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A Thesis
Submitted to
the University of Poona
In partial fulfilment of the requirements
for the degree of

MASTER OF SCIENCE

in
Chemistry

[illegible]

ANUP ANANTRAO [illegible]

Division of Polymer Chemistry
National Chemical Laboratory
Poona-8

([illegible])

KINETICS OF ALKALINE HYDROLYSIS OF POLYACRYLAMIDE IN SOLUTION BY VISCOSITY TECHNIQUE

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ARUN ANANTRAO GUNARI

Division of Polymer Chemistry
NATIONAL CHEMICAL LABORATORY
Poona-8

(1979)

ACKNOWLEDGEMENT

The author wishes to express his sincere appreciation to Dr. S.Gundiah, Scientist, Division of Polymer Chemistry, National Chemical Laboratory, Poona for his inspiring guidance and continued interest throughout the course of this investigation.

He is grateful to Mr.R.A.Kulkarni. for the help and suggestion during this work.

Special thanks are due to the Director, National Chemical Laboratory, Poona, for the permission to submit this research work in the form of a Thesis.

CONTENTS

CHAPTER-I

INTRODUCTION

I.a. General

Polyacrylamides have come to prominence in recent years[1]. The pendant $-CONH_2$ group on the polymer backbone is susceptible towards facile hydrolysis[2]. The resulting macromolecule is an anionic polyelectrolyte. Polyacrylamide can also be treated with formaldehyde and a secondary amine (Mannich reaction) and subsequent quaternization yields a cationic polyelectrolyte[1]. The range of properties that can be obtained by such reactions makes polyacrylamide one of the interesting polymers[1]. Anionic polymers based on polyacrylamides find varied applications[1], as sedimentation aids[1,3] and as flow retarder in secondary oil recovery techniques[1,4] etc.

The kinetics of alkaline hydrolysis of polyamides has been extensively studied[5-8]. These studies are important, both in elucidating the mechanism of the hydrolysis reaction as well as in evaluating the relevant rate constants and their relationship to the structure of the amides.

Solution viscosity measurements are extensively used in polymer characterization[9]. Viscosity measurements in kinetic studies, however, are of limited utility. Viscosity measurements, though earlier employed in studies of kinetics of polymerization reactions[10], have now been superseded by more accurate methods, but continue to be practised for the study of polymer chain degradation kinetics[11]. This investigation is an attempt in evaluating the kinetics of alkaline hydrolysis of polyacrylamide in solution by solution viscosity technique.

I.b. Viscosities of Polymer Solutions

Dilute solution viscosity behaviour of polymers play a very significant part in polymer studies. It was recognised very early[12] that when a polymer is dissolved in a solvent, the resulting high increase in viscosity is due to large dimensions of the macromolecule. This high increase in the viscosity of the solution, renders viscosity measurements an accurate technique requiring relatively less skill and no elaborate experimental set-up. This fact accounts for the wide use of the viscosity technique in polymer characterization. Due to recent advances in theory[13,14], apart from the molecular weights and sizes, significant information on solute-solvent interaction, etc. can also be obtained by viscosity measurements.

The quantity of interest in solution viscosity measurements is the intrinsic viscosity or the limiting viscosity number. Intrinsic viscosity is defined as:

$$\left[\eta_{sp}/C\right]_{C \to 0} \quad \text{or} \quad \left[\ln \eta_r/C\right]_{C \to 0}\text{ , where}$$

η_r is relative viscosity with reference to solvent and η_{sp} is (η_{r-1}). Several extrapolation methods[15] are available for the evaluation of intrinsic viscosity of which, the most widely used are:

$$\eta_{sp/}C = [\eta] + k'[\eta]^2C$$

and $$\ln \eta_r/C = [\eta] - k'' [\eta]^2 C$$

The first of these equations is due to Huggins[16] and the second due to Kraemer[17]. The values of η_{sp}/C or $\ln\eta_r/C$ are evaluated as a function of concentration and intrinsic viscosity is obtained by linear extrapolation of the values of η_{sp}/C or $\ln\eta_r/C$ to zero concentration. For sufficiently low concentration solutions, linearity of both the equations hold good, resulting in negligible uncertainty (< 1%) for the extrapolated intrinsic viscosity. The slope constants k' and k" are complex functions[14] of the thermodynamic and hydrodynamic polymer-polymer and polymer-solvent interactions and can be used as a qualitative estimate of these interactions.

Intrinsic viscosities, apart from being a function of molecular weight, are also influenced by polymer-solvent interaction. It is relatively a measure of the macromolecular dimensions in solutions[13]. Intrinsic viscosity at Flory's theta temperature[18], designated $[\eta]_\theta$, is on a better theoretical foundation. The polymer dimensions in a theta solvent correspond to the unperturbed dimensions[13] and the values of $[\eta]_\theta$ are proportional to the more amenable half-power law with reference to molecular weight.

The viscosity behaviour of polyelectrolytes, is relatively more complicated[19]. The nonionic polymer molecule in solution is represented as a random coil. For polymers carrying ionizable groups, a large increase in the dimensions is brought about by dissociation. A progressive dissociation is brought about even by greater dilution. It would be apparent that the random flight model will not be a true representation of the polyelectrolyte molecule, especially when fully ionized[20]. The important fact from the point of view of the present investigation, is the large changes in the dimensions of the polyelectrolyte during its progressive dissociation. It would be obvious that such large changes in dimension could also be brought about by a change in the number concentration of the ionizable groups.

I.c. Viscosity measurements in Kinetics of Polymeric reactions

The use of solution viscosity measurements for polymer characterization is very well-known. Though not popular to the same extent, viscosity measurements have also been used in kinetic studies. Its well-known use has been in the studies on kinetics of free radical polymerization[10] (for estimating the polymer conversion). The method entails an elaborate calibration, often not of very satisfactory precision. Due to this and other inherent disadvantages, use of viscosity measurements in kinetic studies of polymerization reactions has been totally superseded by the more convenient and precise methods, such as dilatometry[21]. Viscosity measurements on the other hand, continue to be popular in the studies on kinetics of polymer degradation[11,22]. Especially, during the initial stages of degradation, the accuracy of the results obtained is comparable to other methods[23] and this is one of the reasons for the continued popularity of the method.

The purpose of this investigation is to use solution viscosity measurements for studying the kinetics of alkaline hydrolysis of polyacrylamide. The progressive hydrolysis of polyacrylamide results in the polymer chain acquiring an increasing number of ionizable groups. The resultant viscosity changes are sufficiently large. If viscosities of polymers of known extents of hydrolysis are available, the viscosity increase during hydrolysis can be directly correlated with the extent of reaction. This facilitates the evaluation of the rate constant for the hydrolysis reaction.

The accuracy and reliability of kinetic measurements are greatly dependent on the analytical methods used for estimating the extent of reaction. Isolation of the polymer at intermittent conversions, their reprecipitations for purification purposes add to the difficulties. Quantitative precipitation, especially when low molecular weight material is likely to result under drastic hydrolysis conditions, is very difficult to achieve. Elemental analysis such as nitrogen analysis for estimating the residual amide groups, present severe problems. For polyacrylamide and partially hydrolysed polyacrylamide samples very low values are obtained for nitrogen by semi-micro Kjeldahl method[24,25] and N_2 estimation method is thought to be the least reliable for composition analysis of hydrolysed polyacrylamides.

Physical measurements, which allow continuous monitoring of the reaction without the cumbersome necessity of isolating intermittent samples, afford a more reliable, easy and convenient method for following the course of the reaction kinetics. The viscosity method followed in this investigation is one such method and offers these advantages.

Before outlining the method used here, the earlier reported studies on the kinetics of alkaline hydrolysis of polyacrylamide are reviewed.

I.d. Kinetics of alkaline hydrolysis of polyacrylamide

The hydrolysis of an amide is a second-order reaction[5]. The rate of hydrolysis is proportional to both the concentrations of amide as well as acid or alkali. The reaction follows a pseudo first-order rate-law, when one of the reactants is sufficiently in excess. The kinetics of alkaline hydrolysis of polyacrylamide has been studied by several workers and the results are in agreement with the above expectations. However, results reported by different workers differ in several other aspects.

The reaction rate for alkaline hydrolysis of polyacrylamide is faster than the reaction rates for monoamides[5]. The rate slows down as the hydrolysis progresses. Moens and Smets[5] found that the initial rate constant for hydrolysis, which remains almost constant upto about 30$\sim$35% conversion, is about one order magnitude higher than the rate constant at subsequent stages of hydrolysis. Nagase and Sakaguchi[7] observed the rate constant to decrease at even earlier stages of the hydrolysis reaction. Higuchi and Senju[8] obtained a smooth change over from fast to slow reaction as the hydrolysis reaction proceeds. Several investigators[5,8] report limiting conversions, as in the case of the hydrolysis of polymethacrylamide[26], whereas others[2] have been able to achieve total hydrolysis of polyacrylamide to polyacrylic acid.

The hydrolysis reaction of amides is essentially the reaction of hydroxyl ions and the amide groups. Electrostatic interactions, which may be neglected in case of monoamides, become serious in the case of polyamides[27]. High polymer reactions are subject to several limitations due to the inherent macromolecular nature of one of the reactants. Changes in solubility characteristics, irregular substitutions, steric hindrances and distribution of the substituents are a few of the special features of macromolecular reactions which are absent in the similar reactions of the corresponding low molecular weight analogues. The carboxyl group resulting from the hydrolysis of the amide is very likely to be in the ionized state, especially in a strong alkaline medium. Thus, when several of the amide groups on the polyacrylamide molecule are already hydrolysed, electrostatic repulsions between the carboxylate ions and the attacking hydroxyl ions are expected to play a very significant part on the reactivity of the amide group surrounded by the already hydrolysed carboxyl groups on the polymer chain. The large decrease in the reactivity of the amide groups at higher extents of reaction and limiting conversions are mainly due to these electrostatic interactions.

