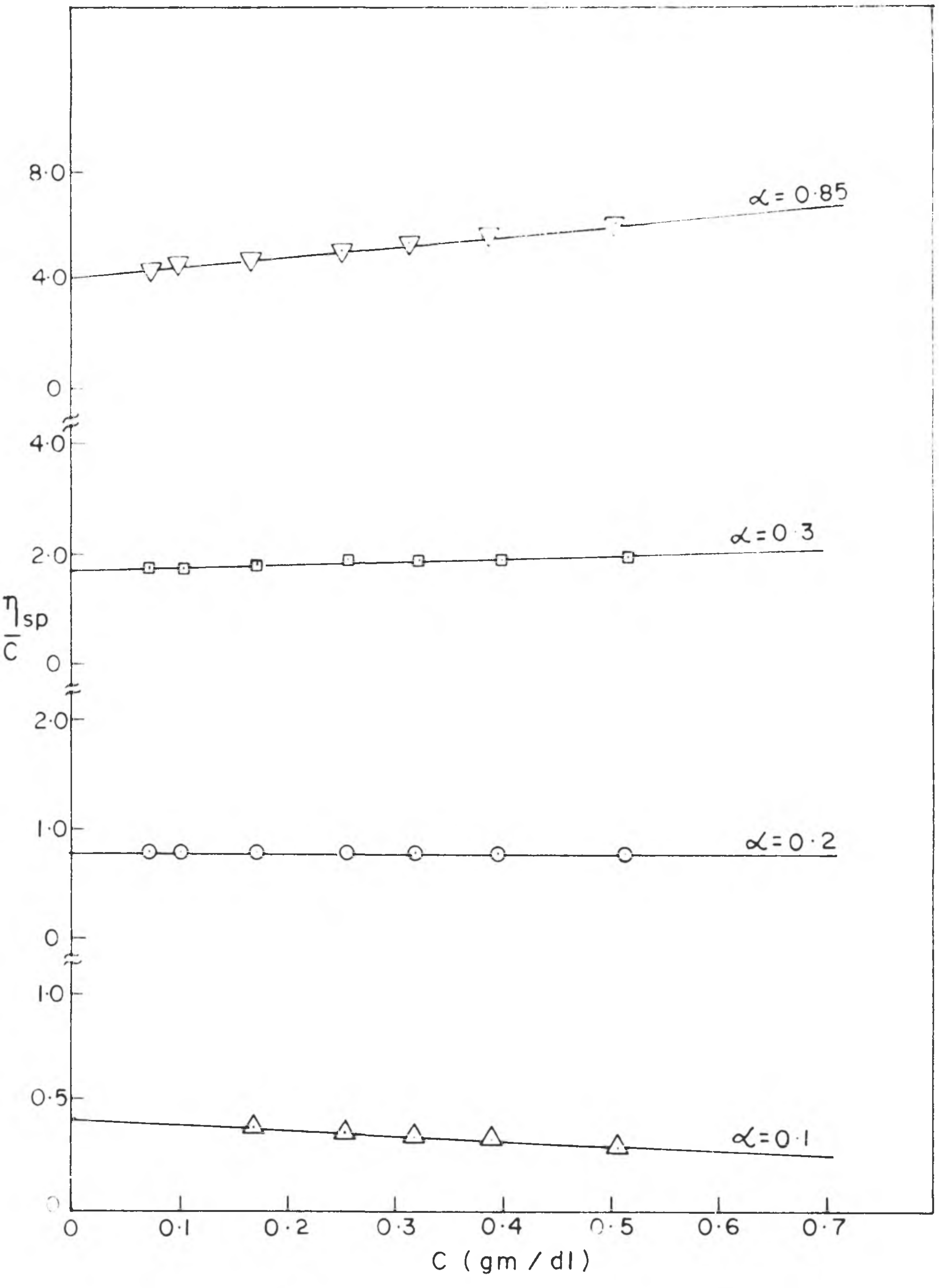


Fig. 24 Huggin's plot of (MA-NVP) copolymer in 0·10M NaCl solution (35·92 mole % NVP)

FUOSS PLOT IN 0.10 M NaCl SOLUTION

Fig.25	0 mole % NVP
Fig.26	2.23 mole % NVP
Fig.27	4.52 mole % NVP
Fig.28	9.51 mole % NVP
Fig.29	15.24 mole % NVP
Fig.30	26.62 mole % NVP
Fig.31	35.92 mole % NVP

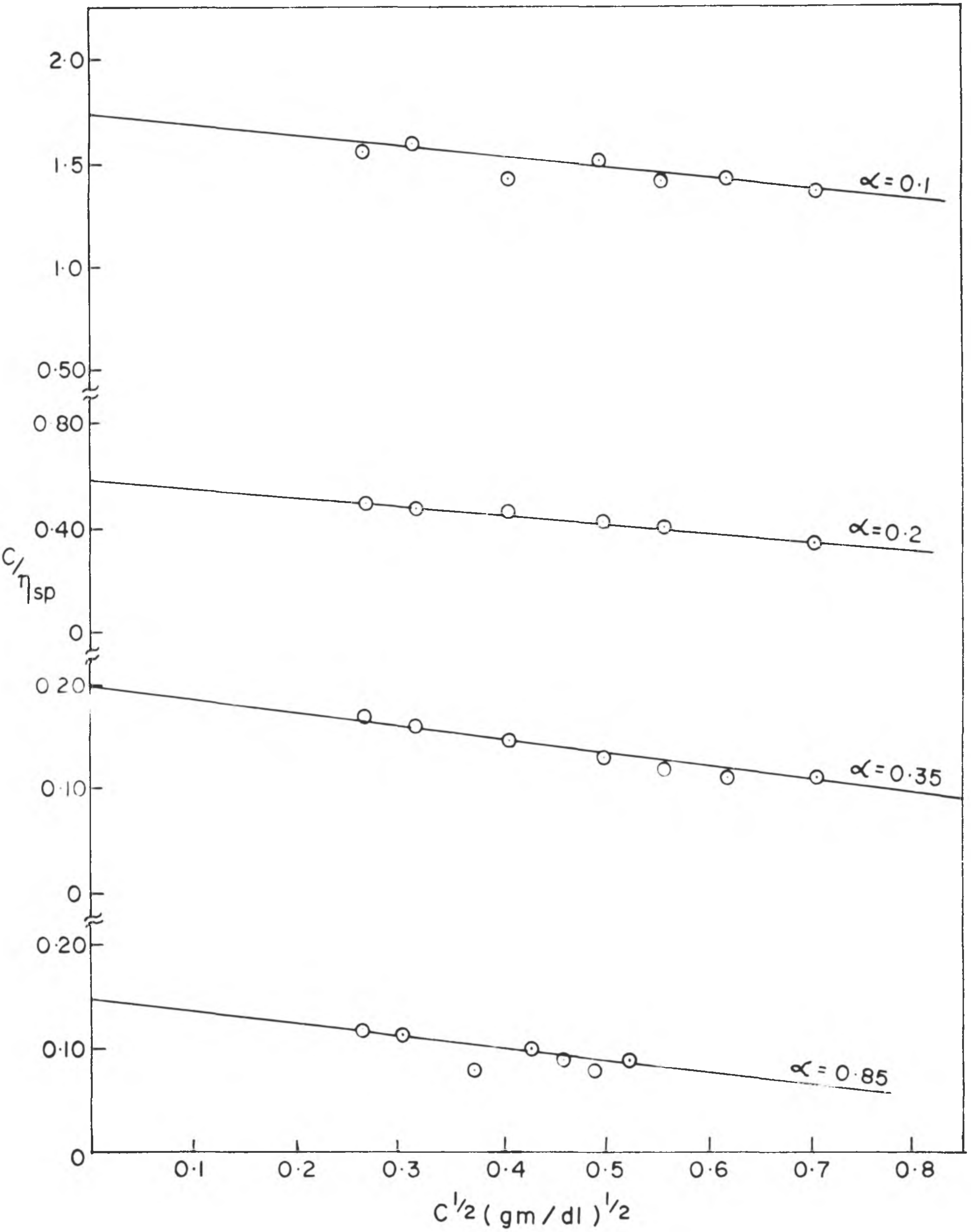


Fig. 25 Fuoss plot of poly (methacrylic acid) in 0·10 M NaCl solution

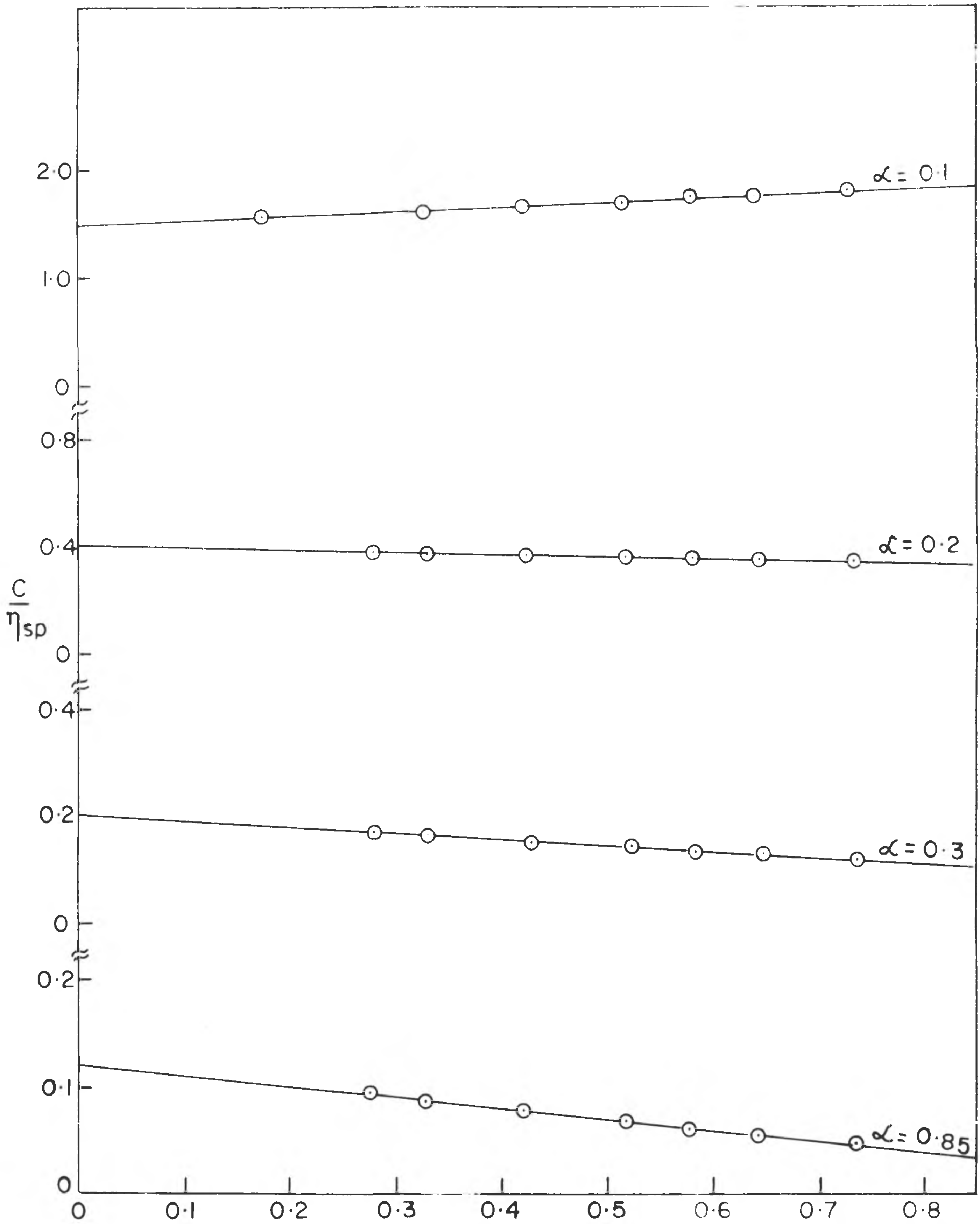


Fig. 26 Fuoss plot of (MA-NVP) copolymer in 0·10 M NaCl solution (2·23 mole % NVP)

