CHAPTER 6

STUDIES ON DILUTE SOLUTION BEHAVIOUR OF PROGRESSIVELY HYDROLYZED POLYACRYLAMIDE IN AQUEOUS SOLUTION

DILUTE SOLUTION BEHAVIOUR OF PROGRESSIVELY HYDROLYZED POLYACRYLAMIDE IN AQUEOUS SOLUTION

6.1 INTRODUCTION AND REVIEW OF PREVIOUS WORKS

In recent years the study of polyelectrolytes has been stimulated by the use of newly available experimental techniques and the introduction of new theoretical concepts. Solutions of polyelectrolyte exhibit a behavior that may differ considerably from that of either uncharged macromolecules or low-molar-mass electrolytes. The origin of this specificity lies in the combination of properties derived from those of long-chain molecules with properties that results from charge-charge interactions. Physical properties of polyelectrolyte solutions have been studied for more than 50 years, but several of them have not yet found a satisfactory theoretical explanation. In many cases a qualitative understanding is available but a quantitative interpretation is still lacking. The study of polyelectrolyte solution has been much more extensively done in aqueous solution than in nonaqueous solution.[1,2] A series of research studies conducted by Fuoss's group in the late 1940s and 1950s demonstrated the general nature of polyelectrolyte behaviour and made an important contribution in establishing major concepts of polyelectrolyte solution.[3-4] Subsequent studies, however, have concentrated on aqueous solution behaviour of polyelectrolyte.[5,6] With respect to the concept of chain expansion due to intramolecular repulsion, scattering techniques were used in addition to classical studies of viscosity.[1,2] The concept of counterion condensation was tested by conductometric measurements of a polyelectrolyte solution, in which the dielectric constant of the solvent was altered and the polyelectrolyte was a copolymer of 4-vinylpyridine and styrene quaternized by n-butyl bromide and the solvent was nitromethane-dioxane mixture covering the dielectric constant from 16.0 to 39.4 (ref. 7). Polyelectrolyte behaviour with respect to solution viscosity was observed for sulphonated polystyrene (PS) ionomers (Na salt) in DMSO, alpha methoxy methanol as well as in DMF (ref.8) This polymer shows similar behavior in acid form also due to dissociation of protons. It was demonstrated by Fuoss and Strauss in one of the first explorations of synthetic polyelectrolyte solution viscosity, that the effect of

charging a polymer chain complicates interpretation of viscosity experiments considerably.[9,10] Unbound rise of reduced viscosity with decreasing concentration for polymethacrylic acid, 2-vinylpyridine-methacrylic acid copolymer, sodium salts of pectin, carboxy methyl cellulose and polyacrylic acid was reported by a number of investigators.[11-14] Yamanaka, Pal and co-workers for dilute solution of sulfonated polystyrene demonstrated very strong shear rate dependence of the reduced viscosity.[15,16] Isoionic dilution method was used by Davis and Russel in their studies on sulfonated polystyrene and the authors found a variation of Huggins constant, K_H from 20 at low ionic strength to 0.8 at maximum ionic strength near 0.1M.[17] Measuring the reduced viscosity as a function of pH Katchalsky and coworkers observed an abrupt increase in reduced viscosity as pH varied above pH 6 for fractions of polymethacrylic acid.[18] Priel and Silberberg observed a complicated dependence of [η] on the mole fraction of ethanol in aqueous solution of polymethacrylic acid and interpreted the results in terms of coil to collapsed chain model.[19] Noda and co-workers observed an increase in the excluded volume parameter as the concentration of added salt decreased for polyacrylic acid and an increase in the apparent excluded volume parameter with the degree of ionization of the polyelectrolyte.[20] McCormick and Johnson[21] have focused their efforts on tailoring macromolecules so that their (three series of N-alkylacrylamide/ acrylamide copolymers containing up to 0.75 mol% of C8, C10, and C12 N-alkylacrylamide monomers) solution viscosity is determined by interplay between intermolecular hydrophobic or ionic interactions of certain chain segments and strong hydration of other segments. Bock and coworkers[22] studied the relationship between the structure and property of hydrophobically associating polymers using a series of copolymers of acrylamide and N-substituted acrylamides and also terpolymers that contain anionically charged carboxyl group. Their results show that hydrophobic association could dominate polymer conformation in solution. Intrinsic viscosities of sodium polystyrene sulfonate (PS) of narrow molecular weight distribution in the absence of coexisting salt were also measured by Ise and coworkers[23]. The possibility of adsorption of the macroions on the glass wall of the viscometer capillary was confirmed to be negligible.

In the polyelectrolyte expansion theory the concentration of low molar mass electrolyte is assumed to be such that electrostatic interactions produce only a perturbation on the inherent dimension of the flexible polyion chain. In a salt free

solution where the electrostatic screening length is controlled by the counter ions of the polyion, by the auto dissociation of water or by dissolved impurities (CO_2), the assumption is not expected to apply. Under these conditions monotonic rise in reduced viscosity is observed and it was suggested that the same results may be found from the chain expansion of the polymer to a rod like conformation. The evidence for this assumption came from an extrapolation of reduced viscosity (η_{red}) using Fuoss equation to obtain apparent intrinsic viscosity. Several groups of authors subsequently demonstrated that the initial rise of reduced viscosity to a maximum during dilution of salt free polyelectrolyte solution is followed by a decrease. It appears that decreasing reduced viscosity at low concentrations following the viscosity maximum can be extrapolated to apparent intrinsic viscosity. It was argued that chains were entangled and decreased in size with concentration in the range where the Fuoss equation was applicable.[24] Similar arguments, based on the homogeneously entangled semi dilute polyelectrolyte solutions, are given by using a scaling approach.[25,26] Some researchers studied the characteristics of polyelectrolyte behaviour using polystyrene based ionomers that had ionic groups randomly distributed along the chain.[27] In their work, the role of intra- and intermolecular interaction on polyelectrolyte behaviour of random ionomer was studied by changing the number of ionic groups per chain, since it was expected that the importance of intramolecular interaction decreased with decreasing number of ionic groups per chain. It was observed that even ionomers with small number of ions per chain showed characteristic polyelectrolyte behaviour. It was suggested that the essential factor causing polyelectrolyte behaviour was intermolecular interactions not intramolecular interactions as is usually assumed in conventional explanations.[28] The use of aqueous polymer solutions in secondary oil recovery has been subject of great interest. It has been reported that[29] more oil may be recoverable by addition of only small quantity of polymers to injection water. The choice of polymer to be added to injection water must take into consideration a number of parameters - the pH of the reservoir, the nature and concentration of salts. The effectiveness of the polymers is related to their molecular weight, the absence of branched chains and solubility in water. The enhanced recovery seems to be a consequence of molecular expansion that results from electrostatic repulsion between the charges carried by the polymer chains. As has already been mentioned that water-soluble synthetic polymers of high molecular weight have given rise to much interest due to their practical application