The electrostatic repulsions coming into play due to the chain connectivity at higher extents of hydrolysis reaction are expected to decrease the rates of hydrolysis at higher conversions. The faster hydrolysis rates for polyacrylamides as compared to monoamides cannot be explained on the basis of the electrostatic interactions. But such higher rates of hydrolysis have been reported for polyacrylamide by several investigators[5,7]. A mechanism similar to the polyfunctional mechanism has been invoked[7] to explain the higher reactivity of the amide group towards hydrolysis in the case of polyacrylamide as compared to the rates of hydrolysis of monoamides. The attack of a hydroxyl ion is postulated to displace the NH_2 group towards the neighbouring amide group thus increasing its susceptibility to hydrolysis.

I.e. Estimation of extent of hydrolysis from viscosity measurements

Alkaline hydrolysis of polyacrylamide, especially at low dilutions, brings about drastic changes in the dimensions of the macromolecule. The resultant carboxyl groups on the polymer chain are almost totally dissociated at highly alkaline conditions existing during the hydrolysis. The polyelectrolyte chain is several times more expanded over an equivalent non-polar polymer molecule of the same degree of polymerization[28]. Hence large and continuous increase in viscosity is observed during the course of the hydrolysis reaction. During the initial stages of the reaction

(0-25%), the viscosities vary linearly[28] with the extent of hydrolysis reaction.

Small quantities of polyacrylamide (from the same sample used for kinetic studies) were initially hydrolysed to different extents by varying the hydrolysis conditions such as the concentrations of polymer and alkali, temperature, time etc. The resultant polymers were isolated by precipitation and purified by reprecipitation. The extents of hydrolysis of the samples were evaluated by potentiometric titration method. For two of the samples the degrees of hydrolysis were estimated by flame photometry,(estimation of total sodium). The values obtained by both the methods were in good agreement. Intrinsic viscosities of the samples were evaluated in 0.1 N NaOH solutions since 0.1 N NaOH was used for most of the hydrolysis experimentation. The flowtimes were linearly extrapolated to zero alkali contact time to correct for further simultaneous hydrolysis during the viscosity determination. A calibration curve was constructed by using the extents of hydrolysis and intrinsic viscosity data so obtained for the hydrolysed samples. This calibration curve was used to estimate the extent of hydrolysis for evaluating the kinetics.

In several kinetic studies, it has been the practice to measure the viscosity of a single concentration polymer solution and to equate the viscosity to intrinsic viscosity[29], the characteristic property of a totally isolated individual macromolecule. Hence from the point of view of kinetic studies, even the viscosity of the polymer solution at a single concentration as measured in the viscometer, especially at low concentrations, may perhaps be practical and sufficiently accurate to obtain meaningful results. However, the intrinsic viscosity will be a better criterion. Intrinsic viscosities of the partially hydrolysed polyacrylamides during the course of the hydrolysis reaction have been evaluated from the measured viscosities of single concentration solutions.

For low concentration polymer solutions, the different viscosity functions, such as reduced viscosity (η_{sp}/C), inherent viscosity ($\ln\eta_r/C$) and intrinsic viscosity ($[\eta]$) are fairly close to each other. The use of reduced viscosity values, in the place of intrinsic viscosity, results in an overestimate and the use of inherent viscosity, an underestimate in the values obtained for intrinsic viscosity. The average of reduced viscosity and inherent viscosity was used as an estimate of intrinsic viscosity for low concentration (<0.2 g/dl) polymer solutions. However, this method is not practical for higher concentration solutions.

The following method was used to estimate intrinsic viscosities from the observed flowtimes for higher concentration polymer solutions ($0.2 > C > 1.0$ g/dl).

The two relevant viscosity-concentration equations are:

$$\eta_{sp}/C = [\eta] + k' [\eta]^2 C \qquad (1)$$

and

$$\ln\eta_r/C = [\eta] - k'' [\eta]^2 C \qquad (2)$$

The two slope constants, k' and k" are related[30] by:

$$k' + k'' = 0.5 \qquad (3)$$

It has been recently reported that the relationship (3) holds good also in the case of aqueous solutions of polyethylene oxide[31]. In the limited range of data obtained for the partially hydrolysed polyacrylamide samples for the calibration purposes, a value of 0.54 was obtained for (k' + k") instead of 0.5 as indicated by equation (3). Considering the higher uncertainty in the slope constants, it is assumed that relation (3) holds good for the present system as well. The estimates of intrinsic viscosities were obtained from flowtimes in the following way[32]:

Subtracting equation (1) from equation (2) and using equation (3),

$$\eta_{sp}/C - \ln\eta_r/C = (k' + k'')[\eta]^2C$$

$$= \tfrac{1}{2}[\eta]^2C$$

$$\text{or} \qquad [\eta] = \sqrt{\frac{2(\eta_{sp}/C - \ln\eta_r/C)}{C}} \qquad (4)$$

The relationship (4) was used to estimate the intrinsic viscosities of polyacrylamides during hydrolysis for polymer solutions of concentrations in the range 0.4 to 0.9 g/dl. As noted earlier, for lower concentration (< 0.2 g/dl) polymer solutions relationship

$$[\eta] \cong \frac{\eta_{sp}/C + \ln\eta_r/C}{2} \qquad (5)$$

was used.

I.f. Outline of the present investigation

The kinetic studies were carried out in a thermostat controlled to better than ± 0.05°C (usually ± 0.02°C). Most of the experiments have been carried out at 50°C. An Ubbelohde viscometer was mounted in the thermostat. Known concentration aqueous solutions of polymer and alkali were pipetted out into the viscometer to achieve the desired concentrations of polymer and alkali. The larger volume solution was first pipetted and after about 15' for reaching thermal equilibrium, the other solution (alkali or polymer whichever was smaller volume) was pipetted with simultaneous starting of a stopwatch to judge the time of reaction. The solutions were mixed by blowing a gentle stream of air through the capillary arm of the viscometer. After about 10', the flowtimes of the solution were periodically determined. The time of hydrolysis was evaluated as the time of start of viscometer reading plus half the flowtime during that viscosity determination. The intrinsic viscosities were obtained from the flowtimes, using either equation (4) or equation (5), depending upon the polymer concentration in the solution. The extent of hydrolysis was read off from the intrinsic viscosity vs. extent of hydrolysis calibration chart constructed using samples of known extents of hydrolysis. The time and extent of reaction data so obtained were used to obtain the kinetic rate constants for hydrolysis.

The time and extent of reaction are related[33] to the relevant rate constants by:

$$\ln a - \ln(a-x) = k_1 t \qquad (6)$$

$$\frac{2.303}{(a-b)} \log \frac{b(a-x)}{a(b-x)} = k_2 t \qquad (7)$$

and

$$\frac{x}{a(a-x)} = k_2 t \qquad (8)$$

k_1 and k_2 are the first-order and second-order rate constants. a, b are the concentration of the two reactants and x the extent of reaction. In the experiments carried out with excess alkali, the pseudo first-order rate constants were determined by linear plots of ln(a-x) vs. t. Equation (7) was used to deduce the second-order rate constant. In one experiment carried out, the concentrations of both the reactants were almost identical and the second-order rate constant was deduced using equation (8).

CHAPTER-II

EXPERIMENTAL

II.a. Polymerization

Acrylamide monomer used for the polymerization was BDH (England) technical grade, with a minimum assay of 98.5% as per the supplier. Typical specifications for technical grade acrylamide monomer[34] are:

Appearance	white, free flowing crystal
Assay	98% min.
Melting point	84-85°C
Water	0.8% max.
Iron as Fe	15 ppm max.
Colour,20% soln. APHA	50 max.
Water insol.	0.2% max.
Butanol insol.	1.5% max.

Bromate/bromide analysis[35] showed the monomer purity as 99.2% and acrylamide was used without further purification. Polymerization was carried out at 65 ± 1°C in aqueous solution. Distilled water, freshly distilled over alkaline $KMnO_4$ was used as solvent for polymerization. The recipe chosen is given in Table.I. Acrylamide solution ($\sim$ 60% in water) was taken in a clean, 2 litre three-necked, round-bottomed flask mounted in the thermostatic bath. Distilled isopropanol was added. Oxygen free nitrogen was purged through the solution for about 30', before raising the temperature of the bath. The solution was heated to about 60°C and pH of the solution was adjusted to 3.5 with 0.1 N H_2SO_4. Polymerization reaction was initiated when the solution temperature reached about 63°C, using 1% solution

Table-I

Polymerization of Acrylamide

Monomer	48.00 g
Water	760.00 g
Isopropanol	31.56 g (40 ml)
pH of the Solution	3.50
$K_2S_2O_8$ (1% solution in water)	0.10 g
Na_2SO_3 (0.10% solution in water)	0.0022 g
Temperature	65°C
Time	1 hr.
Conversion	91%
$[\eta]$ at 30°C, in water	0.8 dl/g
$\bar{M}_v$	1.36×10^5

of potassium persulphate (BDH, analytical reagent grade) and 0.1% solution of sodium sulphite (anhydrous sodium sulphite, analytical reagent grade, Sarabhai Chemicals). The polymerization was carried out under continuous bubbling of nitrogen at 65 ± 1°C. At the end of polymerization (1 hr.) the solution was transferred to a 5 litre beaker and distilled acetone (twice the volume of polymer solution) was added slowly through a dropping funnel under continuous stirring. The separated polymer was allowed to settle. The supernatent layer was decanted and the polymer was dissolved in distilled water and reprecipitated with acetone. 2 g of potassium iodide (BDH, laboratory reagent grade) dissolved in 2-3 ml water was added just before complete precipitation to improve storage stability[36] during reprecipitation. The polymer was washed several times with acetone and dried in a vacuum oven for 2 hrs. at 60°C. The polymer conversion and yield were 91% and 47.7 g respectively. Intrinsic viscosity of the polymer determined in distilled water at 30°C was 0.8 dl/g, corresponding[37] to a molecular weight of 1.36×10^5.

II.b. Partial hydrolysis

Preliminary experiments were carried out to obtain polyacrylamides with differing degrees of hydrolysis. The conditions finally chosen to give a suitable spread of degrees of hydrolysis are shown in Table-II. One of the hydrolysis experiments (expt.7) is described below as an example.