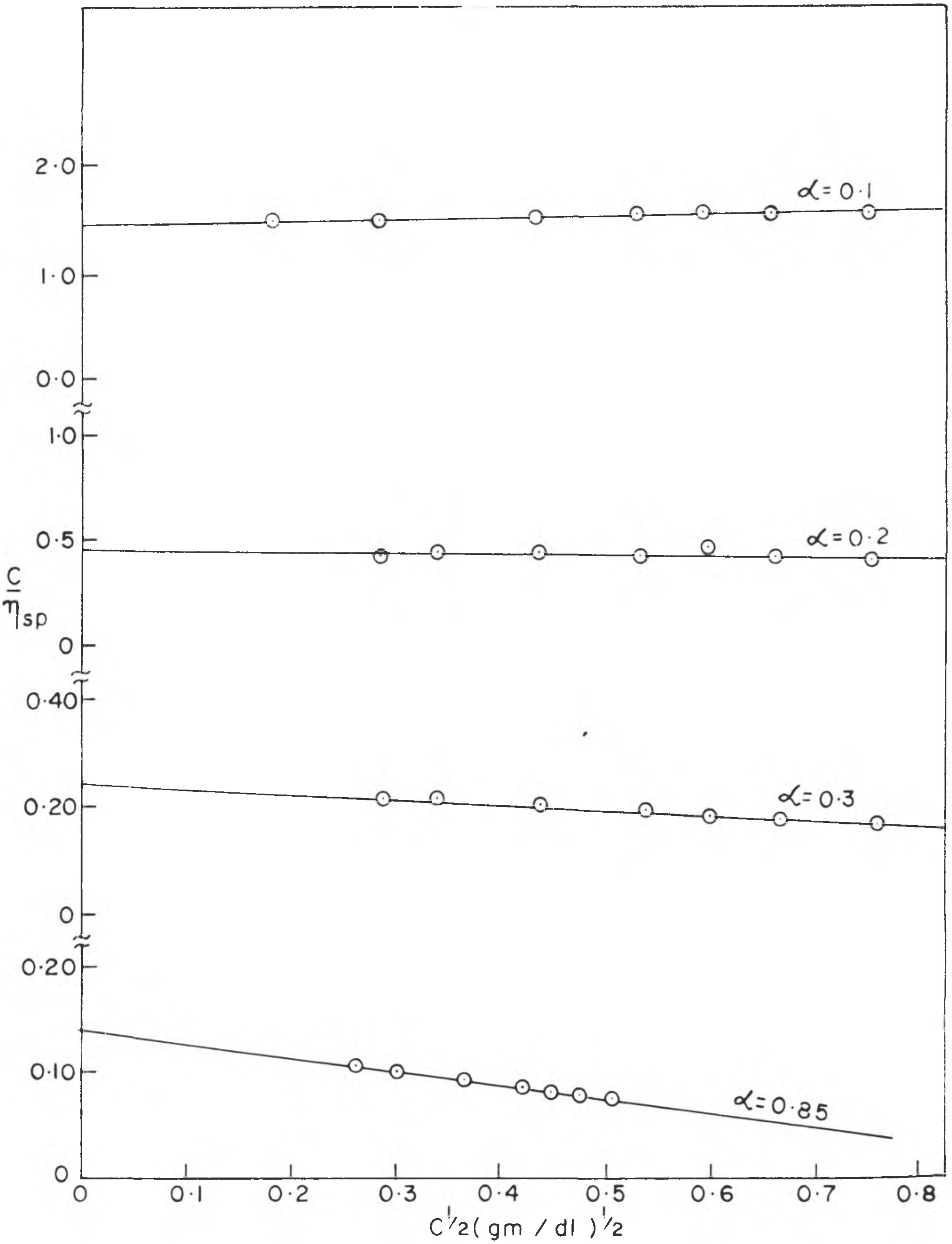


Fig. 27 Fuoss plot of (MA-NVP) copolymer in 0·10M NaCl solution (4·52 mole % NVP)

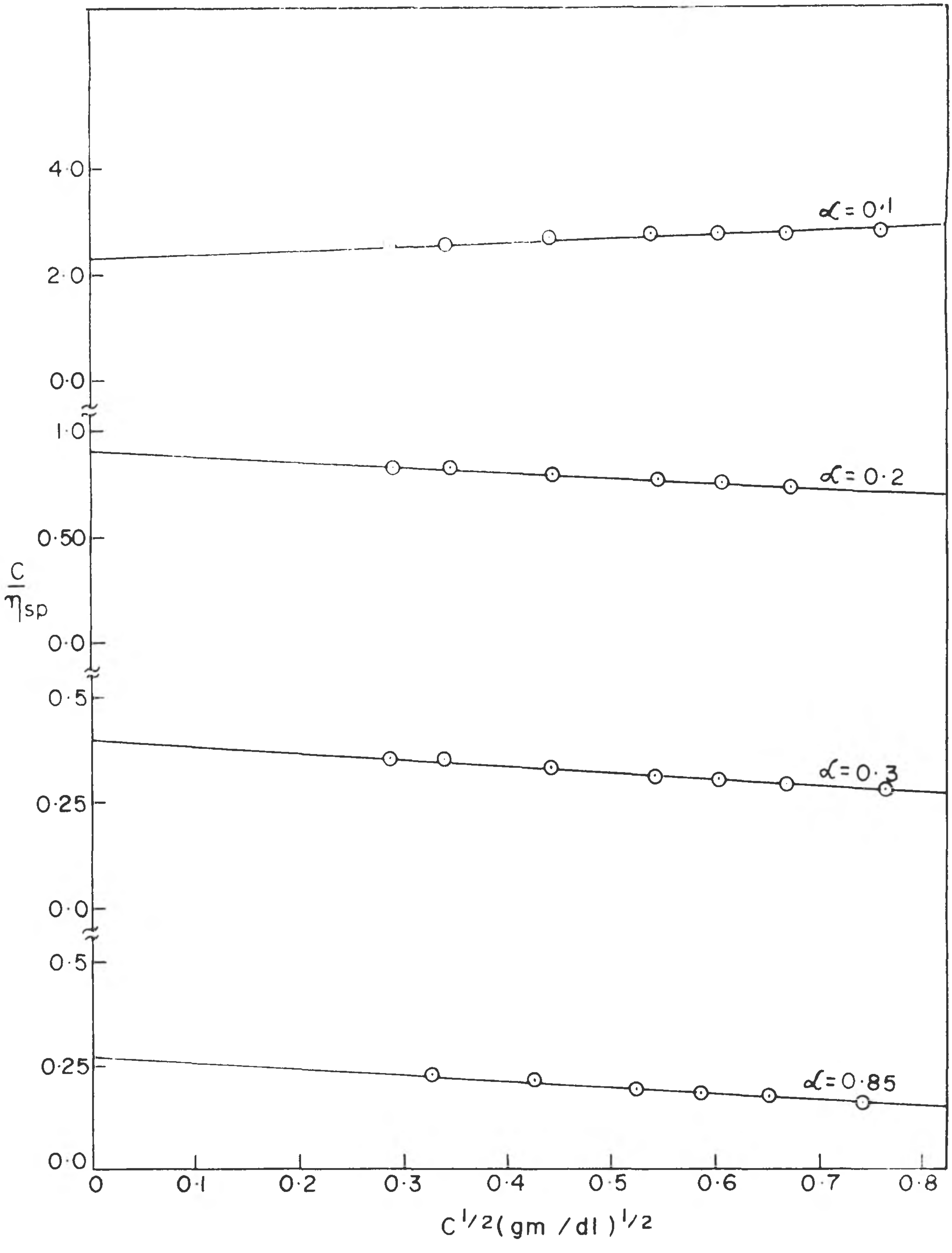


Fig. 28 Fuoss plot of (MA-NVP) copolymer in 0·10M NaCl solution (9·51 mole % NVP)