including the recent application in the preparation of highly viscous solutions in the secondary oil recovery process. One of the widely applied polymers for the above application is carboxyl-modified polyacrylamide (PAM). To understand the role of charged groups on factors that govern the efficiency of PAM in the above use especially in the salt rich waters, a complete molecular characterization is required. In the case of charged PAM the relative dissociation of the ionic groups and the distribution and alignment of the charged dipoles along the chain are expected to play a decisive role on the final state of conformation of the polymer chain.[30] The effect of hydrodynamic field on the viscosity of partially hydrolyzed PAM has been discussed in the literature.[31] The effect of various salt ions on the characteristic of polyelectrolyte in the aqueous solution and the site-binding interaction of salt ions and polymer using Huggins equation has been investigated.[32-36]

Keeping in mind the above, we have investigated the behaviour and properties of unhydrolyzed and hydrolyzed PAM according to the function of factors known to effect the expansion of polyelectrolyte molecules that is, the degree of ionization, polymer concentration and the concentration of added salt. PAM is of interest because it is possible to obtain high molecular weight samples that are easily soluble in water. Moreover, the controlled hydrolysis of PAM samples yield polymers of various charge densities. The effectiveness of the polymer with respect to the above application is related to the extension of the polymer chain. Since the extension of the dissolved chain is related to the charge densities the hydrolysis is thought to be a powerful chemical variable. Moreover, degree of hydrolysis increases salt tolerance of the polyelectrolytes with respect to its solution viscosity. The object of the work is two fold (1) to examine polyelectrolyte behavior of progressively hydrolyzed polyacrylamide with a view to ascertain the degree of polyelectrolytic property shown by an ionomer (LPAM) (2) to examine how the polyelectrolyte behavior is affected on screening of charges of the polyelectrolyte. In view of the above the results of physicochemical studies on dilute solution properties of high carboxyl content (HPAM) and low carboxyl content polyacrylamide (LPAM) in aqueous solution as a function of concentration, pH, added salt and the temperature are reported in this chapter.

In chapter 6 onwards, sometimes unhydrolyzed PAM is also designated as non ionic PAM or NPAM.

6. 2 RESULTS AND DISCUSSION

INTRINSIC VISCOSITY

Factors, which affect the intrinsic viscosity of a polymer, include molecular weight, temperature; shear rate, chain stiffness and topology etc. Values of Huggins coefficient depend on the shear rate, temperature and molecular weight. For expanded neutral polymers in good solvents or for polyelectrolytes, the dependence of $[\eta]$ on the shear rate can be considerable; shear rate extrapolation of the reduced viscosity is needed for quantitative comparison of experiment to theory. The effect of shear rate on the reduced viscosities of dilute polymer solutions in the presence and in the absence of added salts is shown in figures 6.1-6.4. Shear thinning behaviour is observed from the figures. Similar shear thinning behaviour was reported earlier for polystyrenesulphonic acid and its sodium and potassium salts.[37] HPAM and LPAM both are showing shear thinning behavior. The carboxyl content of HPAM is 72 mol% and that of LPAM is 8.2 mol%. Quite obviously the effect of electrical charges should be more for HPAM than that of LPAM. As the concentration of the polymer decreases the effect of shear on solution viscosity increases. On the other hand, as the concentration of added salt increases the polymer solutions become less sensitive to the shear flow. The substantial shear thinning effect of salt-free dilute solutions of hydrolyzed PAM may be attributed to the second order electroviscous effects, which is caused by an electrostatic interaction between macro ions to form an ordered arrangement. For linear macro ions, the flexible nature and orientation of the polymer chains in streaming solvent would also be related to the shear thinning behavior. Concentration dependence of reduced viscosity of HPAM and LPAM in salt free aqueous solutions and in the presence of 0.0125(M) NaCl for HPAM is shown in Figures 6.5-6.10. The reduced viscosity passes through a maximum in reduced viscosity vs. concentration plots. After the maximum point, reduced viscosity decreases continuously on dilution. The sharp increase in reduced viscosity with decreasing concentration can be explained in terms of the expansion of the polymer chain due to progressively enhanced dissociation of the ionisable groups. The more marked dependence of reduced viscosity at lower concentrations seems to be consistent with this explanation. At the maximum point, which is known as overlap concentration, it can be assumed that molecules have reached a final state of expansion and below this concentration the reduced viscosity decreases according to
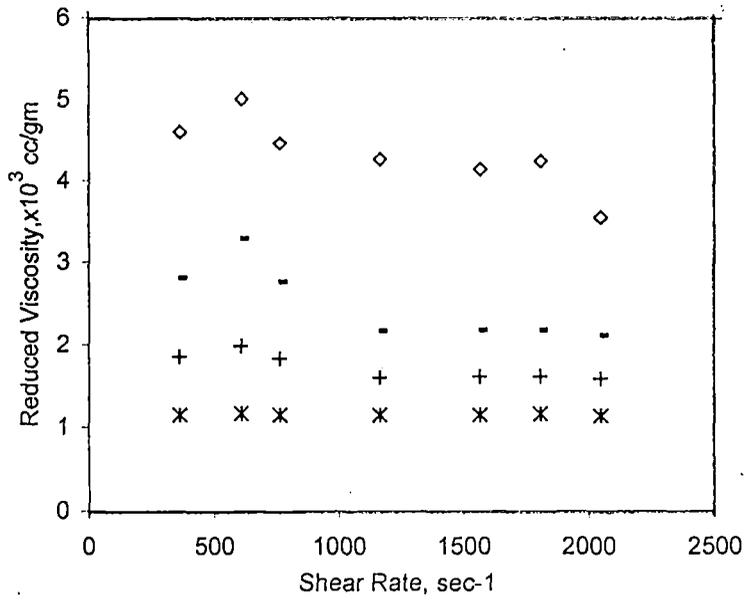
99

Figure:6.1:Reduced viscosity vs. shear rate for LPAM
at different concentrations.