In a clean 250 ml conical flask, 40 g of 5% polymer

Table-II

Partial hydrolysis of polyacrylamide

(Calibration Sample)

Sr. No.	Polyacrylamide (5% aqueous solution in g)	Alkali (ml of 16% solution)	Hydrolysis		Extent of hydrolysis %		[η](dl/g)	
			Temp. (°C)	Time (min.)	Potentiometric method	Flame photometry	0.1 N NaOH at 50°C	0.1 N NaCl at 30°C
1	40.1	15	65	30	36.80	-	2.05	1.87
2	40.1	12	50	30	28.16	28.28	1.91	1.72
3	39.9	4	60	30	22.19	-	1.75	1.68
4	40.1	10	40	30	17.45	-	1.59	1.46
5	39.9	10	30	60	14.75	-	1.45	1.30
6	40.1	10	30	45	9.60	-	1.18	1.10
7	39.9	6	30	15	6.12	6.02	0.94	0.90

solution (accurate to ± 0.1 g) was taken. The conical flask was clamped in the thermostat set at 30° ± 0.01°C. About 15' were allowed for thermal equilibrium and 6 ml of 16% (w/v) alkali solution were added. Simultaneously a stopwatch was started. The contents were mixed by repeated gentle shaking of the flask. After 15', the polymer was precipitated using distilled ethanol as precipitant and reprecipitated from water solution using ethanol. Approximately 0.25 g KI, as a stabiliser, was incorporated during the reprecipitation step. The polymer was washed 2-3 times with alcohol and then dried in a vacuum oven for 3 hrs. at 60°C. All the polymer samples were powdered and stored in sample-tubes in a desiccator over calcium chloride.

II.c. Degree of hydrolysis of partially hydrolysed polyacrylamides

The degrees of hydrolysis of the polymers were determined by potentiometric titration method[38]. pH of the 1% polymer solution was adjusted to 3.3 with 2 N HCl and back titrated to pH 7.0. A systronics expanded scale pH meter type 331 with standard glass and calomel reference electrode was used.

0.3 g (accurate to ±0.01 g) of the polymer was weighed (x) into a 50 ml beaker and 15 ml of distilled water were added. The beaker was covered and the polymer was allowed to swell overnight. The solution was homogenized next day over a magnetic stirrer and diluted with another 15 ml of water. The solution was continuously stirred and the pH of the solution was adjusted to 3.3 with 2 N HCl and back titrated with carbonate free 0.1 N NaOH(N) to pH 7.0 (V). The above procedure was repeated to determine the blank (V_o) taking polyacrylamide sample instead of partially hydrolysed polyacrylamide. The degree of hydrolysis was calculated using the following expression:

$$\% \text{ degree of hydrolysis} = \frac{(V-V_o)xNxM_1}{x\ x10}$$

where M_1 is the molecular weight of the representative monomer unit.

II.d. Viscosity measurements

Viscosity measurements were carried out with an Ubbelohde suspended-level dilution type viscometer in thermostats, controlled to ± 0.01°C at 30°C and better than ± 0.05°C at 50°C as judged by a Beckman thermometer mounted in the thermostats. The viscometer had a 0.4 mm bore and 12.5 cm length capillary, an efflux volume 4.9 ml and an efflux time of 125.2 ± 0.1 secs. for water at 30°C. Kinetic energy corrections were found negligible and hence no corrections were applied. Polymer solutions were prepared by allowing an accurately weighed sample of the polymer to swell overnight in about 10 ml of the solvent in a 25 ml volumetric flask. The solutions were diluted next day to the graduation mark and homogenized. The efflux times for solvent and solutions were determined accurate to ± 0.1 sec.

Water used as solvent in this study was purified in the following manner. Laboratory distilled water was refluxed over alkaline $KMnO_4$ and distilled in an all glass assembly. The distillate was redistilled with reduced amount of $KMnO_4$. Twice distilled water thus obtained (middle-cut fraction) was used throughout the course of the experimentation. The glass assembly used for distilling water was used only for this purpose to prevent contamination. Distilled water was carefully stored in a stoppered glass container and was used within a week.

Intrinsic viscosity of the polyacrylamide sample was determined in distilled water at 30°C. Polymer solution of about 0.2 g/dl concentration was made in a 25 ml volumetric flask and 10 ml of filtered solution were pipetted out into the clean and dry viscometer clamped in the thermostat maintained at 30°C (± 0.01°C). The solution was allowed to attain thermal equilibrium ($\sim$ 15'). Flowtimes for this concentration solution were recorded thrice and generally last two readings agreed to within 0.1 sec. in almost all cases and average of the last two readings was taken as flowtime for that particular concentration solution. 2 ml of water were added to the solution in the viscometer and a gentle stream of air was blown to mix the solution. After thermal equilibrium ($\sim$ 15'), flowtimes were again recorded as described earlier. Similarly 2 ml, 4 ml and 5 ml of water were added for obtaining solutions of varying concentration and flowtimes were determined by the same method for each concentration solution. The corresponding η_{sp}/C values were calculated as $(t-t_o)/C$ where t and t_o are flowtimes for solution of concentration C (g/dl) and for the solvent respectively. A plot of η_{sp}/C vs. C was constructed. Intrinsic viscosity obtained by linear extrapolation of η_{sp}/C vs. C plot was 0.8 dl/g. The molecular weight of the polymer was estimated as 1.36×10^5, using the relationship $[\eta] = k M_v^a$, where $k = 6.31 \times 10^{-5}$ and $a = 0.8$[37].

Intrinsic viscosities of the partially hydrolysed polyacrylamide samples used as calibration standards were determined in 0.1 N NaCl at 30°, 40° and 60°C in the same way as described above. Five solutions of differing concentrations were used and η_{sp}/C values were linearly extrapolated to zero concentration. The values of the intrinsic viscosities obtained at 30°C are included in Table-II.

Intrinsic viscosities of the partially hydrolysed samples of known degrees of hydrolysis were needed in 0.1 N NaOH at 50°C so that the extent of reaction could be estimated from the efflux times for studying the kinetics. The efflux times for the hydrolysed samples in alkali were observed to continuously increase with time of alkali contact due to further simultaneous hydrolysis. In order to evaluate the required intrinsic viscosities, flowtimes were evaluated for solutions of three concentrations, as a function of alkali contact time. The viscosities at zero alkali contact time were evaluated by linear plot of the efflux time versus time of alkali contact. The viscosity measurements were carried out in the following way. The clean and dry viscometer was mounted in a thermostat, maintained at 50°C and 8 ml of 0.125 N NaOH were pipetted out into the viscometer. The alkali solution was allowed to attain thermal equilibrium (~ 15'). 2 ml of polymer solution (2,1 or 0.5 g/dl to achieve 0.4, 0.2 and 0.1 g/dl polymer concentration respectively) were pipetted out into the viscometer with simultaneous starting of a stopwatch to judge the alkali contact time. The solutions were mixed by a gentle blow of air. For solutions of each concentration five flowtimes were recorded continuously and the corresponding η_{sp}/C values were calculated. The η_{sp}/C values were extrapolated to zero alkali contact time as shown in Fig.1, to obtain corrected values of η_{sp}/C. The values of η_{sp}/C thus obtained, were linearly extrapolated to zero concentration as shown in Fig.2, to obtain intrinsic viscosities of the partially hydrolysed polyacrylamides in 0.1 N NaOH at 50°C.

II.e. Kinetics of alkaline hydrolysis of polyacrylamide

The rate of alkaline hydrolysis of polyacrylamide was followed in a viscometer by continuously determining the flowtimes of the polymer solution, containing requisite alkali and polymer at the desired temperature. The procedure followed was similar to that used for determining intrinsic viscosities of partially hydrolysed polyacrylamides in 0.1 N NaOH. Separate aqueous solutions of polymer and alkali were prepared and mixed in the viscometer. The concentrations of alkali and polymer were such that, the solutions when mixed in the ratio of 4:1 desired concentrations of alkali and