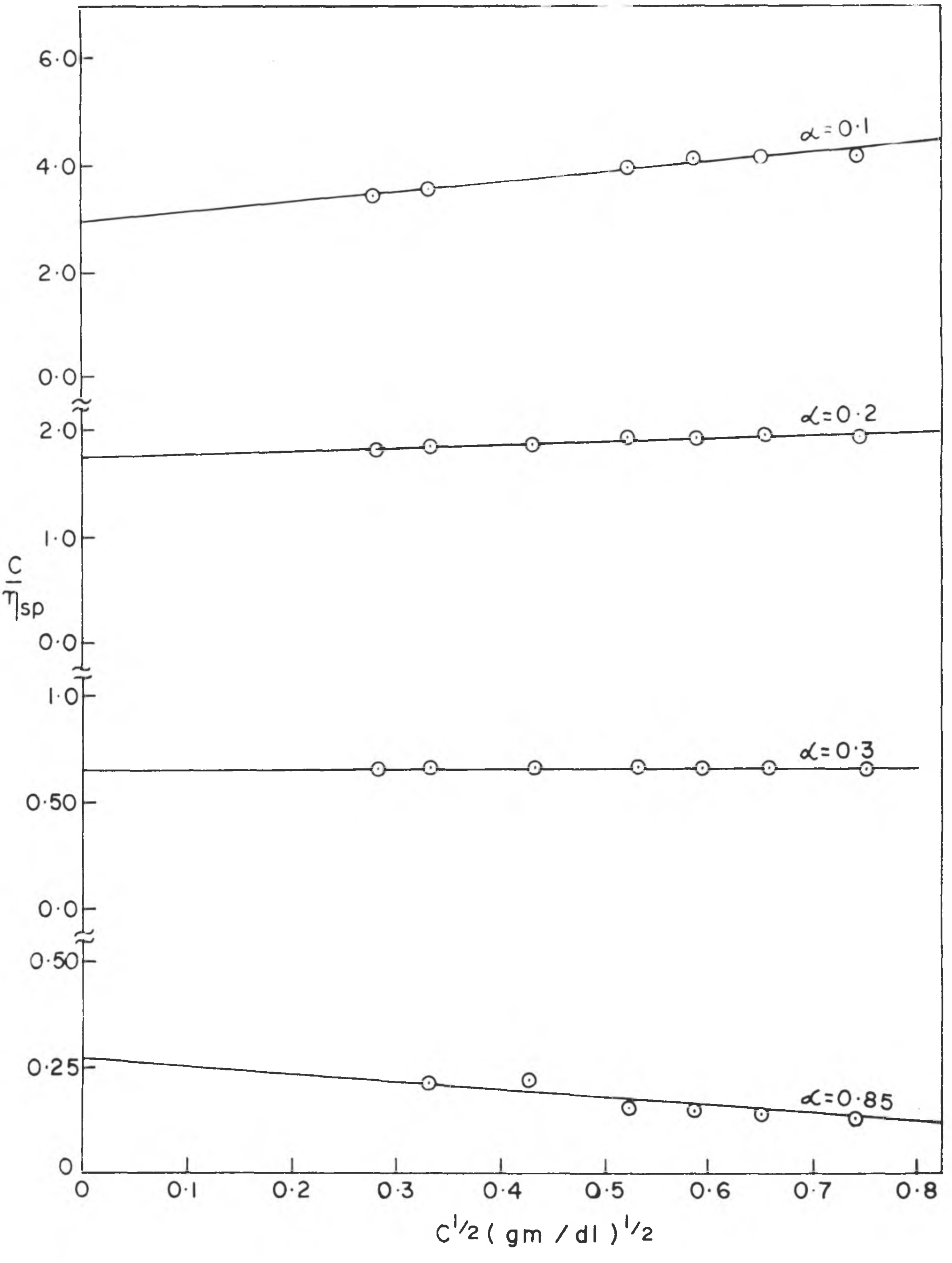


Fig. 29 Fuoss plot of (MA-NVP) copolymer in 0·10 M NaCl solution (15·24 mole % NVP)

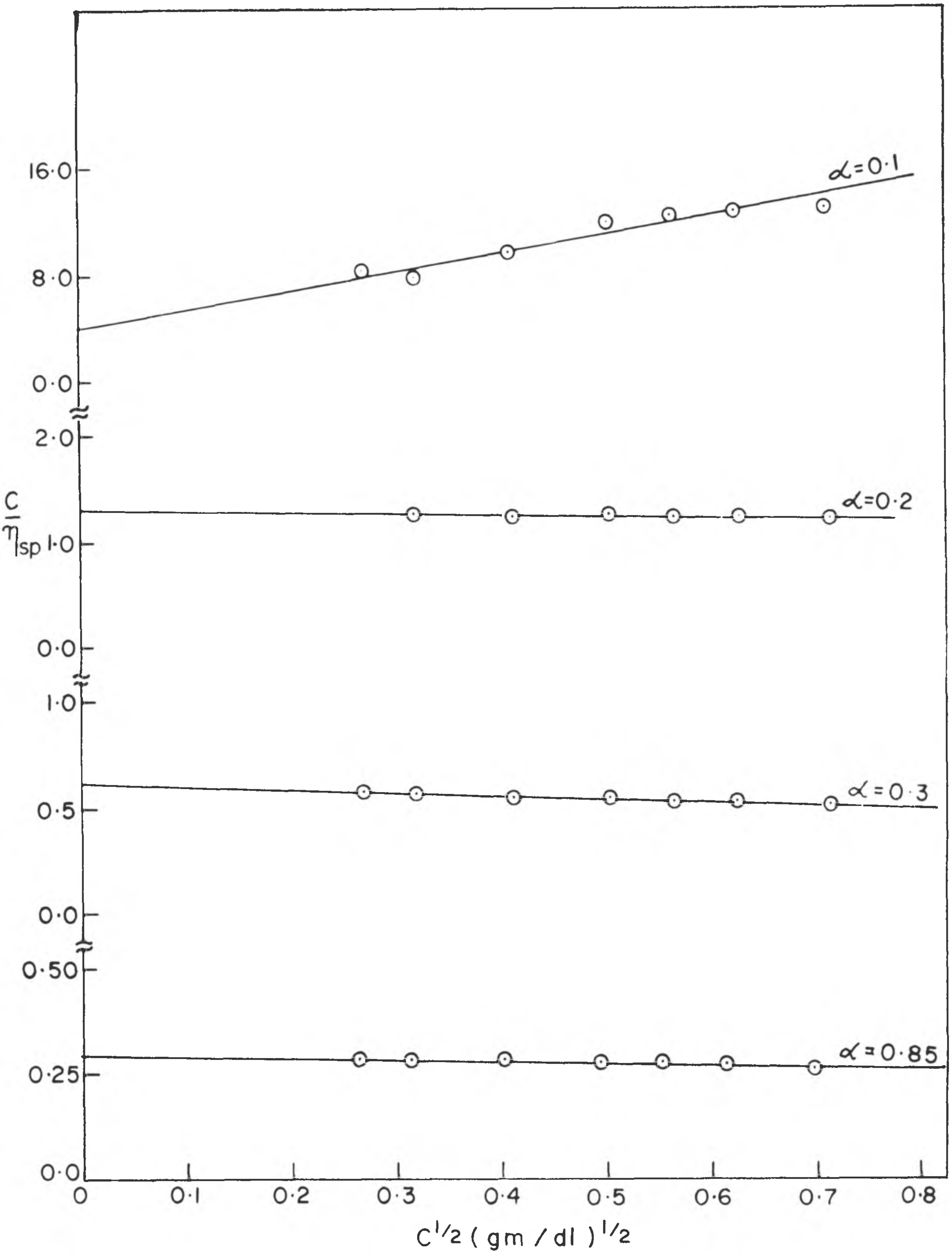


Fig. 30 Fuoss plot of (MA-NVP) copolymer in 0·10M NaCl solution (26·62 mole % NVP)

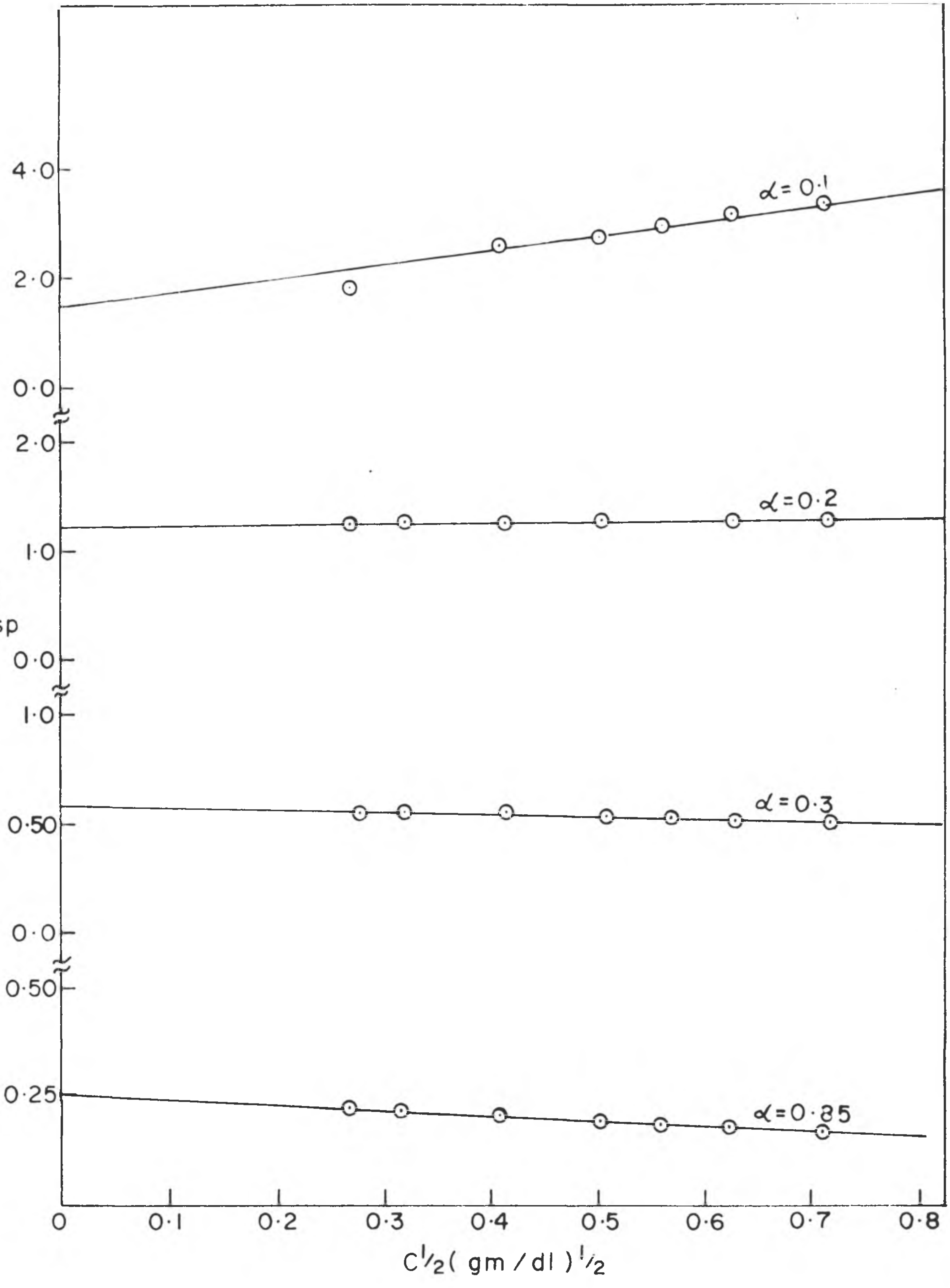


Fig. 31 Fuoss plot of (MA-NVP) copolymer in 0·10M NaCl solution (35·92 mole % NVP)

CHAPTER-IV

DISCUSSION

4. DISCUSSION

4.1. Copolymerisation Studies

4.1.1 Introduction

The copolymerisations were carried to high conversions and the experimentally determined monomer feed-copolymer composition data were treated by both the YBR differential procedure[45] using average monomer feed values and by the Mayo-Lewis integrated equation[31] resolved by Joshi's procedure[46] to compute r_1 and r_2.