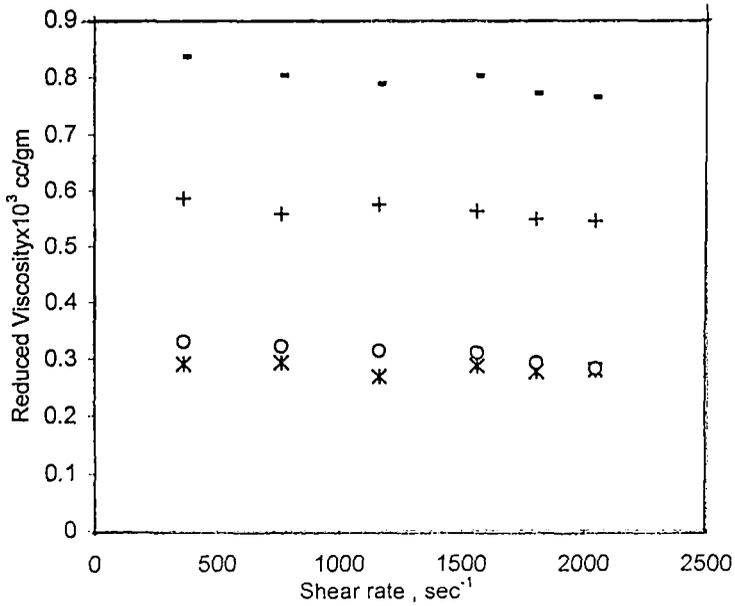✗0.00244gm/cc +0.00122gm/cc −0.0006gm/cc ◇0.0003gm/cc

Figure:6.2:Reduced viscosity vs.shear rate of
HPAM(conc.=0.00061gm/cc) in presence of
various concentration(N) of NaCl.
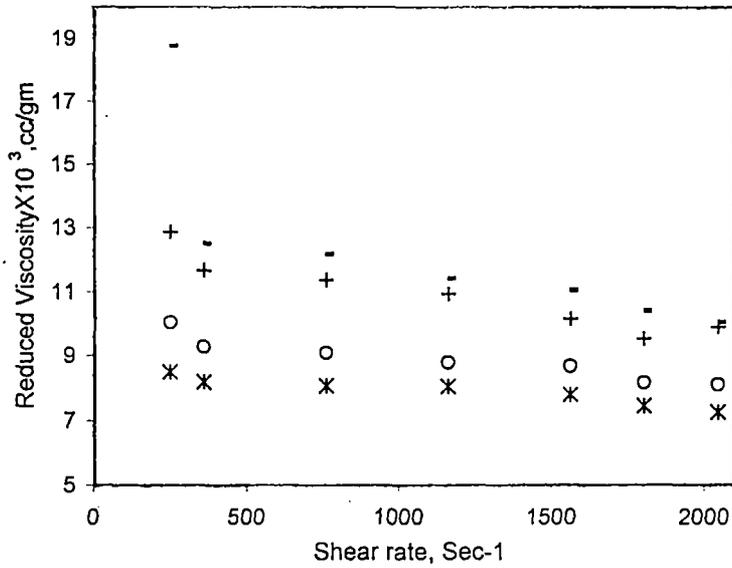
✗0.25(N)NaCl O0.12(N) NaCl +0.05(N)NaCl −0.025(N)NaCl

Figurea;6.3: Reduced viscosity vs.shear rate of HPAM
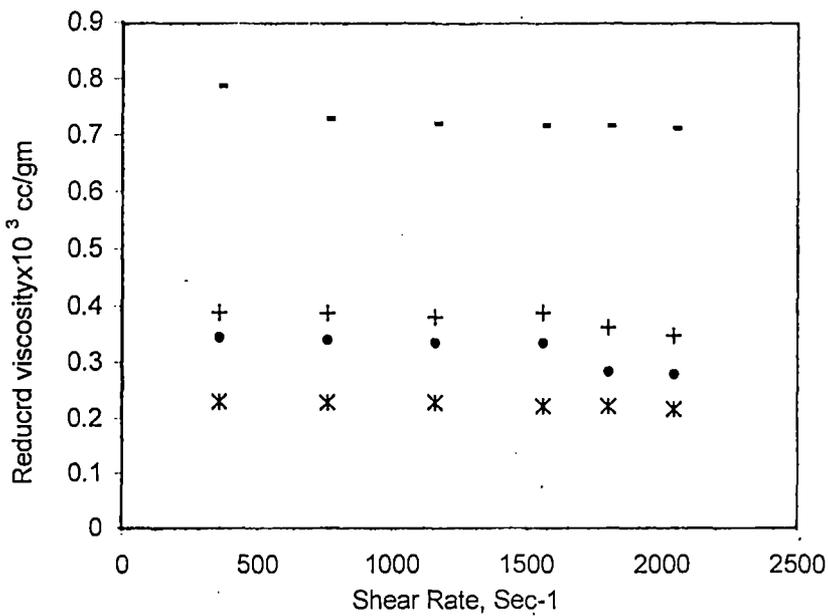at different concentration(gm/cc):Legends are same as
that LPAM.

Figure:6.4: Reduced viscosity vs.shear rate of
LPAM(conc.=0.00061gm/cc) in presence of various
concentration(N) of NaCl.

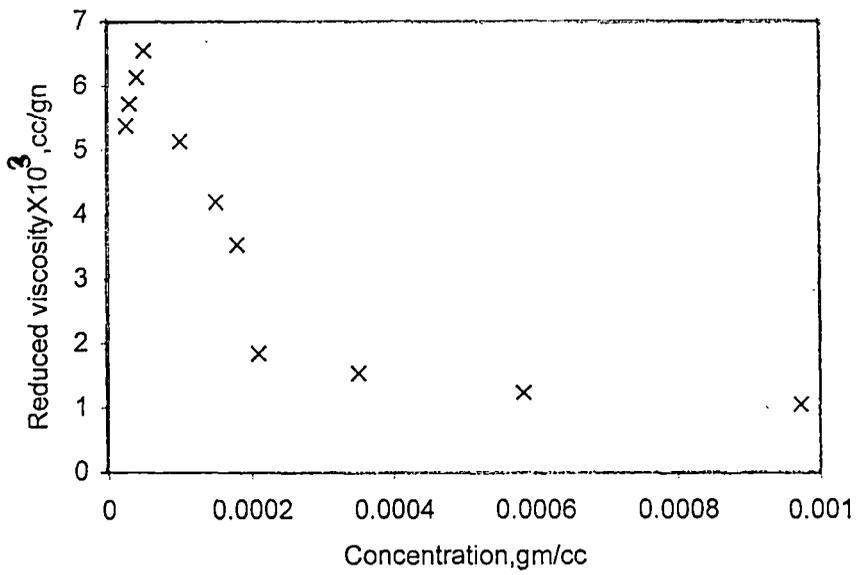✕ 0.1(N)NaCl ● 0.05(N)NaCl + 0.025(N)NaCl ▪ 0.0125(N)NaCl