FIG. 1

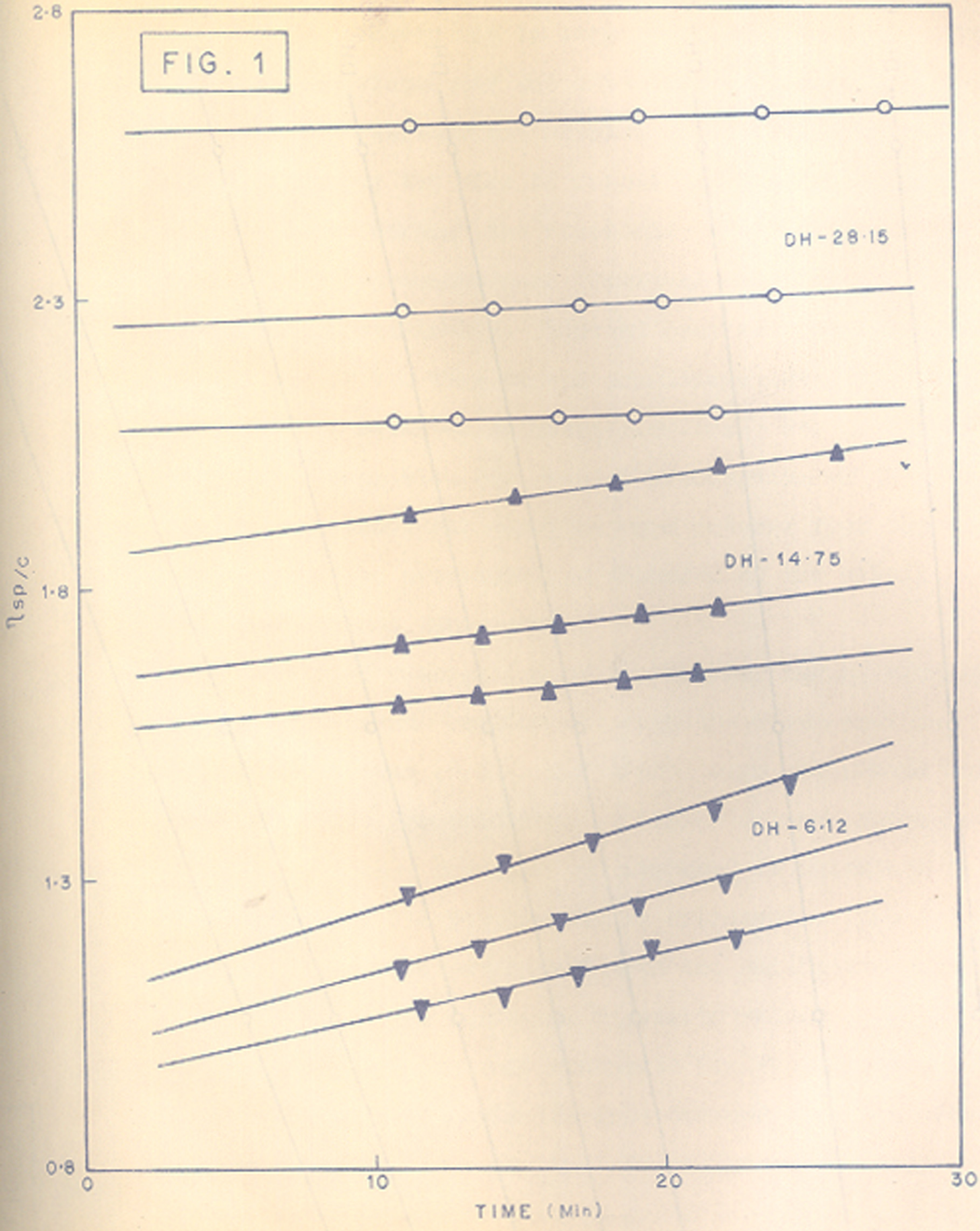
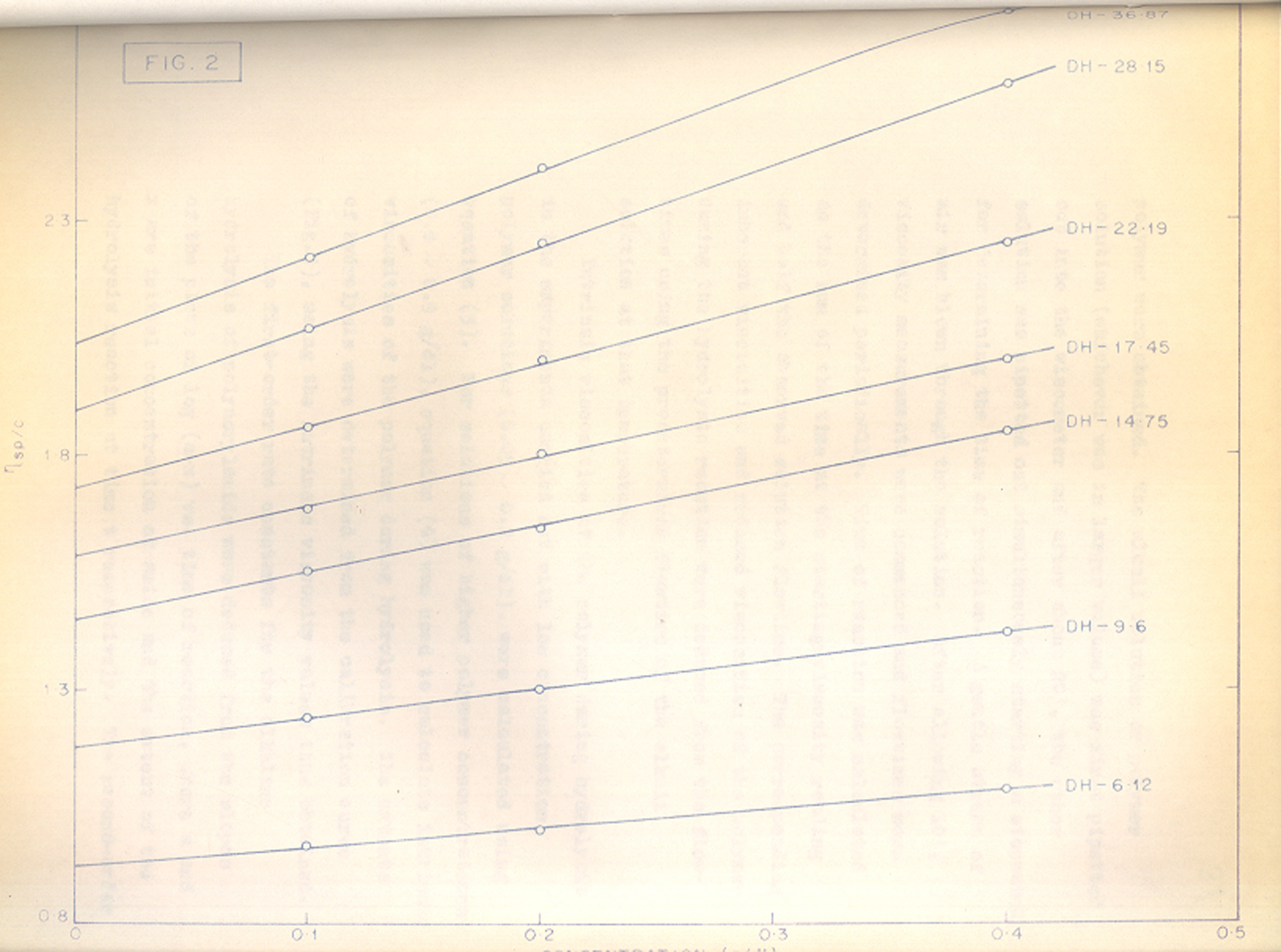


FIG. 2


DH-36·87
DH-28·15
DH-22·19
DH-17·45
DH-14·75
DH-9·6
DH-6·12
$\eta_{sp/c}$
2·3
1·8
1·3
0·8
0
0·1
0·2
0·3
0·4
0·5
CONCENTRATION (g/dl)

polymer were obtained. The alkali solution or polymer solution (whichever was in larger volume) was first pipetted out into the viscometer and after about 20', the other solution was pipetted out simultaneously starting a stopwatch for determining the time of reaction. A gentle stream of air was blown through the solution. After allowing 10', viscosity measurements were commenced and flowtimes were determined periodically. Time of reaction was calculated as the sum of the time at the starting of viscosity reading and half the observed solution flowtime. The corresponding inherent viscosities and reduced viscosities of the polymer during the hydrolysis reaction were deduced from the flowtimes using the predetermined flowtime of the alkali solution at that temperature.

Intrinsic viscosities of the polymer during hydrolysis in the experiments carried out with low concentration polymer solutions (0.05 ~ 0.2 g/dl), were calculated using equation (5). For solutions of higher polymer concentrations (0.4 ~ 0.9 g/dl), equation (4) was used to calculate intrinsic viscosities of the polymer during hydrolysis. The extents of hydrolysis were determined from the calibration curve (Fig.3), using the intrinsic viscosity values thus obtained.

The first-order rate constants for the alkaline hydrolysis of polyacrylamide were deduced from the slopes of the plots of log (a-x) vs. time of reaction, where a and x are initial concentration of amide and the extent of the hydrolysis reaction at time t respectively. The second-order

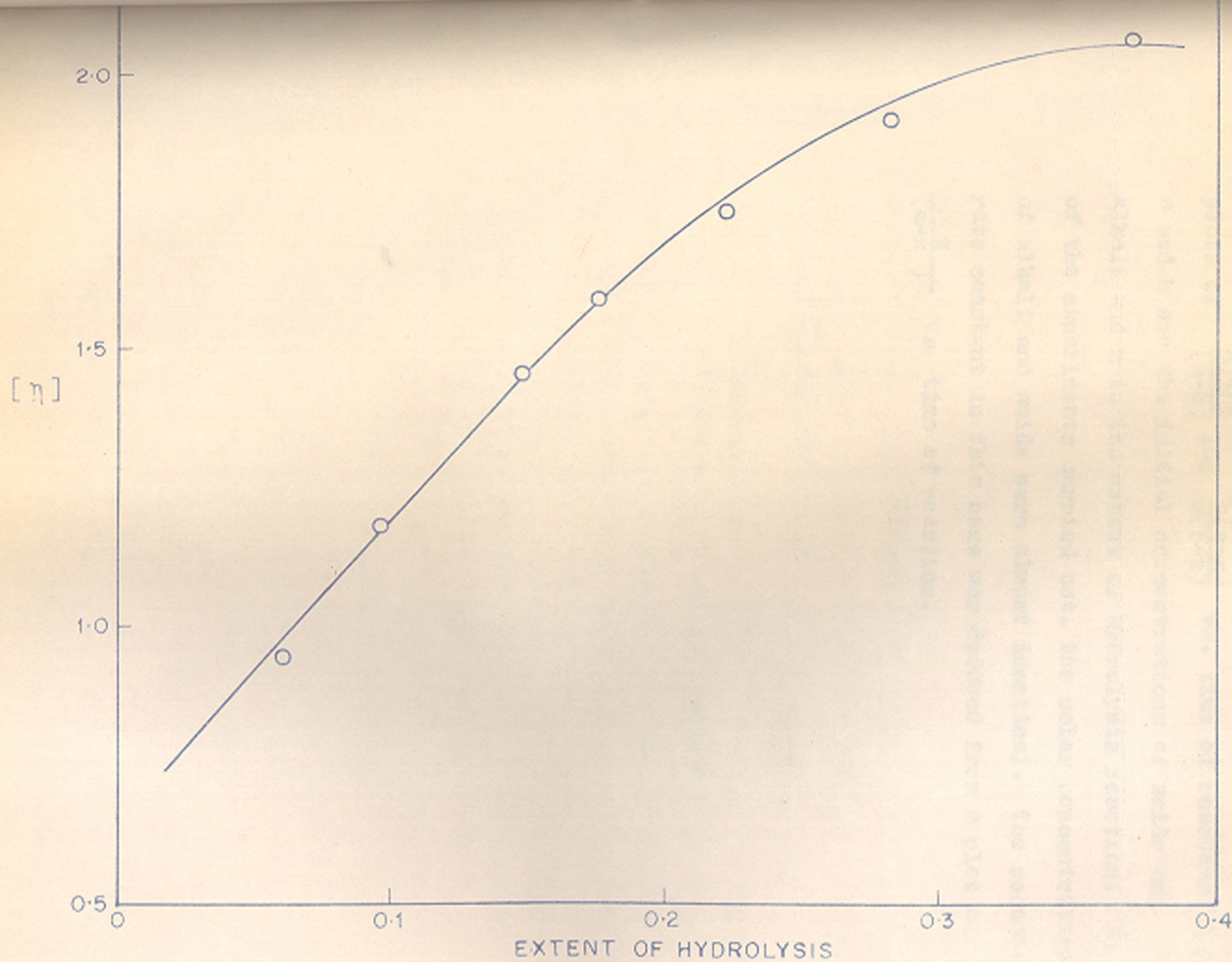


FIG. 3

rate constants were determined from the slopes of the plots of $\frac{2.303}{(a-b)} \log \frac{b(a-x)}{a(b-x)}$ vs. time of reaction, where a and b are the initial concentrations of amide and alkali and x is the extent of hydrolysis reaction. In one of the experiments carried out, the molar concentrations of alkali and amide were almost identical. The second-order rate constant in this case was deduced from a plot of $\frac{x}{(a-x)}$ vs. time of reaction.