The solutions of r_1 and r_2 obtained by the two methods are not drastically different inspite of very high conversions ($<70\%$) in some experiments. Joshi has pointed out the close agreement between the differential YBR and the integrated equation after a survey of a large number of experimental data[46]. In the four systems investigated in the present work, the agreement in a good number of cases is well within 10%. The systems are discussed in the light of the data obtained by the solution of the integrated equation since it accounts for the drift in the monomer concentrations with copolymerisation and,hence, is more exact. The experimental results are compared with the existing results of the same system under different conditions. The systems acrylic acid-acrylamide and methacrylic acid-acrylamide polymerised to relatively low conversions, were also treated by the recently prepared Kelen-Tüdös[49,50] method and these two systems are discussed on the basis of the observed results[148].

4.1.2 Acrylic acid-N-vinyl Pyrrolidone

The system, investigated by Van Paesechen and Smets in bulk at 75°C[136] and by Chapiro and Le Dean Trung[134] in toluene, ethanol, DMF and in bulk, gives conflicting values for the monomer reactivity ratios (Table-42). Chapiro et al observed that the reactivity ratios were nearly the same in bulk, toluene and in ethanol. Copolymers formed in DMF contained a somewhat larger fraction of acrylic acid, caused possibly by the formation of a complex between acrylic acid and dimethyl formamide. However, the differences between the compositions did not exceed 10 to 15%. Various physical measurements like phase diagram[135], flow time and infra-red analysis of the monomer mixtures reveal a strong molecular interaction between the two monomers. A kinetic study of the polymerization of acrylic acid in the presence of poly(N-vinyl pyrrolidone) in dilute aqueous solutions has also revealed a polymer complex, of poly(N-vinyl pyrrolidone) and the polymerized acrylic acid, which precipitated during the course of the polymerization[137,138]. The formation of association complex between the monomers, however, does not seem to control the copolymerization[134]. The copolymerizations in these investigations had been carried to low conversions and the monomer reactivity

Table-42: **Monomer Reactivity Ratio of the Copolymerization System Acrylic acid (r_1) N-vinyl Pyrrolidone (r_2) in Water at 30±0.05°C**

Reaction condition pH	Differential Method[45]		Integrated Equation[46]		Conversion range (weight %)	R_p(of AA)x10^5 mole/lit.-sec(19)
	r_1	r_2	r_1	r_2		
Ion free, 4	5.39±1.72	0.072±0.128	5.26±1.51	0.078±0.108	13.0 - 70.0	3.60
Ion free water, 5	1.36±0.30	0.30±0.12	1.32±0.29	0.31±0.17	17.0 - 56.0	2.10
Ion free water, 7	8.58±0.52	-0.035+0.017	8.12±0.43	0.019±0.011	10.5 - 35.0	0.43
Ion free water, 8	8.94±0.44	0.19±0.034	6.66±0.63	-0.084±0.016	23.0 - 65.0	1.90
Ion free water, 9	8.43±0.43	0.014±0.02	7.22±0.37	0.010±0.019	16.0 - 65.0	8.90
1 M NaCl, 6.5	6.29±0.68	-0.088±0.017	5.87±0.63	-0.077±0.020	8.7 - 48.0	
Bulk[136]	1.3	0.15				
Toluene[134]	0.48	0.05				
DMF[134]	0.67	0.03				

ratios were determined from the differential form of the copolymer composition equation.

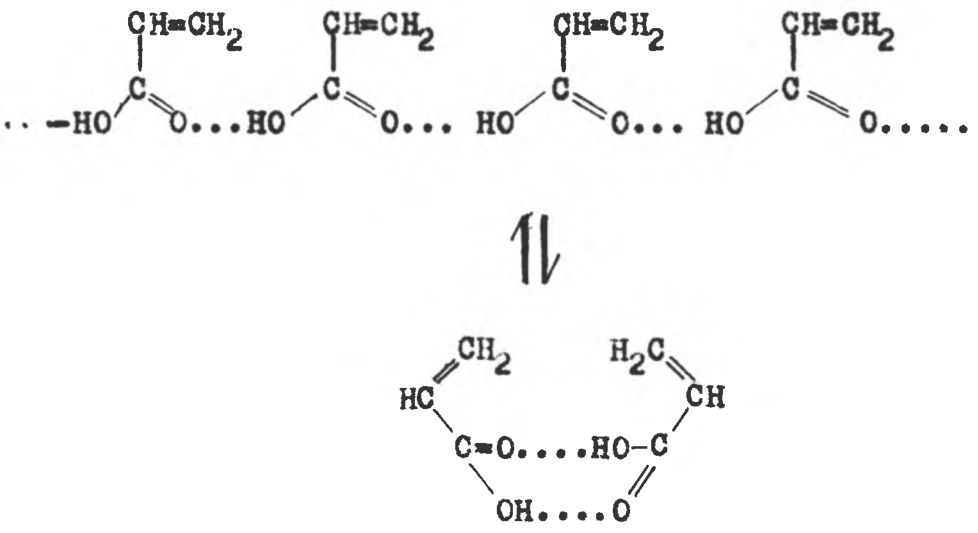
In the present investigation the copolymerisation of acrylic acid with N-vinyl pyrrolidone was conducted at pH 4,5,7,8 and 9 in ion free water and at pH 6.5 in 1 molar sodium chloride solution[122]. The computed r_1 (for acrylic acid) and r_2 (for N-vinyl pyrrolidone) are presented in Table-42.

The reactivity ratio for acrylic acid drops from 5.26at pH 4.0 when 45% of the monomer is ionized [pKa for acrylic acid = 4.2 and pKa of Poly(acrylic acid) is 6.4][19] to 1.3 at pH 5.0 when nearly 86% of the monomer is ionized. In this pH range, the copolymer chain is predominantly unionized. The r_1 increases to 8.1 at pH 7.0 and fluctuates between 6 and 7 as the pH is raised from 7.0 to 9.0. Addition of 1 molar sodium chloride at pH 6.5 slightly reduces r_1 to 5.8 (r_1 = 8.1 at pH 7.0), which is however similar to its value at pH 4.0. A minimum in r_1 = 1.3 observed at pH 5.0 is due to the electrostatic repulsion between the ionized monomer molecules approaching the growing copolymer chain. A further decrease in r_1 would be expected above pH 5.0 as the growing copolymer chain also begins to ionize. At pH 6.0, for instance, the polymeric acid is already 40% ionized. The higher value of r_1 in this range (6.6 - 8.1 in the pH range 7.0 - 9.0) can partly be understood by examining the homopolymerisation rate R_p of acrylic acid ($R_p x 10^5$ for AA is 3.6, 2.1, 0.43, 1.9 and 8.9 at pH 4, 5 and 6,7,8 and 9)[19]. Though R_p has a minimum in the pH range 5-7, it sharply increases and exceeds the values at pH 4.0 when the pH is 8.5. The polyacid anions are capable of binding cations present in aqueous solutions[139,140]. The propagating copolymer radicals may also be considered as being composed of divided ion pairs[16-18]. The electrostatic repulsion between the like charged monomeric ions and the ionised growing copolymer radicals approaching each other are diminished, increasing thereby the probability of addition of the ionised monomer. Homopolymerisation rates are directly proportional to r_{11} (or k_p, the propagation rate constant) as the termination rate constant is independent of pH as shown by rotating sector measurements (Table-1)[19].

In the present system, N-vinyl pyrrolidone does not ionise and hence 'k_{12}' is invariant with pH. Therefore $r_1(=k_{11}/k_{12})$ may be assumed to be proportional to k_p and hence the rate of polymerisation of acrylic acid. The data on sodium ion binding (both loose and tight binding) to polyacrylic acid[139,140] shows that 50,63 and 65% of the Na^+ ions are bound to the polymeric acid at pH 6,7 and 7.5 respectively. This ion binding considerably reduces the negative charge density on the polymer backbone. Consequently the electrostatic repulsive interactions between the ionised monomer units and the growing polymer chain are minimised. The cations present in the system partially shield the negative charges on the ionized monomers, resulting in the faster rate of addition of the monomer units to the growing copolymer chain. This is reflected in the increase of r_1 in the alkaline range. The r_2 values for N-vinyl pyrrolidone are small, either positive or negative in all cases except at pH 5.0. Together with the standard deviation, r_2 can be taken to be equal to zero. The r_2 value of 0.3 at pH 5.0 may probably be due to the lowering of the local concentration of ionised acrylic acid monomer at the site of addition, giving a better chance for the incorporation of N-vinyl pyrrolidone molecule and hence a copolymer richer in N-vinyl pyrrolidone. At pH 6.5, when the polymer is about 50% ionised and the monomer is totally ionized, addition of 1 molar sodium chloride restores the r_1 to the situation where the monomer is only partially ionised. It is assumed that the pKa of the copolymer of acrylic acid and N-vinyl pyrrolidone is close to the pKa of poly(acrylic acid). This is evident from the fact that the copolymers obtained from different monomer feed ratios are always richer in acrylic acid. Since the r_1 is considerably greater than unity, and the r_2 is nearly equal to zero, the copolymers would consist of long sequences of acrylic acid interrupted by short units of N-vinyl pyrrolidone, which is a close approximation to poly(acrylic acid).

The reactivities of acrylic acid and N-vinyl pyrrolidone towards copolymerization in bulk has shown the former to be a more reactive monomer[136]. The recent study of Chapiro et al, as already discussed[134], has also shown a small reactivity for N-vinyl pyrrolidone (Table-41).

The smaller values of r_1 obtained by Chapiro et al[134] for acrylic acid are in variance from the results obtained in the present investigation in aqueous solution. This can be partially explained on the basis of plurimolecular aggregation of acrylic acid monomer in aqueous solution[141] leading to a long sequence of the monomer interrupted by a few units of N-vinyl pyrrolidone. In hydrocarbon solvents these aggregations break down to individual monomer units microscopically distributed in a way similar to their macroscopic distribution in the system as a whole. Therefore a slight solvent effect is observed in DMF, as compared to toluene, a hydrocarbon solvent.


(1)

(2)

The possibility of carboxylic acids associating (I) linearly has been reported for formic and acetic acids[142,143]. These plurimolecular aggregates with a very short half life, assumed on thermodynamic considerations to represent only a minor fraction of the hydrogen bonded associations, are in a dynamic equilibrium with the more abundant dimer (II). The high viscosity observed for acrylic acid and its solution in high dielectric constant solvents is explainable in terms of plurimolecular aggregates[134]. Copolymerisation of acrylic acid under conditions favouring the formation of these aggregates will lead to a long sequence of acrylic acid resulting in poly(acrylic acid) blocks. Addition of benzene and other hydrocarbon solvents decreases the viscosity of acrylic acid solutions[134]. Simultaneously there is a considerable fall in the reactivity. Under these conditions the plurimolecular aggregates may assumed to be dissociated[141].