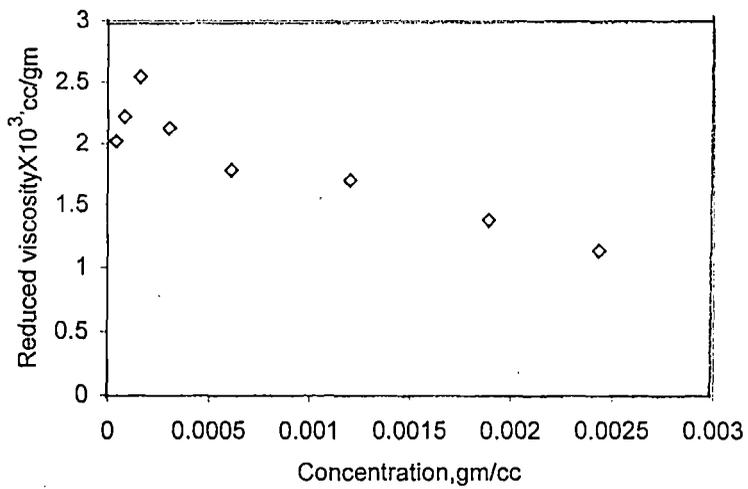Figure:6.5:Reduced viscosity vs. concentration (below and avove overlap concentration) plot for HPAM at 303K.

Figure:6.6:Reduced viscosity vs.concentratiom(below and above overlap concentration) plot for HPAM in presence of 0.0125(N) NaCl at 303K.
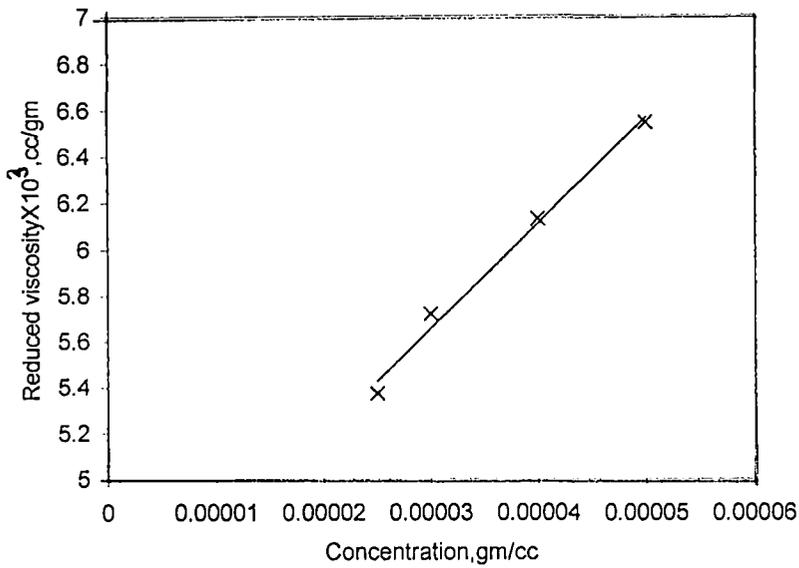
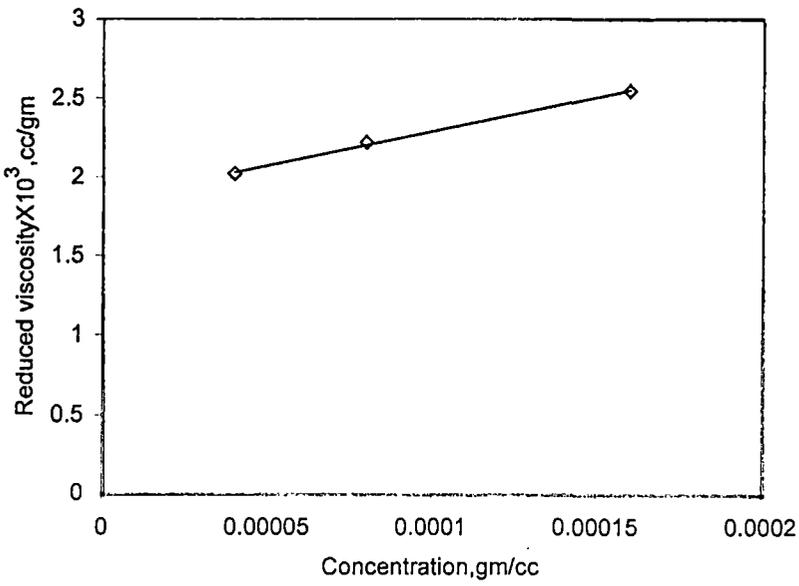Figure:6.7:Reduced viscosity vs concentration(below overlap concentration) plot for HPAM.