CHAPTER-III

RESULTS AND DISCUSSION

III.a. Polymerization

Solution polymerization technique is a convenient method for the polymerization of acrylamide[39]. The advantages are the ease of polymerisation, good polymerization rates, high conversions and reproducible polymerization results. The polymer used in this study was obtained by solution polymerization technique using the recipe given in Table-1 as described in Chapter-II.

The viscosity-average molecular weight of the polymer used in the study is 1.36×10^5. Polyacrylamides used in the study of alkaline hydrolysis by different workers differ widely with respect to their molecular weights. Polymeric reactions are generally carried out in solutions. These reactions are subject to several restrictions which are absent in the reactions of their low molecular weight analogues. Polymeric reactions are characterized by high viscosities of the reaction medium. Changes in solubility characteristics during the reaction, irregular substitutions, substituent distributions, steric hindrances, strong electrostatic interactions etc. are several of the special features of the polymeric reactions coming into play essentially due to chain connectivity and large dimension of one of the reactants. Viscosities of the reaction medium may play a significant role only when the reaction is diffusion controlled and such reactions (and/or stages of the reactions where viscosity determines the course of the reaction) may be expected to be molecular weight dependent. Other factors are expected to be almost independent of molecular weight. This is especially true when the molecular weight of the polymer exceeds the critical molecular weight for segmental overlap to occur (mol.wt. about 50,000 or more). The rates of the reaction such as the rates of alkaline hydrolysis of polyacrylamide are not expected to be greatly molecular weight dependent and a comparison should be permissible between results obtained by different workers, inspite of differing molecular weights of the polymer sample used. The range of the molecular weight of the polymer used in the study was mainly determined on the basis of its suitability for convenient and reliable viscosity measurements.

III.b. Estimation of extent of reaction from viscosities

The alkaline hydrolysis of polyacrylamide brings about large changes in the viscosity of the medium, especially when the hydrolysis is carried out in low concentration polymer solutions. This increase in viscosity is mainly due to the polymer acquiring a polyelectrolyte character as a result of partial hydrolysis. The large and continuous increase in viscosity, was utilized for determining the extent of reaction during the course of the hydrolysis reaction.

Most of the hydrolysis experiments were carried out in 0.1 N NaOH at 50°C. Hence intrinsic viscosities were determined in 0.1 N NaOH at 50°C, for a series of partially hydrolysed polyacrylamides with predetermined extents of hydrolysis. A $[\eta]$ - extent of hydrolysis calibration chart was constructed. The extent of hydrolysis during the hydrolysis experiment for obtaining the rate constants were determined with the help of the calibration chart.

It was observed that the flowtimes of the partially hydrolysed polyacrylamides in 0.1 N NaOH continuously increased during viscosity determination, due to the further simultaneous hydrolysis. Viscosities were determined as a function of alkali contact time for each concentration solution of the partially hydrolysed polyacrylamides. Viscosities corresponding to zero alkali contact time (hence no further hydrolysis and characteristic of the polymer used) were determined by linear extrapolation of the viscosities to zero alkali contact time. Typical data obtained for three samples are shown in Fig.1. It is observed that further hydrolysis during viscosity measurements was negligible in the case of samples of higher degrees of hydrolysis. But it was very severe in the case of samples of low degrees of hydrolysis. The corrections for simultaneous hydrolysis during viscosity determination amounted to 2-32% depending on the extent of hydrolysis of the sample, a higher correction being needed for the samples of low degrees of hydrolysis. The corrected viscosities were extrapolated to zero concentration to obtain intrinsic viscosities of the samples in 0.1 N NaOH at 50°C as shown in Fig.2.

The extents of hydrolysis in the partially hydrolysed polyacrylamides used as calibration standards were determined by potentiometric titration method (Table-II). For two of the samples the extents of hydrolysis were determined by flame photometry (estimation of total Na). The values of the extents of hydrolysis obtained by both the methods are included in Table-II. There is a close agreement between the extents of hydrolysis estimated by the two methods showing that the potentiometric titration method is a reliable technique for determining the extent of hydrolysis in the partially hydrolysed polyacrylamides.

Fig.3 depicts the calibration chart obtained and shows the variation of intrinsic viscosity of partially hydrolysed polyacrylamide at 50°C in 0.1 N NaOH with the extent of hydrolysis reaction. A continuous increase in intrinsic viscosity with the extent of hydrolysis is observed and intrinsic viscosity varies almost linearly with the extent of reaction upto about 25% hydrolysis. Intrinsic viscosity is not very sensitive to the extent of reaction above 30% hydrolysis. Fig.3 was used to estimate the extent of reaction during hydrolysis for determining the kinetic rate constants. The almost linear extent of reaction versus intrinsic viscosity plot (Fig.3) minimizes the uncertainty in the extent of reaction determined during the hydrolysis experiment for evaluating the kinetic rate constants.

III.c. Kinetic measurements

Kinetics of alkaline hydrolysis of polyacrylamides was followed viscometrically. Separate solutions of polymer and alkali were pipetted out to achieve desired concentrations

Table-III

Rate of hydrolysis of polyacrylamide at 50°C

[Polyacrylamide] 0.1 g/dl
[NaOH] 0.1 N
Solvent flowtime 90.2±0.1 sec

Start of viscometer reading 't_o'	Flow time in secs. 't'	Time of reaction ($t_o + t/_2$)	η_r	[η]*	Extent of reaction** (x)	log (a-x)
10' 5"	98.7	10' 54.35"	1.0942	0.92	0.065	$\bar{1}$.9708
20'	100.2	20' 50.10"	1.1109	1.08	0.090	$\bar{1}$.9590
30'	101.4	30' 50.70"	1.1242	1.20	0.110	$\bar{1}$.9494
45'	103.5	45' 51.75"	1.1475	1.42	0.146	$\bar{1}$.9314
60'	104.8	60' 52.40"	1.1619	1.55	0.171	$\bar{1}$.9184
75' 25"	106.3	76' 8.15"	1.1785	1.71	0.204	$\bar{1}$.9010
105'	108.2	105' 54.10"	1.1996	1.90	0.266	$\bar{1}$.8656
145'	109.7	145' 54.85"	1.2162	2.05	-	
175'	110.9	175' 55.45"	1.2295	2.17	-	
235'	112.6	235' 56.30"	1.2483	2.34	-	
295'	113.8	295' 56.90"	1.2616	2.46	-	
355'	114.8	355' 57.40"	1.2727	2.56	-	
475'	116.0	475' 58.00"	1.2860	2.68	-	
595'	116.8	595' 58.40"	1.2949	2.77	-	
715'	117.5	715' 58.75"	1.3027	2.83	-	

* $[\eta] = \dfrac{\eta_{sp}/C + \ln \eta_r/C}{2}$

** obtained from the calibration curve (Fig.3) of polymer and alkali. Larger volume solution was first pipetted out and with the addition of the second solution, the time of hydrolysis was counted to have begun. The procedure of taking the larger aliquot first in the viscometer and mixing the smaller volume of the other solution was followed in every case to minimize temperature in-homogeneity during the initial period of the hydrolysis reaction. From the measured flowtimes, intrinsic viscosities of the polymer were calculated using equation (5) for solutions of low polymer concentration (< 0.2 g/dl). For higher concentration polymer solutions the values of intrinsic viscosities during hydrolysis were calculated using equation (4). The extent of reaction was determined with the help of Fig.3 using the intrinsic viscosities so determined.