4.1.3 Methacrylic acid-N-vinyl Pyrrolidone

The system has been investigated by Kabanov et al[18] in ion free water and in 2 molar sodium chloride solution at pH 8 when methacrylic acid as well as the growing copolymer chain are predominantly ionized. The system has also been investigated by Chapiro et al[134] in DMF and methylene chloride solutions using gamma ray initiation at room temperature and at 42°C by Endo et al[145] using azo bis isobutyronitrile as initiator. Their results are conflicting in nature. Chapiro et al[134] observed reactivity ratios as $r_1(MA) = 4.7\pm0.1$ and $r_2(NVP) = 0.07\pm0.02$ while Endo et al[145] reported copolymers of almost constant composition over a wide range of monomer feed (Table-4).

In the present investigation the copolymerisation behaviour of methacrylic acid and N-vinyl pyrrolidone was investigated at pH values 2,3,4,5,6,7,8,9 and 10 in ion free water and also in 1 molar sodium chloride solution at pH 3,7 and 10. The monomer reactivity ratios observed, r_1 for methacrylic acid and r_2 for N-vinyl pyrrolidone, are presented in Table-43.

The experimental results clearly indicate that in the investigated pH range methacrylic acid adds faster than N-vinyl pyrrolidone to the growing copolymer chain. N-vinyl pyrrolidone shows enhanced rate at pH 7 and 8. The r_1 drops from 6-8 at pH 2-3 to 2.9 at pH 4 (when about 30% of the monomer is ionized), continues to be low (4.9 - 4.0) in the pH range 5-7 and drops to 0.92 at pH 8.0 when in addition to the total ionisation of methacrylic acid, 92% of the growing poly(methacrylic acid) chain is also ionized. As the pH is increased to 10, the r_1 shows a gradual increase to 3.6. In the presence of 1 molar sodium chloride, r_1 remains fairly constant (r_1=4.9 - 4.4) in the pH range 3-10.

Table-43: Monomer Reactivity Ratios for Copolymerization System Methacrylic acid (r_1) N-vinyl Pyrrolidone (r_2) in Water at 30±0.05°C

Reaction condition, pH	Differential Method[45]		Integrated Method[46]		Conversion range (weight %)	$R_p \times 10^5$ (of MA) mole/lit.sec. at 60°C
	r_1	r_2	r_1	r_2		
2, Ion free water	6.87±0.39	-0.035±0.025	6.49±0.42	-0.038±0.028	4.9 - 46.0	
3, Ion free water	8.62±0.17	-0.059±0.005	8.34±0.14	-0.006±0.003	6.0 - 37.0	3.4
4, Ion free water	2.99±0.18	-0.035±0.016	2.99±0.18	-0.032±0.015	8.5 - 12.0	1.7
5, Ion free water	5.99±1.11	0.073±0.106	4.90±0.91	0.052±0.086	17.0 - 70.0	0.57
6, Ion free water	4.33±0.17	-0.026±0.009	4.00±0.10	-0.027±0.006	4.8 - 61.0	0.11
7, Ion free water	4.17±0.28	0.291±0.05	4.03±0.29	0.28±0.062	5.7 - 43.0	0.11
8, Ion free water	1.23±0.52	-0.011±0.047	0.92±0.29	0.67±0.19	5.7 - 28.0	0.23
9, Ion free water	2.33±0.39	0.039±0.065	2.33±0.38	0.037±0.035	11.6 - 20.0	0.52
10, Ion free water	3.59±0.23	-0.313±0.036	3.58±0.23	-0.031±0.035	6.0 - 22.0	0.98
3, 1 M NaCl	5.01±0.42	0.28±0.12	4.90±0.40	0.27±0.12	6.5 - 32.0	
7, 1 M NaCl	4.42±0.38	-0.084±0.042	4.44±0.39	-0.059±0.044	9.0 - 31.0	
10, 1 M NaCl	4.45±0.20	-0.031±0.02	4.43±0.19	-0.030±0.019	4.3 - 23.0	

The homopolymerisation rate of methacrylic acid is known to vary with the pH of the medium[16-19]. The rate registers a gradual fall, in the pH range 1-6, with minimum at the pHs corresponding to the pK_a of methacrylic acid [pK_a = 4.32][19] and the pK_a of poly(methacrylic acid) [pK_a = 7.0][19]. The rate then shows a slow gradual increase in the pH range 7-12. As the pH of the medium is increased the monomeric acid begins to ionise and the monomer-monomer electrostatic repulsive interactions become prominant in the vicinity of the pK_a of the monomeric acid thereby decreasing the rate. With further increase in pH, the pendant carboxyl groups of the growing polymer chain begin to ionize and monomer-growing polymer electrostatic repulsive interactions also come into play around the pK_a of the polyacid resulting in a further decrease in the rate (Fig.1). At pH 8.5, the electrostatic repulsion between the monomer units in the polymer is maximum[19] and hence electrostatic repulsion between the ionized growing polymer chain and the approaching ionized monomers may also be assumed to be maximum.

In the present investigation the minimum observed for r_1 at pH 8 (0.92) can thus be accounted for. With further increase in pH, the negative charges on the carboxyl ions are partially shielded by the Na^+ ions introduced into the system for pH adjustments. The monomer-monomer and monomer-growing copolymer chain repulsive interactions are reduced marginally, resulting in a faster rate of addition of methacrylate anion to the growing copolymer chain. The rate of addition of N-vinyl pyrrolidone remains invariant with pH. The r_1, therefore, shows a gradual increase from 0.92 at pH 8 to 3.58at pH 10. The increase in r_1 in the alkaline pH, though noticeable, is not as pronounced as in the acrylic acid-N-vinyl pyrrolidone system. This parallels the homopolymerisation behaviour of the two acids (Fig.1). Polymethacrylate anion binds sodium ion to a much lesser extent than polyacrylate anion[18]. Thus, at high pH the electrostatic repulsive interactions in the system methacrylic acid-N-vinyl pyrrolidone still persist to a significant extent resulting in a less dramatic increase in r_1 in the alkaline range. Cation binding to polyelectrolyte is specific[19]. The kinetic investigation of polymerization of methacrylic acid in the alkaline range (pH 9.5) shows that the rate is influenced by the type of cation present[146]. This may largely be attributed to the different capacities of the respective cations to form ion pairs at the propagating end of negatively charged polymer radicals. If the pH adjustment is made with the aid of trimethylamine, the enhancement in rate in the alkaline pH is appreciable for methacrylic acid but is only marginal for acrylic acid[18] (Fig.2). The feasibility of hydrophobic interaction between poly(methacrylic acid) radicals and triethylamine probably contributes to the stabilisation of the ion pair[18].

A significant increase in r_1 is noted at high pH in the presence of 1 molar sodium chloride and the r_1 values are somewhat restored to those at pH 5-7. However, r_1 values are still much lower than that observed under the nonionic situation presumably because the added sodium chloride disrupts the hydrophobic interactions and the plurimolecular aggregates responsible for the high rate of polymerisation at low pH[144]. Methacrylic acid exists predominantly as a dimer and the hydrophobic interactions between the methacrylic acid monomer and the growing poly(methacrylic acid)chain is broken by NaCl[147].

In the present discussion it is assumed that the pK_a of poly(methacrylic acid-co-N-vinyl pyrrolidone) is nearly the same as the pK_a of poly(methacrylic acid) since the copolymers obtained are always richer in methacrylic acid. The reactivity ratios of N-vinyl pyrrolidone are very small either negative or positive and together with the standard deviations may taken to be zero. Thus, the copolymers have a long sequence of methacrylic acid units interrupted by very short intervals of N-vinyl pyrrolidone. The relatively high r_2 values (0.28 and 0.67) at pH 7 and 8 may perhaps be due to the decrease in the rate of addition of methacrylate anion to the predominately ionized propagating copolymer radicals. Hence, an unionised N-vinyl pyrrolidone molecule will have a greater chance of addition yielding copolymers richer in N-vinyl pyrrolidone. Kabanov et al[18] in their rather limited study of this system report $r_1 = 0.65$, $r_2 = 0.33$ and $r_1 = 0.90$, $r_2 = 0.30$ at pH 8.0 in ion free water and in 2 molar sodium chloride solution respectively. The computational procedure was not described in their work and the increase in r_1 is not appreciable in the presence of NaCl. Comparison of the reactivity ratios observed in the present investigation with those arrived at by Kabanov et al[18], should be treated with caution. The Fineman and Ross treatment most probably applied to these calculations is inadequate in comparison with the YBR differential method and Mayo-Lewis integrated equation used in the present investigation.

4.1.4 Acrylic acid-Acrylamide

Copolymerizations of the system acrylic acid-acrylamide were investigated at pH values 2,4,6, 8 and 9 in ion free water and at pH 2,4 and 6 in 1 molar sodium chloride solution. The observed monomer reactivity ratios r_1 (for acrylic acid) and r_2 (for acrylamide) are represented in Table-44[125].