Figure:6.8:Reduced viscosity vs. concentration (below overlap concentration) plot for HPAM in presence of 0.0125(N) NaCl.
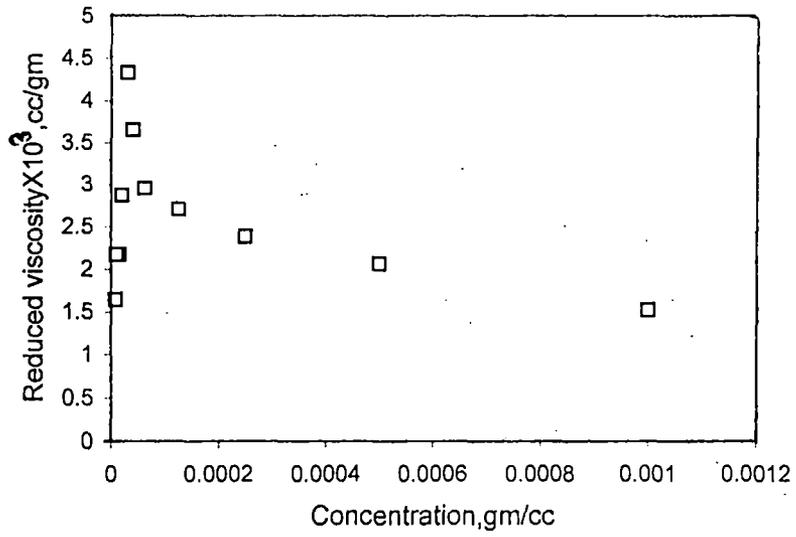
Figure:6.9: Reduced viscosity vs. concentration(below and above overlap concentratiopn) plot for LPAM.
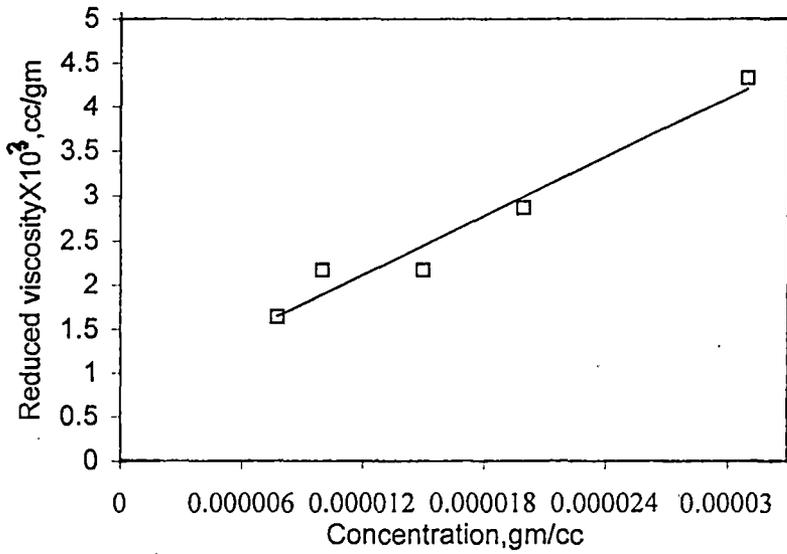

Figure:6.10: Reduced viscosity vs. concentration(below overlap concentration) for LPAM at 303K.

Huggins equation as has already been mentioned in chapter 5. The overlap concentration (C*) depends on the added salt concentration and on the ion content of the polymer. The magnitude of the reduced viscosity at the maximum decreases when salt concentration increases and the ion content of the polymer decreases. This behavior may be attributed to the electrostatic long-range interactions above the overlap concentration of the polymer. The C* values of HPAM and LPAM are found to be 5.0×10^{-5} and 3.0×10^{-5} g/ml respectively. The overlap concentration of LPAM in the presence of 0.0125M NaCl and above is not detectable but for HPAM it is 1.6×10^{-4} in presence of 0.0125M NaCl. This value of overlap concentration is substantially higher than that in the absence of salt. At lower concentration regions (C < C*), the reduced viscosity decreases linearly with dilution and the extrapolation to zero concentration yields the intrinsic viscosity $[\eta]$.[38] Hydrolyzed PAMs exhibit higher reduced viscosity than their neutral counterpart.

The effect of NaCl concentration on the shear corrected reduced viscosity of LPAM and HPAM is also examined .The effect of various NaCl concentrations ranging from 0.20 to 0.0125M on the reduced viscosity of HPAM and LPAM is illustrated in figure 6.11. A significant decrease in reduced viscosity apparently occurred with an increase of NaCl concentrations. Linear extrapolation of reduced viscosity to zero polymer concentration, which is normally done to determine intrinsic viscosity for non-ionic polymers, could not be applied in the present system because of the deviation from linearity. However, at high concentration of NaCl, 0.1M for HPAM and 0.05M for LPAM, a simple linear extrapolation is possible for reduced viscosity – concentration linearity due to nonpolyelectrolytic nature of the polymers under this condition. Addition of NaCl to the polymer solution increases the ionic strength of the solution outside the polymer coil relative to that of inside and also reduces the thickness of the bound layer. As a result, contraction of the polymer chain takes place. When the polymer solution is diluted in presence of a low but fixed NaCl concentration the overall ionic strength decreases. This decrease in overall ionic strength results in an increase in the distance over which electrostatic interaction can be manifested. This causes an increase in intermolecular interactions and the expansion of the polymer chain occurs. On the other hand, the decrease in zero shear reduced viscosity with polymer concentration at higher concentration of NaCl may be ascribed to the complete screening of the electrostatic potential around the bound charges resulting in the manifestation of nonpolyelectrolytic behaviour.

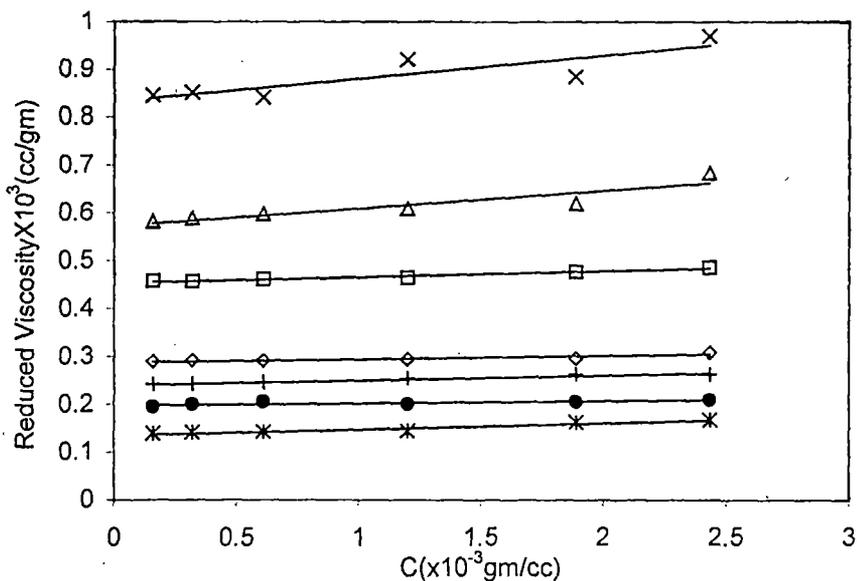*Figure:6.11* :Reduced Viscosity vs. Concentration plot for
HPAM and LPAM in presence various concentration of NaCl.