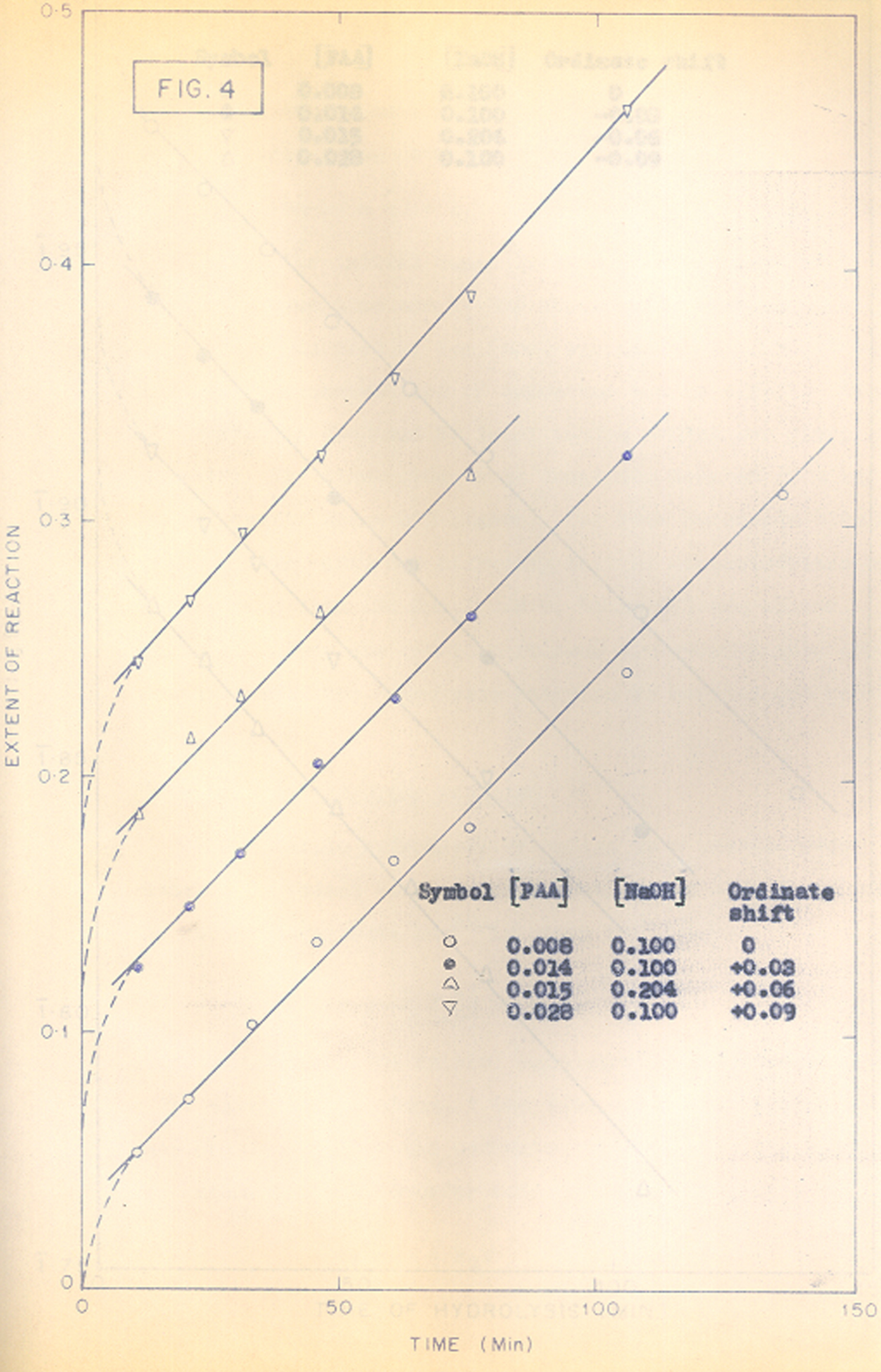
Typical data obtained during the hydrolysis experimentation and the method of calculations are illustrated in Table-III as an example. Column 1 lists the time of the start of the viscosity reading after the second solution (polymer or alkali) was pipetted out into the viscometer. Column 2 records the observed flowtimes. The uncertainty in the determination of flowtimes is generally ± 0.1 sec. The time of reaction used for the evaluation of the kinetic rate constants was determined as the sum of the time at the start of the viscosity reading and half the flow-time during that viscosity determination. These values are listed under column 3 of Table-III. Column 4 shows the values of the relative viscosities and the estimated intrinsic viscosities by using one of the two expressions [equations (4) or (5)] described earlier, are tabulated in column 5. The extents of reaction obtained from the intrinsic viscosities (column 5) with the help of Fig.3 are given in column 6. The data listed in column 3, and 6 were used to determine the relevant (depending on the concentrations of amide and alkali) first-order or second-order rate constants for the hydrolysis reaction. Data beyond 30% hydrolysis was not used due to the insensitivity of the intrinsic viscosity to extent of reaction beyond 30% hydrolysis (Fig.3).

The variation in the flowtime with the extent of hydrolysis is easily seen by the results given in column 2 of Table-III. Usually the difference between any two successive viscosity determination amounted to over one second. The data indicate the convenience and the accuracy with which the kinetics can be evaluated by this method.

III.c(i). First-Order reaction

The rates of hydrolysis of polyacrylamide may be treated as a pseudo first-order reaction under conditions where the concentration of one of the reactants remains almost unchanged during the course of the reaction. Several hydrolysis experiments were carried out with excess alkali. Fig.4 shows the variation of the extent of reaction with time. The data can be represented by straight lines. These plots could be used to calculate the pseudo first-order rate constants for hydrolysis of polyacrylamide. However, a more accurate estimate is possible with the use of the integrated

FIG. 4



Symbol	[PAA]	[NaOH]	Ordinate shift
○	0.008	0.100	0
●	0.014	0.100	+0.03
△	0.015	0.204	+0.06
▽	0.028	0.100	+0.09

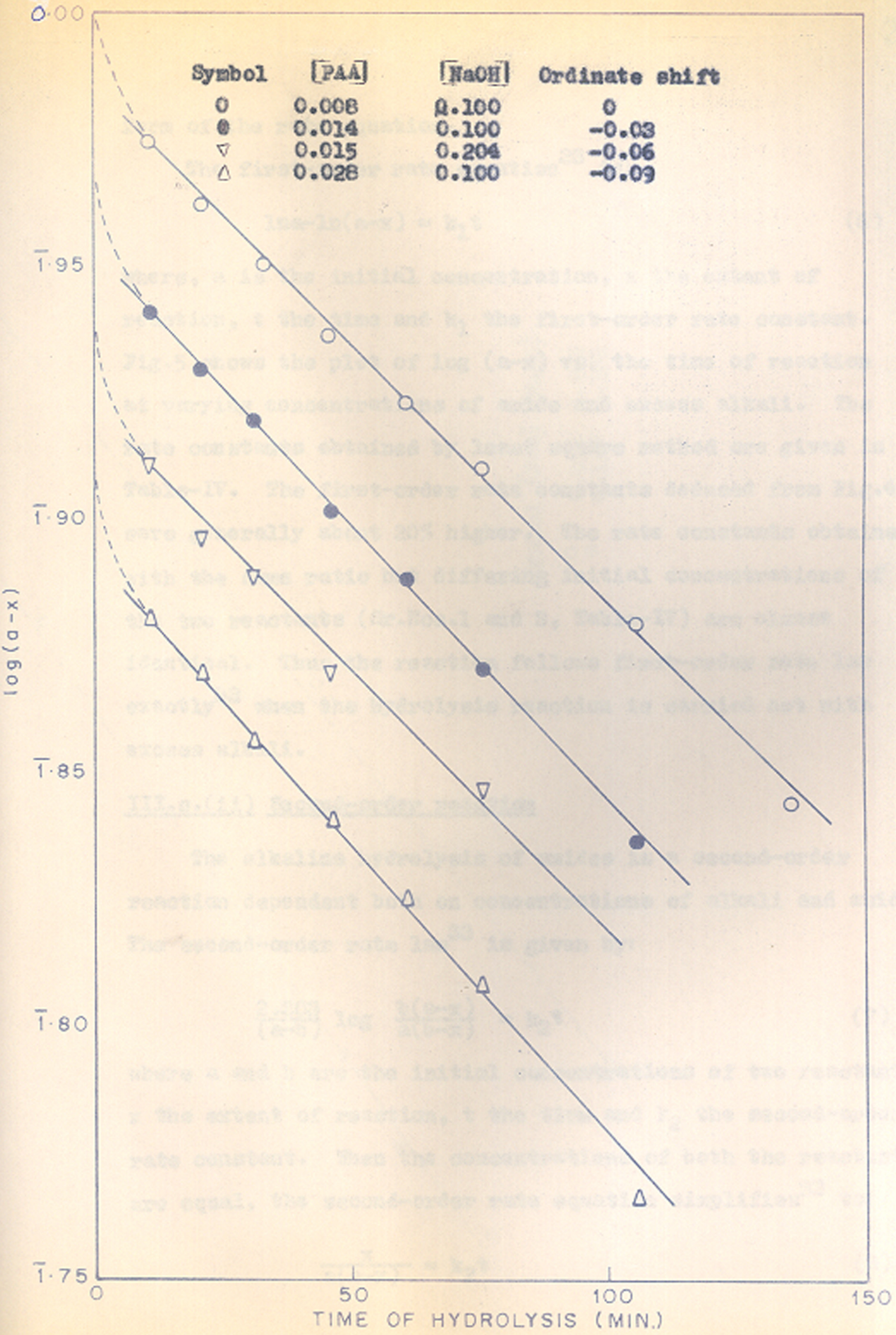

0.00
Symbol [PAA] [NaOH] Ordinate shift
○ 0.008 0.100 0
● 0.014 0.100 -0.03
▽ 0.015 0.204 -0.06
△ 0.028 0.100 -0.09
$\bar{1}$·95
$\bar{1}$·90
$\bar{1}$·85
$\bar{1}$·80
$\bar{1}$·75
log (a-x)
0
50
100
150
TIME OF HYDROLYSIS (MIN.)

FIG 5

form of the rate equation.

The first-order rate equation[33] is:

$$\ln a - \ln(a-x) = k_1 t \qquad (6)$$

where, a is the initial concentration, x the extent of reaction, t the time and k_1 the first-order rate constant. Fig.5 shows the plot of log (a-x) vs. the time of reaction at varying concentrations of amide and excess alkali. The rate constants obtained by least square method are given in Table-IV. The first-order rate constants deduced from Fig.4 were generally about 20% higher. The rate constants obtained with the same ratio but differing initial concentrations of the two reactants (Sr.Nos.1 and 3, Table-IV) are almost identical. Thus the reaction follows first-order rate law exactly[33] when the hydrolysis reaction is carried out with excess alkali.

III.c.(ii) Second-order reaction

The alkaline hydrolysis of amides is a second-order reaction dependent both on concentrations of alkali and amide[5]. The second-order rate law[33] is given by:

$$\frac{2.303}{(a-b)} \log \frac{b(a-x)}{a(b-x)} = k_2 t \qquad (7)$$

where a and b are the initial concentrations of two reactants, x the extent of reaction, t the time and k_2 the second-order rate constant. When the concentrations of both the reactants are equal, the second-order rate equation simplifies[33] to:

$$\frac{x}{a(a-x)} = k_2 t \qquad (8)$$

FIG. 6

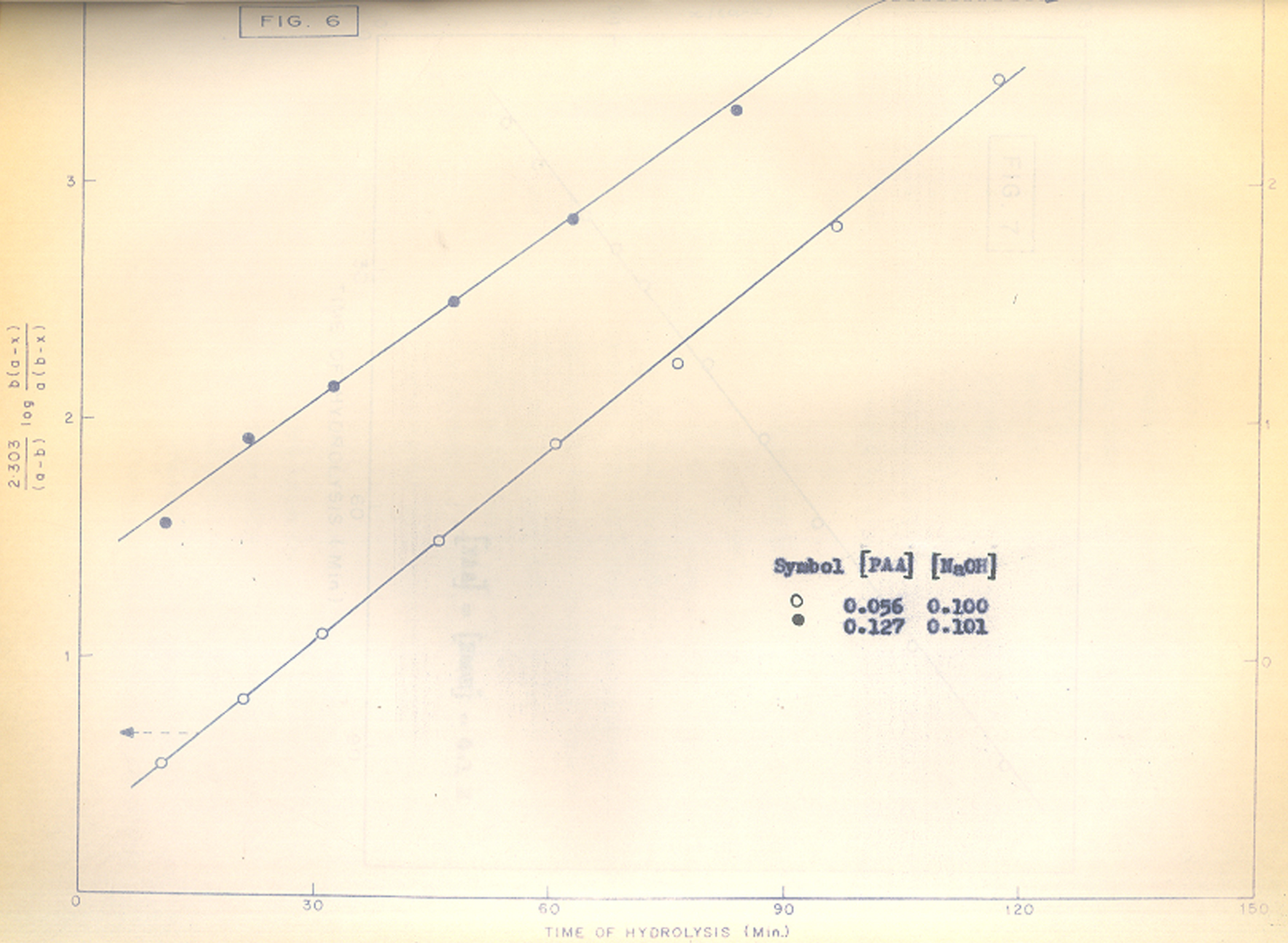
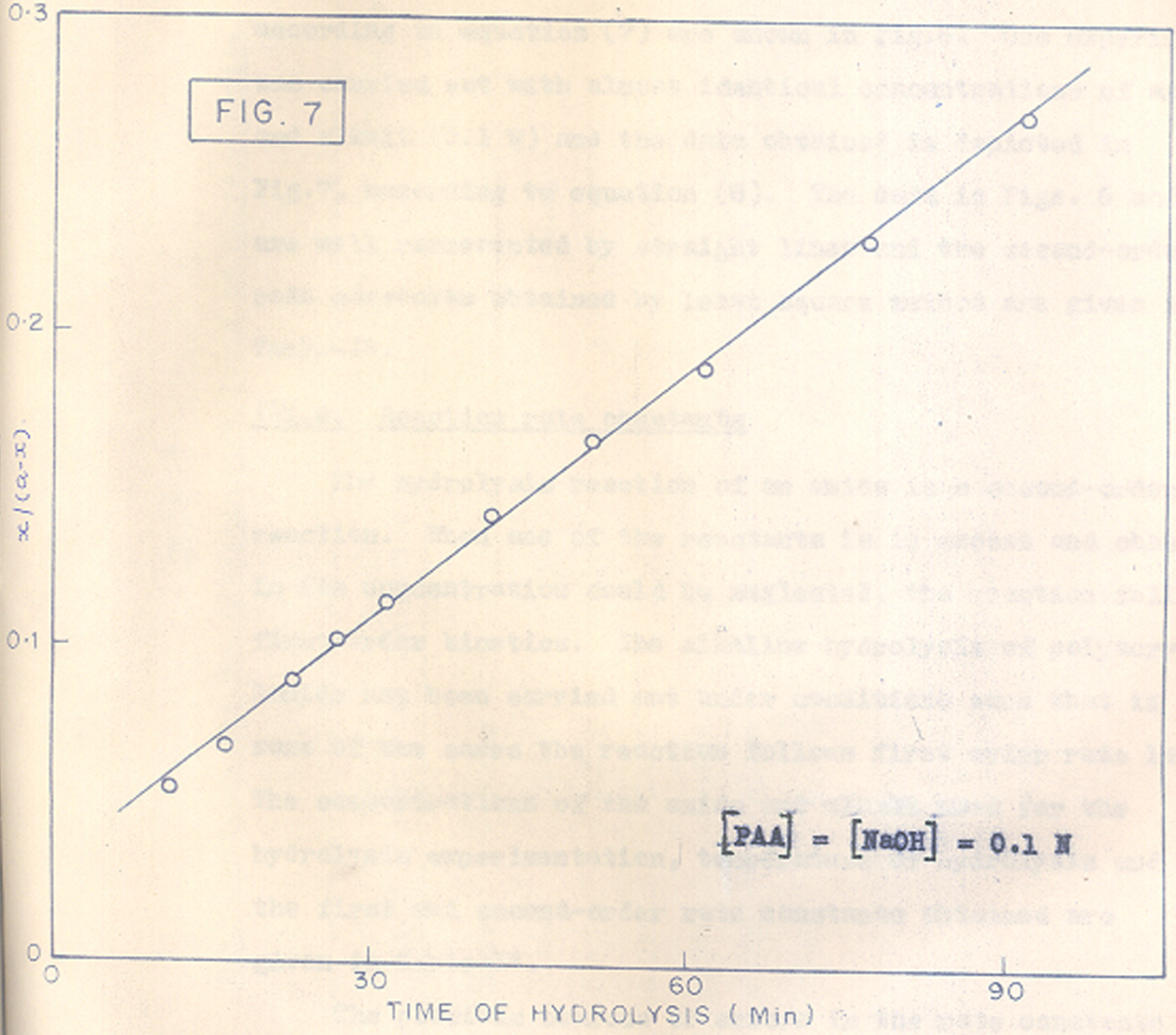

$\frac{2.303}{(a-b)} \log \frac{b(a-x)}{a(b-x)}$
0
1
2
3
0
1
2
0
30
60
90
120
150
TIME OF HYDROLYSIS (Min.)
Symbol [PAA] [NaOH]
○ 0.056 0.100
● 0.127 0.101

FIG. 7



The extent of reaction versus time of reaction plots for two varying concentrations of amide (0.056 and 0.127 moles/lit) with the same concentration of alkali (0.1 N) according to equation (7) are shown in Fig.6. One experiment was carried out with almost identical concentrations of amide and alkali (0.1 N) and the data obtained is depicted in Fig.7, according to equation (8). The data in Figs. 6 and 7 are well represented by straight lines and the second-order rate constants obtained by least square method are given in Table-IV.

III.d. Reaction rate constants

The hydrolysis reaction of an amide is a second-order reaction. When one of the reactants is in excess and changes in its concentration could be neglected, the reaction follows first-order kinetics. The alkaline hydrolysis of polyacrylamide has been carried out under conditions such that in some of the cases the reaction follows first order rate law. The concentrations of the amide and alkali used for the hydrolysis experimentation, temperature of hydrolysis and the first and second-order rate constants obtained are given in Table-IV.

The possible sources of errors in the rate constants obtained are due to the uncertainties in the determination of time and the extent of reaction. The uncertainty in the evaluation of extent of reaction is in turn dependent on the uncertainties in the estimation of intrinsic viscosities from the measured flowtimes as well as the reliability of

Table-IV

Rate constants for the alkaline hydrolysis of polyacrylamide

Sl.No.	PAA (g/dl)	[PAA] moles/lit	[NaOH] moles/lit	Temp. °C.	$k_1 \mathrm{x} 10^{5*} \mathrm{sec}^{-1}$	$k_2 \mathrm{x} 10^{4} \mathrm{dm}^3 \mathrm{mole}^{-1} \mathrm{sec}^{-1*}$
1	0.054	0.008	0.100	50	3.89 ± 0.14**	-
2	0.100	0.014	0.100	50	4.19 ± 0.25**	-
3	0.105	0.015	0.204	50	3.71 ± 0.37**	-
4	0.200	0.028	0.100	50	4.54 ± 0.44**	-
5	0.396	0.056	0.100	50	-	4.50 ± 0.31**
6	0.708	0.100	0.101	50	-	4.45 ± 0.44**
7	0.901	0.127	0.101	50	-	3.96 ± 0.38**

* Obtained by least square method,

** uncertainty corresponds to twice the uncertainty in intrinsic viscosity.

the calibration curve established correlating the extents of reaction to the intrinsic viscosities of the partially hydrolysed polyacrylamides. Of these the errors in the determination of the intrinsic viscosities of the calibration samples and the time of reaction can be neglected. The linearity of the extents of reaction versus intrinsic viscosity plots especially below 25% conversion (Fig.3) minimizes the errors in the estimation of extents of reaction from the intrinsic viscosities. Hence the major source of error in the rate constants determined is the uncertainty in the estimated values of intrinsic viscosities from the observed flowtimes of solutions at single concentration.

As discussed above, the probable uncertainty in the rate constants is due to the extrapolation method used for determining the intrinsic viscosities of the polyacrylamides during reaction from viscosities of solutions at single concentration. The viscosity-concentration data obtained for calibration standards in 0.1 N NaOH at 50°C were used to estimate the uncertainty in the values of intrinsic viscosity used in the evaluation of rate constants. The two methods of extrapolation used viz. equations (4) and (5) resulted in an uncertainty of 1.8 to 5.9% in the values of intrinsic viscosities depending on the concentration of the polymer solutions. The total uncertainty in the rate constants listed in Table-IV are assumed to be twice the uncertainty in the evaluation of intrinsic viscosity by the use of equations (4) or (5).