The r_1 for acrylic acid is maximum (0.92) at pH 2 where less than 1% of the acid is ionised. It decreases sharply to 0.32 at pH 4 corresponding to 45% ionisation of acrylic acid (pKa 4.2)[19]. The lowering of r_1 is caused by electrostatic charge repulsions among the

Table-44: Monomer Reactivity Ratios of the Copolymerization System Acrylic acid (r_1) Acrylamide (r_2) in Water at 30±0.05°C

Reaction condition, pH	Differential Method[45]		Integrated Method[46]		Conversion range (weight %)	$R_p \times 10^5$ (of AA) mole/lit.-sec. at 60°C
	r_1	r_2	r_1	r_2		
Ion free water, 2	0.93±0.79	0.23±0.33	0.92±0.82	0.25±0.36	28.8 - 70.7	10.3
Ion free water, 4	0.30±0.06	0.56±0.09	0.32±0.05	0. 57±0.07	11.4 - 63.4	3.6
Ion free water, 6	0.34±0.20	0.89±0.64	0.34±0.20	0.85±0.62	34.2 - 77.3	0. 3
Ion free water, 8	0.63±0.01	0.12±0.01	0.63±0.004	0.12±0.004	35.0 - 40.25	1.9
Ion free water, 9	0.30±0.10	0.95±0.21	0.30±0.10	0.95±0.20	10.3 - 45.75	8.9
1 M NaCl, 2	0.93±0.39	0.33±0.17	0.94±0.38	0.34±0.16	20.0 - 40.50	
1 M NaCl, 4	0.91±0.24	0.67±0.13	0.92±0.25	0.68±0.13	28.0 - 68.5	
1 M NaCl, 6	0.29±0.19	0.93±0.57	0.28±0.20	0.86±0.59		

ionised monomer molecules approaching the growing copolymer radical. The r_1 remains low (0.3[illegible]) at pH 6 when in addition to the nearly complete ionizationof the monomeric acid, the acrylic acid units in the copolymers would also predominately ionize. The pK_a of poly(acrylic acid) is 6.4[19] and in the acrylic acid-acrylamide copolymers obtained in the present work, the pKa would shift to lower values since the mean sequence length of acrylic acid units are not long for all the monomer feed ratios. In other words, the pKa may be assumed to be nearly equal to 6. As discussed for the earlier systems, at this pH, monomer-growing polymer electrostatic repulsive interactions will also be felt in addition to the electro static repulsions between ionized monomers. This trend is similar to the homopolymerization behaviour of acrylic acid as a function of pH. To recapitulate the earlier systems, the rate of polymerization of acrylic acid, at different degrees of ionisation, is directly proportional to the corresponding propagation rate constant k_p, the termination rate constant k_t remaining invariant with pH, as shown by the rotating sector measurements[19]. Therefore, $r_1 (= k_{11}/k_{12})$ may be taken to be proportional to K_p [and hence R_p of acrylic acid], assuming the invariance of k_{12}, the rate constant for the addition of non-ionizing acrylamide unit to an acrylic acid unit. The homopolymerisation rates (R_p) of acrylic acid determined by pH independent initiation at

60°C are (R_px10^5) equal to 3.6, 2.1, 0.43, 1.9 and 8.9 at pH 4,5 (6 and 7),8 and 9 respectively[18] (Fig.1). As shown earlier the higher rates in alkaline pH are caused by sodium ion binding to the growing polyacrylate anion, partially neutralising the negative charges on the growing polymeric chain[139,140], as well as on the ionized monomer molecules, thereby facilitating greater monomer addition. The increase in r_1 at high pH values is thus understandable. However, the low value of 0.3 for r_1 at pH 9 is unexplainable. The high value of r_2 at pH 9 (r_2=0.95) suggests faster incorporation of acrylamide units in the copolymers, resulting in low acrylic acid content. Addition of 1 molar sodium chloride solution to the system at pH 4 restores r_1 from 0.32 (in ion free water) to 0.92, the value at pH 2. Addition of 1 molar sodium chloride solution to the system at pH 6 contributes only to a partial increase of acrylic acid addition in the presence of acrylamide. A greater concentration of the electrolyte is needed to completely screen the charges and bring about a condition similar to that at low pH. The presence of acrylamide in the system seems to play a negative role in the addition of acrylic acid units at high pH, in contradiction to the homopolymerisation behaviour of acrylic acid. It is not clear whether the alkali metal ion binding to acrylic acid is affected. The r_2 for acrylamide shows a gradual increase with pH except at pH 8.0, where it is low. Addition of

1 molar sodium chloride to the system results in a sharp increase of r_2 at pH 4 and 6. A few experiments were conducted on the homopolymerization of acrylamide at pH 4, 6 and 10 using the same initiator system $K_2S_2O_8/Na_2S_2O_4$ and 1 molar concentration of monomer in the presence and in the absence of 1 molar sodium chloride. The rate of polymerization showed 3-10 fold increase in the presence of NaCl. The increase in r_2 can only be explained in terms of faster addition of acrylamide units in the presence of sodium chloride.

The system has also been investigated in water at low and high pH values by Bourdais[22], in benzene by Smets et al[21] and more systematically as a function of pH in the range 1.77 to 6.25 by Cabaness et al[24]. They observed an inversion in the reactivity ratios (Table-5). However, it is incorrect to compare their data with the data in the present work for the following considerations (a) the monomer feed in their experiments are of the order of millimolar concentrations as against a constant total concentration of 1 mole/litre in the present work. Monomer-monomer interactions like plurimolecular aggregations will be less prominent in the dilute solutions used by Cabaness (b) the copolymerizations were carried out at 60°C as against 30°C in the present investigation (c) Cabaness et al have carried copolymerizations to low conversions and the experimental data were treated by Fineman and Ross linearization method[41] which is shown to have limitations[46,55] as compared to the Mayo-Lewis integrated copolymerization equation[31] used in the present investigation.

4.1.5 Methacrylic acid-Acrylamide

The reactivity ratios r_1 for methacrylic acid and r_2 for acrylamide as a function of degree of ionization of methacrylic acid, are tabulated in Table-45.

The copolymerization data of this system corroborates with the homopolymerization rate of the monomeric acid better than the system acrylic acid/acrylamide. The r_1 for methacrylic acid (MA) is maximum at pH 4 and drops sharply till the pH 6 (r_1 is 2.81, 1.94 and 0.19 at pH 4, 5 and 6 when 30%, 82% and 93% of the monomer is ionized.). The decrease of r_1 is again understandable in terms of electrostatic charge repulsions between the reactive species. The pK_a of poly(methacrylic acid) is 7.0[19]. The sequence length of methacrylic acid in the growing copolymer chain, computed from the monomer reactivity ratios at pH 6 and 7, is not too long. The pK_a of the copolymer would tend towards a lower value. Hence, the minimum of r_1 at pH 6-7 is also caused by the repulsion between the negatively charged propagating polymeric ion and the monomer ions. In the alkaline range, as expected from the arguments presented for the foregoing systems, faster addition of methacrylic acid to the copolymer chain and

Table-45: Monomer Reactivity Ratios of the Copolymerization System Methacrylic acid (r_1) Acrylamide (r_2) in Water at 30±0.05°C

Reaction condition, pH	Differential Method[45]		Integrated Method[46]		Conversion range (weight %)	$R_p \times 10^5$ (of MA) mole/lit.-sec. at 60°C. Ref.19
	r_1	r_2	r_1	r_2		
Ion free water, 4	2.84±0.47	0.20±0.07	2.81±0.44	0.20±0.07	7.0 - 26.25	1.7
Ion free water, 5	1.35±0.35	0.30±0.13	1.94±0.35	0.30±0.12	9.90- 16.8	0.7
Ion free water, 6	0.19±0.08	0.55±0.08	0.19±0.08	0.55±0.08	12.75- 24.60	0.11
Ion free water, 8	0.32±0.002	0.53±0.001	0.32±0.004	0.53±0.003	8.50- 39.2	0.23
Ion free water, 9	0.34±0.05	0.57±0.06	0.34±0.05	0.58±0.06	13.0 - 26.60	0.52
Ion free water, 10	0.38±0.06	0.51±0.06	0.39±0.06	0.51±0.06	5.5 - 54.5	0.98
1 M NaCl, 4	1.84±0.48	0.35±0.17	1.79±0.45	0.35±0.16	9.4 - 50.15	
1 M NaCl, 6	0.22±0.06	0.76±0.13	0.21±0.06	0.75±0.13	21.2 - 30.15	
1 M NaCl, 10	0.52±0.07	0.24±0.02	0.51±0.07	0.22±0.02	36.1 - 63.5	

simultaneously an increase in r_1 (to 0.32, 0.34 and 0.39 at pH 8,9 and 10 respectively) results but never approaching the r_1 values at low pH. This is because the Na^+ binding to the poly(methacrylic acid) units is much lower as compared to that of poly(acrylic acid)[18]. In the unionized state at low pH methacrylic acid is present as aggregates stabilized by hydrophobic interactions. This results in high values for r_1. At higher pH partial shielding of the electrostatic repulsive interactions by the Na^+ ions introduced results in a marginal increase in r_1. The r_1 values,however, do not approach that at low pH. Introduction of 1 molar sodium chloride at pH 4 results in a decrease in r_1 (1.79), instead of an increase over the r_1 value observed at the same pH in ion free water. This must be due to the disappearance of methyl-methyl hydrophobic interactions in the presence of sodium chloride leading to the breakdown of the aggregates of the reacting species. The breakdown of these aggregates is similar to the denaturation of proteins in the presence of strong electrolytes. Such hydrophobic interactions between the units of poly (methacrylic acid)[141] as well as the hydrophobic association of water soluble substituted hydrocarbons (e.g. alanine)[35] are well known. In the absence of sodium chloride the r_1 is as high as 2.81at pH 4,in sharp contrast to its values at other pH. In the presence of 1 molar sodium chloride the r_1 at pH 10 (0.51) registers only a 30% increase over its value of 0.39 in ion free water. The added electrolyte concentration is not sufficient to bring about the complete shielding of the ionic centres.

The r_2 values of acrylamide show a gradual rise with respect to pH, increasing from 0.20 at pH 4 to 0.58 at pH 9. In the presence of sodium chloride, the r_2 at pH 4 showed a 75% increase in keeping with a similar trend observed in the homopolymerization rate of acrylamide in sodium chloride solution. However, the r_2 value of 0.22 at pH 10, 1 molar sodium chloride is too low and is unexplainable.

4.1.6 Evaluation of Kelen-Tüdös Method[148]

The systems acrylic acid-acrylamide and methacrylic acid-acrylamide were copolymerized to high conversions (5-60%), at different pHs as mentioned earlier, and the monomer reactivity ratios r_1 and r_2 were computed by the Mayo-Lewis integrated equation[31] using a modified computer procedure[46]. The salient features of these systems are: (i) the reacting monomeric acid (AA,MA) ionizes predominantly during the reaction especially at pH > pK_a of the acids (pK_a of AA = 4.2 and pK_a of MA = 4.32)[19] and (ii) the copolymeric acid formed during the course of the reaction also predominantly ionizes in the vicinity of the pK_a of poly(acrylic acid) and poly(methacrylic acid) [pK_a of P(AA) = 6.4 and P(MA) = 7.0][19]. In these systems, in addition to free radical reactivities which control copolymerization, electrostatic charge interactions between the ionized carboxyl groups are also present and the binary copolymerization equation may not be ideally applicable. Recently Kelen and Tüdös[49] proposed a new differential equation for the evaluation of monomer reactivity ratios. It has been shown to be the most reliable form of the differential methods based on the well known monomer feed-copolymer composition equation[50]. The equation also determines the prerequisite for the applicability of the differential equation to the system. The equation has, since, been tested and found suitable for a number of cationic copolymerization data by Kennedy[50].

It was pointed out[49] that the binary copolymerization equation tends to become inapplicable if the reacting system has irregularities arising from intra and inter molecular interactions between the reacting species. In view of the fact that the Kelen Tüdös method was found to be well applicable to cationic copolymerization reactions which generally proceed to high conversions and are presumably not free from inter molecular interactions between the reacting species, it was felt worthwhile to test the reliability of the r_1 and r_2 values obtained by the Kelen-Tüdös procedure for high conversion free radical copolymerization systems. The r_1 and r_2 obtained by the Mayo-Lewis integrated copolymer equation are used as reference for comparison.