◇0.2(N),HPAM ☐0.1(N),HPAM △0.05(N),HPAM
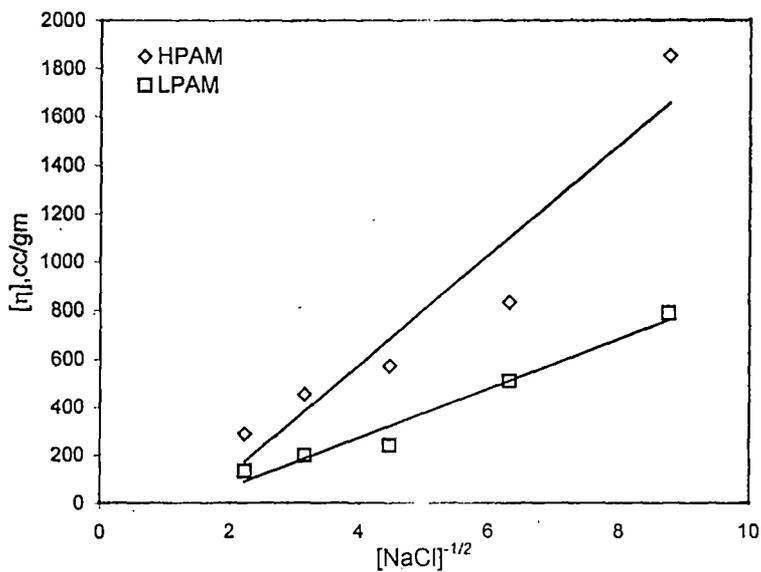
✕0.025(N),HPAM ✳0.1(N),LPAM ●0.05(N),LPAM

Figure:6.12 :Intrinsic viscosity of carboxyl modified
polyacrylamide as a function of NaCl concentration.

HPAM requires more NaCl than LPAM for the screening of bound charges due to presence of higher numbers of carboxyl sites per polymer chain. It may be recalled that the number of carboxyl sites are 8.2 and 72 mole% for LPAM and HPAM respectively. Intrinsic viscosities of HPAM and LPAM in salt free solution and in the presence of various amount of NaCl are shown in the Table-6.1. The above concept of chain contraction of the anionic polymers in presence of NaCl is clear from the presented data. A plot of intrinsic viscosity vs. $C_{NaCl}^{-1/2}$ for both the polymers is presented in figure-6.12. This linear behavior is typical of polyelectrolytes. In the presence of added electrolytes, charge-charge repulsions between the anionic sites are shielded, leading to a decrease in the hydrodynamic volume because the polymer coils assume less extended conformation. These results have demonstrated that the viscosity behavior of a random ionomer (LPAM) is basically similar to that of a polyelectrolyte in aqueous solution. The above observation that even ionomer (LPAM) with small ion content show characteristic polyelectrolyte behavior is important. The chain expansion due to intramolecular electrostatic repulsion, which is used to explain the observed increase in reduced viscosity with concentration, may not necessarily be sufficient to cause a marked increase in viscosity at low polymer concentration for LPAM. In this context it may be argued that there is still a possibility that some polymer chains may have larger number of ionic groups in random ionomers and may lead to some chain expansion due to mutual repulsion of like charges resulting in an increase in viscosity.

Table 6.1 Intrinsic Viscosity of hydrolyzed PAM in presence of various concentrations of NaCl.

Conc. of NaCl (M)	HPAM, $[\eta]$, cc.g^{-1}	LPAM, $[\eta]$, cc.g^{-1}
0.2000	287	123
0.1000	452	134
0.0500	571	197
0.0250	830	239
0.0125	1853	511

EFFECT OF pH

Since hydrolyzed PAMs behave as polyelectrolytes, the effect of pH on the reduced viscosity should be important. The results of our investigation on the reduced viscosity of carboxyl modified PAMs at different pH are shown in figure 6.13-6.14 (Only a few representative concentrations of each PAM are shown in figures). For LPAM, the reduced viscosity increases with pH and it reaches its maximum value at pH 6 and decreases at higher pH. However, for HPAM, although similar trend in reduced viscosity vs pH plot is observed, reduced viscosity is found to be maximum at pH 9. At low pH when degree of ionization is small and the repulsive interaction between undissociated carboxyl and amide groups is absent an impermeable hyper-coiled conformation of the polymer chain results. On the other hand when the pH is increased overall negative charge increases due to higher degree of ionization. As a consequence polymer chain experiences more inter-unit repulsion resulting in an extended rod like structure. In the case of LPAM, ionization is almost complete (detail in next section) at pH 6.0 and it shows highest reduced viscosity at this pH. Similarly, HPAM also exhibits maxima in its reduced viscosity vs. pH plot at pH 9.0, where the ionization of the carboxyl sites are almost complete. After complete dissociation of ionizable groups, reduced viscosity decreases with pH due to shielding of the charge repulsion between charged groups of the LPAM chains. In the case of HPAM, however, this shielding is not apparent in the presence of larger number of charged groups in the chain. Similar observation has also been reported previously in the studies performed on fractions of poly methacrylic acid over a concentration range of 2 to 17 mg/ml[18].

VOLUME RELATED PARAMETER

The volume related parameter (V_E) is a function of temperature and is a measure of volume of the solvated polymer molecules. Viscosity values of LPAM and HPAM are used to calculate the volume related parameter (V_E) of the polymer. As has been mentioned recently, V_E can be used to determine the shape of protein molecules and some acrylate copolymers[39] in solutions. V_E is obtained by plotting Y against C (concentration of polymer), where