The reactivity of the amide group towards hydrolysis has been reported to vary with conversion. Moens-Smets[5] observed that at about 35 to 40% hydrolysis, the rate decreases almost by one order of magnitude. Nagase-Sakaguchi[7] observed a decrease in the reactivity at still lower conversions and Higuchi-Senju[8] observed a continuous change of reactivity of the amide group towards hydrolysis as conversion proceeds. The results obtained in this study show a constant reactivity of the amide group towards hydrolysis in the conversion ranges of 5-30%. In this respect the results obtained here are in agreement with those of Moens-Smets[5].

The decrease of reactivity of the amide group towards hydrolysis at high conversions can be accounted for, on the basis of the electrostatic repulsions of the carboxylate ions of the already hydrolysed neighbouring groups and the attacking hydroxyl ion. Several theoretical attempts[40-43] have been made to account for varied reactivity of amide groups depending upon the number (zero, one or two) of the already hydrolysed groups in its neighbourhood. However, calculation of the variation of the reactivity with conversion by the expressions obtained is difficult and the expressions obtained[40-43] are perhaps more meaningful for studying the composition distribution during the course of the hydrolysis reaction.

The reactivity of the amide group in polyacrylamide towards alkaline hydrolysis is constant in the conversion range of 5-30% in confirmity with the results reported by Moens-Smets[5]. However, the extent of reaction versus time plots given in Fig.4 and similar plots obtained at other concentrations of amide and alkali indicate a positive intercept corresponding to about 4-5% hydrolysis at zero time of reaction. Hence the results obtained in the study indicate about 4-5 times higher reactivity of the amide group towards hydrolysis at almost the beginning of the hydrolysis reaction (5%). The neighbouring group effect has been invoked[7] to explain higher reactivity at early stages of the hydrolysis reaction. A mechanism similar to the 'concerted'[44] polyfunctional mechanism has been proposed[7]. Due to considerable segmental overlaps, it is possible that this effect would be noticeable only at the initial stages of the reaction as noticed in this investigation.

As earlier noted, the kinetic constants obtained for the hydrolysis of polyacrylamide should be essentially independent of molecular weight of the polyacrylamide used, and a direct comparison should be possible between the results obtained by different workers. Moens-Smets[5] have reported a second-order rate constant of 6.66×10^{-4} dm^3 $mole^{-1}$ sec^{-1} for the alkaline hydrolysis of polyacrylamide at 55°C. Using the value of 57.39 KJ/mole (13.7 Kcal/mole) for the activation energy reported by Moens-Smets[5], the second-order rate constant for the alkaline hydrolysis of polyacrylamide at 50°C is obtained as 4.8×10^{-4} dm^3 $mole^{-1} sec^{-1}$.

Table-V

Activation energy

Temp. °C	kx10^5 sec^{-1}	-log k	T°(K)	10^3/T
30	1.10	4.96	303.1	3.299
40	2.05	4.69	313.1	3.194
50	4.19	4.38	323.1	3.095
60	7.02	4.15	333.1	3.002

E = 55.9 KJ mole^{-1} (13.35 Kcal mole^{-1})

This is in good agreement with the value of $(4.5\pm0.4)\times10^{-4}$ $dm^3\ mole^{-1}\ sec^{-1}$ obtained in this study for the second-order rate constant for alkaline hydrolysis of polyacrylamide.

III.e. Activation energy

The activation energy represents the energy that the reactant molecules must possess before they can form a transition state. The value of the activation energy is evaluated by determining the rate constants for the reaction at different temperatures. The temperature dependence of the rate constants is represented by the Arrheniaus equation:

$$k = A \exp(-E/_{RT})$$

where A is the pre-exponential or the frequency factor and E the activation energy.

The calibration curve (Fig.3) correlating the intrinsic viscosities to the extents of reaction was constructed by determining intrinsic viscosities of the calibration samples in 0.1 N NaOH at 50°C. This presented the cumbersome necessity of correcting the viscosities obtained for further simultaneous hydrolysis during the course of viscosity measurements. Only an approximate value of activation energy was aimed at in this investigation. Hence it was assumed that the conformation of polyelectrolyte (partially hydrolysed olyacrylamide) is mainly influenced by the ionic str the solution and independent of the nature of species. Viscosity measurements were there

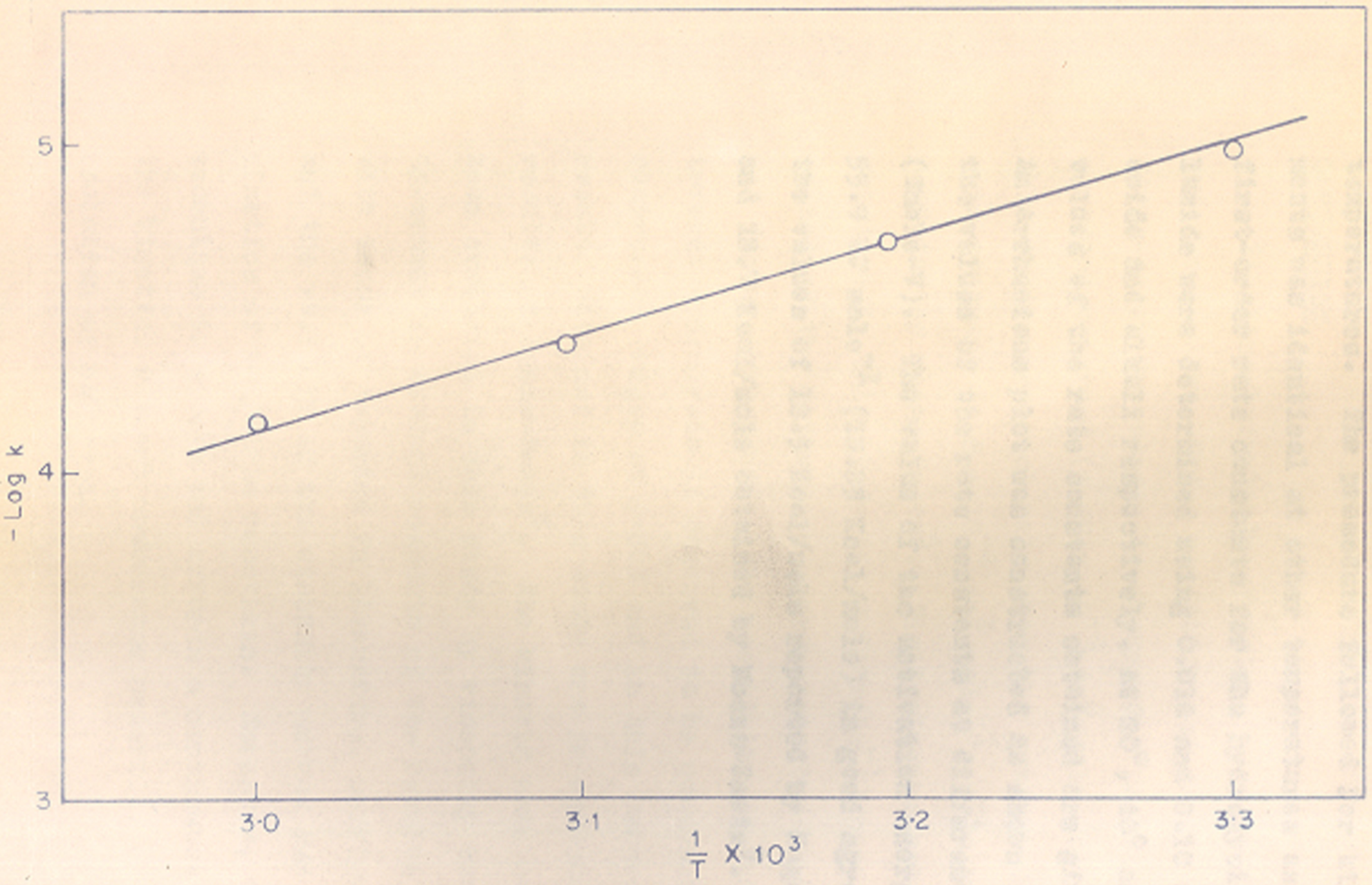


FIG. 8

in 0.1 N NaCl for obtaining calibration curves at other temperatures. The procedure followed for kinetic measurements was identical at other temperatures as well. The first-order rate constants for the hydrolysis of polyacrylamide were determined using 0.014 and 0.10 moles/lit amide and alkali respectively, at 30°, 40° and 60°C. The values of the rate constants obtained are given in Table-V. An Arrhenius plot was constructed as shown in Fig.8, using the values of the rate constants at different temperatures (Table-V). The value of the activation energy obtained is 55.9 KJ $mole^{-1}$ (13.35 Kcal/mole) in good agreement with the values of 13.5 Kcal/mole reported by Nagase-Sakoguchi[7] and 13.7 Kcal/mole obtained by Moens-Smets[5].

CHAPTER-IV

CONCLUSION

Alkaline hydrolysis of polyacrylamide follows second-order rate law. Under conditions of excess alkali pseudo first-order dependence is observed. The second-order rate constant obtained (4.45×10^{-4} dm^3 mole^{-1}sec^{-1}) at 50°C in this study agrees closely with the estimated second-order rate constant (4.8×10^{-4} dm^3 mole^{-1}sec^{-1}) from the data reported by Moens-Smets[5]. Similarly the activation energy obtained in this study (55.9 KJ mole^{-1}) agrees with the values of the activation energy reported by Moens-Smets[5] and Nagase-Sakaguchi[7]. The reactivity of the amide group towards hydrolysis is observed to be constant in the conversion ranges of 5-30% and in this respect also the results obtained in this study are in agreement with the results of Moens-Smets[5]. The kinetic rate constants have been evaluated in this study by viscosity technique. The agreement in several respects of the results obtained, with those of reported in literature, confirms the utility and the validity of the viscosity method for studying the kinetics of polymeric reactions. Moreover, the viscosity technique is simple and affords a continuous scanning of the kinetics without cumbersome necessity of intermittent isolation of polymers.

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