The Kelen-Tüdös equation was treated by the method of least squares and r_1 and r_2 for MA-AM and AA-AM systems are listed in Table-46. The MA-NVP and AA-NVP systems do not yield satisfactory values since the conversions are too high and therefore the test results are not discussed. It will suffice to say that conversions above 50% are generally unsuitable for treatment of data.

A comparison of r_1 and r_2 obtained from the Kelen-Tüdös procedure[49] with those computed from the standard integrated equation[31] shows that except for cases of conversion higher than 40% (the deviation in these cases from the integrated equation being in the range > 7-9%) the deviations are less than 5%. It is interesting to note that the deviations are only in the range 0.5 - 4% in systems when the conversion does not exceed 50% and an excess of a strong electrolyte (.e.g. 1 molar sodium chloride) is present to suppress the electrostatic interactions between the reacting species (AA-AM, pH 4 and 2 in the presence of 1 molar sodium chloride and MA-AM, pH 4, 1 molar sodium chloride). At higher conversions, as in the system MA-AM, pH 10, 1 molar sodium chloride, the deviation becomes more pronounced. Although it is too drastic to make generalization from the limited number of experiments examined, it can be said with certainty that the Kelen-Tüdös method can be applied to copolymerization data with conversions at least upto 25-30% without much loss in

Table-46: Evaluation of Kelen-Tudos Method for High Conversion Copolymerisation Data
(a) Acrylic acid-Acrylamide (b) Methacrylic acid-Acrylamide Systems

Reaction condition, pH	Weight percent conversion	Mayo-Lewis integrated equation		Kelen-Tudos method		Percentage deviation	
		r_1	r_2	r_1	r_2	r_1	r_2
(a)							
Ion free water, 4	7-19	2.805	0.201	2.936	0.194	+4.67	-3.48
Ion free water, 9	13-26	0.340	0.575	0.317	0.590	-6.76	+2.61
Ion free water, 10	5-54	0.390	0.514	0.402	0.468	+3.07	-8.95
1 M NaCl, 4	7-49	2.015	0.294	2.011	0.308	-0.20	+4.54
1 M NaCl, 10	36-63	0.512	0.224	0.542	0.245	+5.86	+9.37
(b)							
Ion free water, 6	34-77	0.338	0.853	0.358	0.832	+5.58	-2.40
Ion free water, 9	10-45	0.304	0.950	0.303	0.956	-0.33	+0.63
1 M NaCl, 2	20-40	0.941	0.336	0.936	0.326	[illegible]	[illegible]
1 M NaCl, 4	4-47	0.920	0.681	0.930	0.680	[illegible]	[illegible]

precision of r_1 and r_2. Average monomer feed values (Eqn.60) should be used for computation in equation 15.

4.2 Potentiometric and Viscometric Studies on MAA-NVP Copolymers: Collapsed Conformation of Poly(methacrylic acid) Chain

The free energy $-\Delta F^o/N$ of transition from uncharged compact globular to the hypothetically uncharged expanded form for poly(methacrylic acid) in 0.10 molar sodium chloride solution [in the concentration range (3 to 5)x10^{-2} equivalents/litre] computed from its titration curve (Fig.11) is equal to 158 cal $mole^{-1}$ which is in fair agreement with the value of 165 cal $mole^{-1}$ reported[7] for the same polymer in 0.50 molar sodium chloride solution in the same concentration range. It has been pointed out[7], however, that the average value of $-\Delta F^o/N$ for poly(methacrylic acid) obtained from the conflicting values of different workers amounted to 136 cals $mole^{-1}$ with high values of 190 cal $mole^{-1}$ found by Ptitsyn[3] and 220 cal $mole^{-1}$ by Conio et al[98]. The value of 158 cal $mole^{-1}$ obtained in this work is taken as the reference for the poly(methacrylic acid) chain. The titration curves for methacrylic acid-N-vinyl pyrrolidone copolymers (Fig.5-17) show a progressive decrease in the area of the loop between the experimental titration curve, the extrapolated curve and the pK_o on the ordinate with increasing N-vinyl pyrrolidone content. The characteristic 'hump' disappears for the copolymers with 26 and 36 mole percent N-vinyl pyrrolidone. The titration behaviour of poly(methacrylic acid) and methacrylic acid-N-vinyl pyrrolidone copolymers in ion free water (Figs. 5-10) show a similar trend. The copolymer compositions are presented in Table-41. The free energy values are listed in Table-47 and are graphically plotted against the mole percent of N-vinyl pyrrolidone in Fig.33. The progressive decrease in the $-\Delta F^{0}/N$ values is indicative of the gradual destabilization of compact structure with increase in the mole percent of N-vinyl pyrrolidone. The compact structures are nonexistant at N-vinyl pyrrolidone contents greater than 16 mole percent in the methacrylic acid N-vinyl pyrrolidone copolymers. The titration curves for high N-vinyl pyrrolidone content copolymers nearly resemble those of poly(acrylic acid) in which no significant conformational changes occur at low degrees of ionization. The viscosity plots of these copolymers in 0.10 molar sodium chloride solutions show similar characteristics of molecular size (Fig.32). The $[\eta]$ values of all the polymers lie nearly in the same range at $\alpha = 0.1$ but show divergence at higher values of α. The curves for 2.33 and 4.52 mole percent N-vinyl pyrrolidone copolymers lie close to the poly(methacrylic acid) curve, while the values for higher mole percent copolymers lie for below. The steep rise in the hydrodynamic volume with α for poly(methacrylic acid) and the too low N-vinyl pyrrolidone content

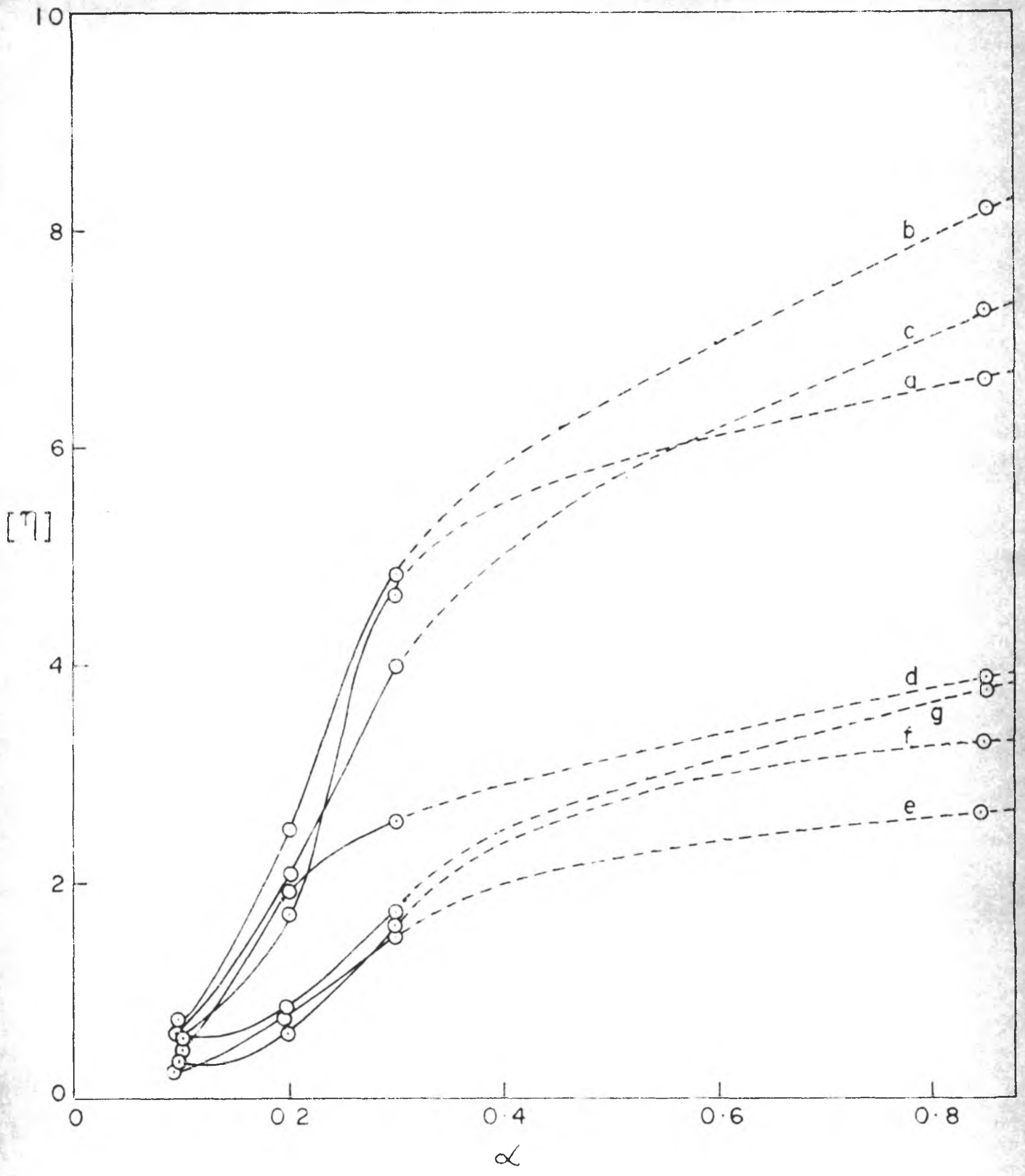
Table-47: Conformational Free Energies, pK_o Values and Intrinsic Viscosities at Different Degrees of Ionization in 0.10 M NaCl Solution at 30±0.05°C

Polymer	Mole percent NVP	pK_o	$-\Delta F^o/N$ cal/mole	$[\eta]$ dl gm^{-1} x 10			
				$\alpha = 0.1$	$\alpha = 0.2$	$\alpha = 0.3$	$\alpha = 0.85$
Poly(MA)	0	4.0	158	5.79	17.0	46.2*	66.5
Copoly(MA-NVP) I	2.23	4.1	100	7.01	25.0	48.0	81.9
Copoly(MA-NVP) II	4.57	4.5	71	6.66	20.3	39.6	72.4
Copoly(MA-NVP) III	9.51	4.85	65	4.25	19.0	25.3	39.0
Copoly(MA-NVP) IV	15.24	4.80	58	3.39	5.88	15.6	33.3
Copoly(MA-NVP) V	26.62	-	-	2.38	7.40	15.3	26.6
Copoly(MA-NVP) VI	35.92	-	-	6.13	8.16	17.0	38.1