$$Y = (\eta_r^{0.5} - 1)/C \, (1.35 \, \eta_r^{0.5} - 0.1) \qquad\qquad 1$$
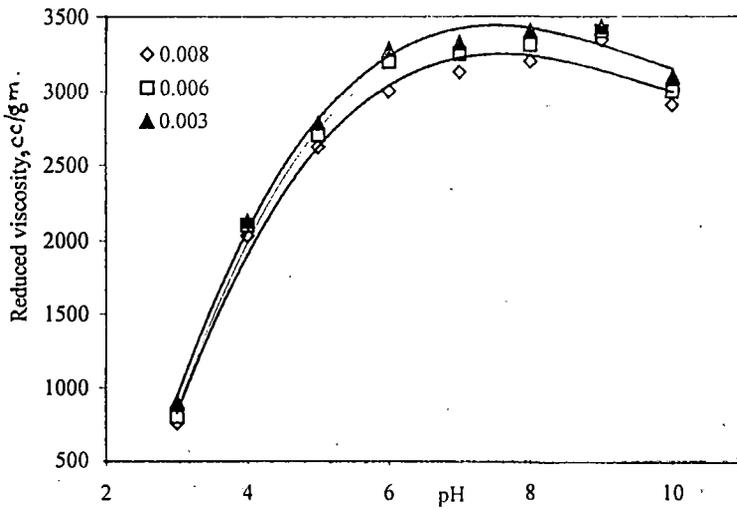
Figure:6.13 :pH vs. reduced viscosity for HPAM at different of polymer concentration (gm/ml).
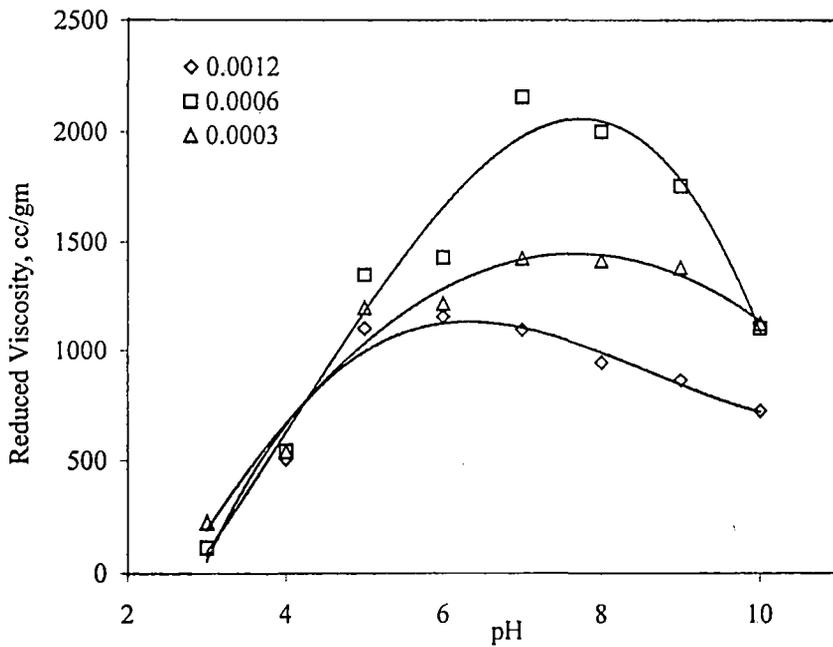

Figure:6.14:pH vs. reduced viscosity for LPAM at different concentrations (gm/ml) of polymer.

(here η_r is relative viscosity). The plot is linear and when it is extrapolated to C=0 the intercept yielded V_E as

$$Lt_{C \to 0} Y = V_E. \qquad\qquad 2$$

Plots are shown in the figure 6.15-6.16. From table 6.2 it is seen that with an increase in salt concentration the volume related parameter of LPAM as well as HPAM molecules decreases. This result is expected from their intrinsic viscosity data. Shape factor values of LPAM suggest that polymer molecules are of rigid sphere configuration in presence of low concentration of added salt. On the other hand, HPAM molecules have the tendency of attaining a shape other than spherical in such a solution. Both the polymer molecules, however, assume spherical shape in presence of higher concentration of salt.

Table 6.2 Shape factor and volume related parameter for hydrolyzed PAM in presence of various concentrations of NaCl.

NaCl (N)	HPAM		LPAM	
	$V_E(dl.g^{-1})$	ν	$V_E(dl.g^{-1})$	ν
0.2000	111	2.58	48	2.56
0.1000	153	2.95	53	2.53
0.0500	159	3.59	78	2.52
0.0250	294	2.82	93	2.57
0.0125	-	-	181	2.82

POTENTIOMETRIC MEASUREMENTS

Values of dissociation constant (pK$_a$) were calculated using Henderson-Hasselbalch equation [40] (eq. 3) .The mole % ionic character of the polymers was found to be 72 and 8.2 for HPAM and LPAM respectively.

$$pK_a = pH - \log \alpha/1-\alpha \qquad\qquad 3$$

where α is degree of ionization of the polymer sites. Plots of pH vs. log $\alpha/1-\alpha$ (figure6.17) are made to determine n value (equation 4), which measures the
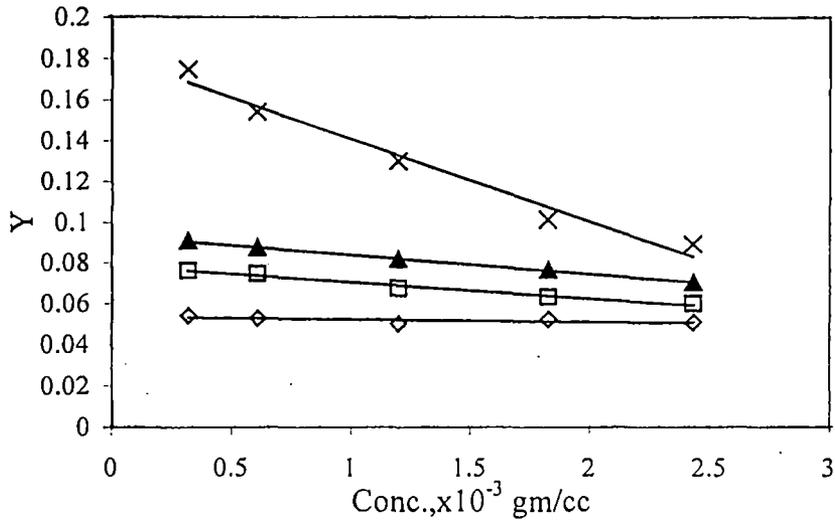
Figure:6.15: Y vs. Conc. for LPAM in presence of various concentration of NaCl.

◇ 0.1000(N)   □ 0.0500(N)   ▲ 0.0250(N)   ✕ 0.0125(N)
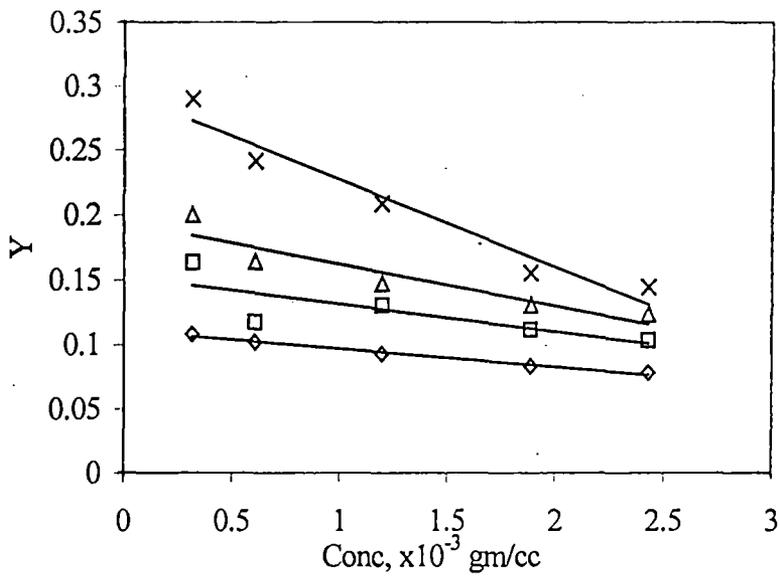

Figure:6.16 :Y vs. conc. for HPAM in presence of various conc. of NaCl.