* $[\eta]$ for $\alpha = 0.35$

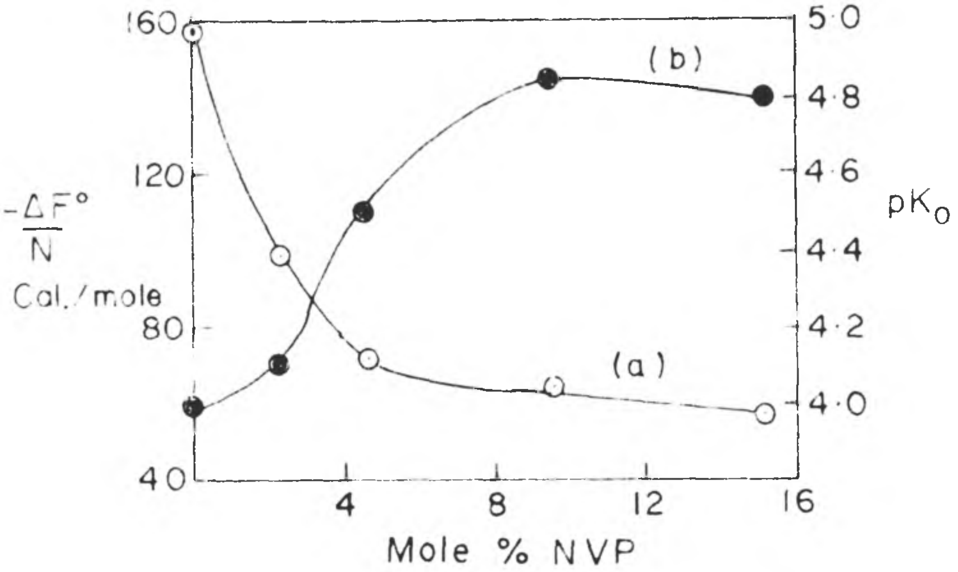
$|\eta|$ vs α PLOTS OF PMA AND MA-NVP COPOLYMERS
in 0.10 M NaCl Solution

Fig.32 a) 0% NVP
b) 2.23% NVP
c) 4.52% NVP
d) 9.51% NVP
e) 15.24% NVP
f) 26.62% NVP
g) 35.92% NVP



a) 0 % NVP, b) 2·2 mole % NVP, c) 4·5 mole % NVP, d) 9·5 mole % NVP, e) 15·2 mole % NVP, f) 26·6 mole NVP, g) 36 mole NVP

Fig. 32 [η] Vs α plots of P(MA) and (MA-NVP) copolymers in 0·10 M NaCl solution



a) Free energy of conformational transition as a function of mole % NVP

b) pK_0 as a function of mole % NVP

Fig 33

copolymers is of similar nature, ultimately reaching a maximum value at $\alpha = 0.85$ which corresponds to the maximum extension of the poly(methacrylic acid) chain[5,19]. The $[\eta]_{\alpha = 0.85} / [\eta]_{\alpha}$ ratios are not high for high N-vinyl pyrrolidone content copolymers, suggesting the existance of relatively expanded structures even at low α in these copolymers. The 'S' shaped nature of these curves suggest a cooperative breakdown of compact structures as suggested for the pure poly(methacrylic acid) chain[92]. The viscosities are for unfractionated polymers and the data can be used only for a qualitative interpretation of the general hydrodynamic behaviour of these copolymers. However, the features revealed in the potentiometric titration data are brought out. The potentiometric titration data are unaffected by the molecular weight and molecular weight distribution of the polymers[7].

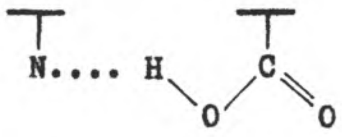
It has been pointed in the experimental section that the copolymers contain single N-vinyl pyrrolidone unit distributed among long sequences of methacrylic acid in a random manner, with the average lengths of the methacrylic acid sequences decreasing with increase in N-vinyl pyrrolidone content, the average length shortening to nearly 3 and 2 for 26.62 and 35.92 percent N-vinyl pyrrolidone contents. The decrease in the conformational free energy with increase in N-vinyl pyrrolidone content (Fig.33) indicates that the methyl-methyl hydrophobic contacts are not favoured by 'dilution' of the methyl sequences by N-vinyl pyrrolidone, a nonionic hydrophilic monomer. The lowest N-vinyl pyrrolidone content samples (2.23 and 4.52 mole percent) have about 40 and 20 methacrylic acid sequences and show the existance of compact structures, but of lesser stability. The 15.24 N-vinyl pyrrolidone mole percent copolymer, which still shows a slight contraction, has only an average of 5 methacrylic acid sequences. Lower methacrylic acid sequences do not bring about any measurable contraction as shown in the titration curves for the 26.62 and 35.92 N-vinyl pyrrolidone mole percent copolymers (Fig.16, 17).

It was shown from the viscosity studies of poly (methacrylic acid) by Ptitsyn[5] that the long range electrostatic interaction parameter obtained from the Stockmeyer-Fixman plots has only a slight dependence on α, when $\alpha < 0.2$, suggesting that the long range interactions have practically no effect on the dimensions of poly(methacrylic acid) molecules. In other words, these interactions are not considerable.

Likewise, long range interactions of methyl groups do not seem to occur, in which case, the molecules of higher N-vinyl pyrrolidone contents should fold. As pointed out by Ptitsyn[92] about 30 units of methacrylic acid sequences are required to bring about a stable collapsed molecule. This requirement is met in the 2.23

mole percent N-vinyl pyrrolidone copolymer with 44 units of MA and partly in the 4.52 mole percent N-vinyl pyrrolidone copolymer with 20 units of MA sequence and the compact structures are found in them though with slightly lesser stability. Only weak hydrophobic contacts are possible at shorter sequence lengths. An instance is known, however, in which only 40 percent of methyl groups in a long chain polymer[143] showed considerable collapse in aqueous solution at neutral pH. This is a terpolymer of glutamic acid, lysine and alanine (3:3:4 mole ratio) in fairly random sequence with relatively long sequences of alanine in which electrostatic attraction between the negative glutamate side chains and positive lysyl side chains compact the molecule in addition to hydrophobic alanine-alanine contacts. Such a situation does not arise in the methacrylic acid-N-vinyl pyrrolidone copolymers with all the ionizable groups carrying the same negative charge.

The decrease in tendency to collapse may also be partly attributed to the hydrophilic shielding of the methyl groups by the N-vinyl pyrrolidone side chains. Such a shielding also occurs in pure poly(methacrylic acid) at high values of α when carboxyl groups are ionised, as pointed out by Ptitsyn[92]. The destabilisation of collapsed structures even at low pH, with increase in N-vinyl pyrrolidone content in the poly(methacrylic acid) chain can possibly be attributed to the hydrophilic shielding of the methyls by pyrrolidone ring in addition to the dilution of the methyl sequences. This partly can explain the relative instability of the 2.23 and 4.52 mole percent N-vinyl pyrrolidone compolymers in spite of having long methacrylic acid sequences. The intrinsic pK (pK_o) values increase with the N-vinyl pyrrolidone content (Fig.33) indicating the hindrances in the proton release from the carboxyl groups. Interaction between the carboxyl groups and pyrrolidone rings are also well known[138]. Hydrogen bonded interactions of the type proposed[150] between the acidic hydrogen (from phenols) and the pyrrolidone ring could exist in the case of carboxyl groups. These interactions have to be:



between neighbouring units and might also hinder the free movement of polymer segments obstructing the relatively short range methyl-methyl contacts at low degrees of ionization.

CHAPTER-V

CONCLUSION

5. CONCLUSION

5.1 Copolymerization

Aqueous solution copolymerizations of ionisable monomers [acrylic acid (AA) and methacrylic acid (MA)] with nonionizable water soluble monomers [N-vinyl pyrrolidone (NVP) and acrylamide (AM)] show a dependence on the pH of the reaction medium. The variation in the monomer reactivity ratios of the acids show a definite trend with respect to the degree of ionization of both the monomer and the growing polymer acid, as well as with the degree of sodium ion binding to the polymer, hydrophobic interactions and plurimolecular aggregations[122-125]. The reactivity ratios for the two acids vary with the degree of ionisation in parallel to their homopolymerization behaviour.

The r_1 values (AA,MA) are rather high at low pH and drop to a minimum around the pH corresponding to the pK_a of monomeric acids when monomer-monomer electrostatic repulsive interactions come into play. The reactivity ratio continues to be low as the pH is increased and drops to a second minimum in the vicinity of the pK_a of the growing polyacid when monomer-polyion repulsions come into play. Further increase in pH leads to an increase in the value of r_1, nearly approaching its value at low pH for acrylic acid systems. However, the increase in the reactivity ratio for methacrylic acid is only marginal. This difference is due to much less Na^+ ion binding to poly methacrylate ion and the absence of polymer-monomer aggregates as a result of the disappearance of hydrophobic interactions normally present at low pH in methacrylic acid systems. Addition of an excess of a strong electrolyte like sodium chloride at high pH nearly restores the reactivity of acrylic acid to its low pH value systems by the complete shielding of the repulsive electrostatic interactions, by appreciable Na^+ binding to the carboxyls. Addition of sodium chloride to methacrylic acid systems disrupts the hydrophobic interactions and hence the increase in the reactivity ratio of methacrylic acid, in the presence of added electrolyte at high pH, is only marginal. The smaller effect of Na^+ in methacrylic acid system is also due to the much less Na^+ binding to the same.

The reactivity ratio of NVP generally are very small either positive or negative and together with the standard deviations can be taken to be zero. The reactivity ratio of acrylamide on the other hand show a gradual increase with increase in pH.

These trends in the variation of the reactivities of the ionizing monomers in copolymerisation will be of considerable help in synthesizing water soluble copolymers of different compositions and sequence lengths, which are simpler models for biological polyelectrolytes.

5.2 Potentiometric and Viscometric Studies

The study of copolymers of methacrylic acid and N-vinyl pyrrolidone with long sequences of methacrylic acid interrupted at random by single segments of the nonionic hydrophilic monomer, N-vinyl pyrrolidone, shows that the collapsed structure of poly(methacrylic acid) chain is progressively destabilized as the length of methacrylic acid sequences, is reduced. The compact structures are nonexistant at N-vinyl pyrrolidone content greater than 16 mole percent. The results indicate that the long range methyl-methyl hydrophobic contacts by segmental motion in a random coiled polymer like poly (methacrylic acid) at low pH are ineffective in bringing about the collapse of the molecule. As predicted from the hydrodynamic studies on poly(methacrylic acid), the short range interactions involving ≈ 30 segment lengths are essential to compact the molecule. The destabilisation of the collapsed structure could also arise from additional factors like the shielding of the hydrophobic methyl groups by the hydrophilic pyrrolidone rings.

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