◇ 0.2000(N)   □ 0.1000(N)   △ 0.0500(N)   ✕ 0.0250(N)

average electrostatic repulsion between charges on the chain according to the modified Henderson-Hasselbalch equation

$$pH = pK' + n \log \alpha/1-\alpha.$$
<div style="text-align:right">4</div>

Calculated values of α, pK_a, pK' and n are given in the table 6.3. In water, both pK' and n are higher for HPAM (5.78 and 2.08 respectively) than that of LPAM (4.96 and 1.33 respectively). This is a result of greater charge-charge repulsion due to higher charge density along the chain of HPAM. The increased electrostatic repulsion with increasing carboxyl content causes decreased stability of ionic groups, thereby raising the pK_a value[40].

Table 6.3 Acid strength (pKa) and degree of dissociation of hydrolyzed PAM.

HPAM					LPAM				
pH	α	n	pKa	pK'	pH	α	n	pKa	pK'
4.18	0.143		4.96		3.7	9.33		4.68	
4.86	0.286		5.26		3.9	16.0		4.62	
5.53	0.428		5.65		4.3	3.30		4.60	
6.11	0.571	2.08	5.98	5.78	4.6	46.6	1.33	4.65	4.96
6.69	0.714		6.29		5.0	62.66		4.77	
7.32	0.857		6.54		5.6	77.33		5.06	
					6.6	92.0		5.54	

The pK' values in salt free solution show a greater conformational changes. At low degree of dissociation where there is little charge-charge repulsion, the polymers appear to be in a compact, random coil conformation. As the degree of dissociation increases, the repulsion between charges increases and the conformation of the chain changes to an extended almost rod like molecule with maximum size coming at $\alpha =1$.
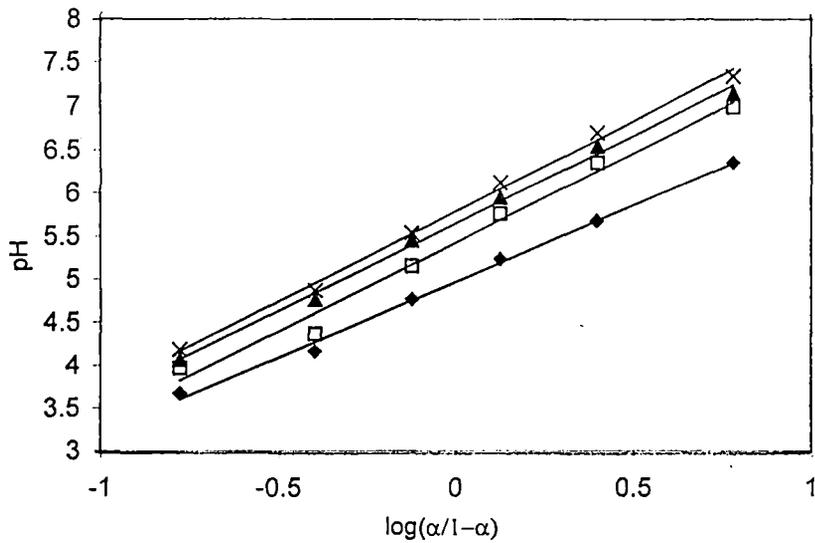
Figure 6.17:Plot of pH vs. log ($\alpha/1-\alpha$) for HPAM in presence of various concentration of KCL.
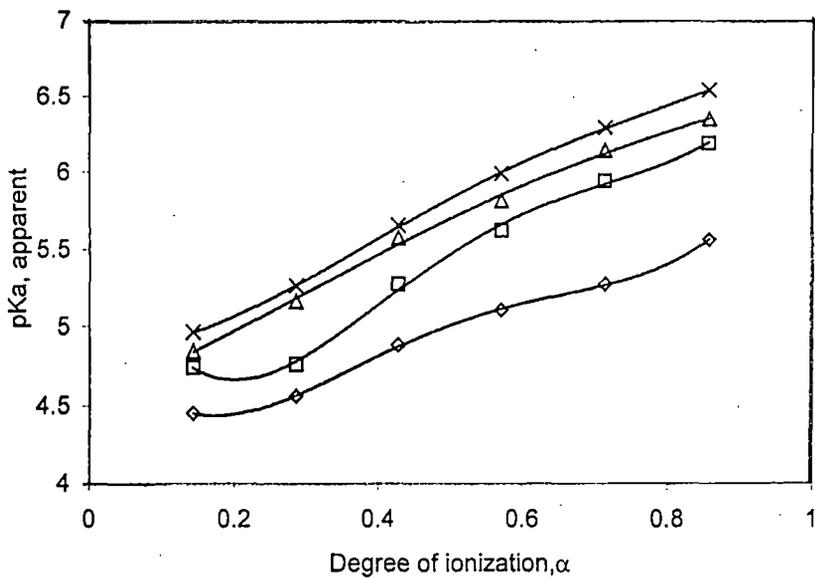
◆ 0.1(N)KCl □ 0.01(N)KCl ▲ 0.001(N)KCl ✕ Pure water

Figure:6.18:Potentiometric titration of HPAM in presence of various concentration of KCl; pKa vs.α

◇ 0.1(N)KCl □ 0.01(N)KCl △ 0.001(N)KCl ✕ Pure water.

Table 6.4 Acid strength (pKa) of hydrolyzed PAM in presence of various concentrations of added salt.

System	pK'	n
Pure Water	5.78	2.08
0.001(N) KCL	5.64	2.06
0.010(N) KCl	5.42	2.02
0.100(N) KCl	4.97	1.76

To investigate the effect of added electrolyte on the chain conformation of the polymers, potentiometric titration were also performed in presence of various concentration of KCl in aqueous solution. From the table 6.4 it is seen that as the electrolyte concentration increases pK' values as well as the n decrease. This may be explained by the slight acidity of the KCl solution and the greater stability of the anionic groups of the polymer chain caused by association with potassium cation. Furthermore, the polymer chains are much more tightly coiled in an electrolyte solution and thus enhancing the possibility of H-bond formation between the carboxylate groups and acrylamide units in the chain due to their closer proximity. The pK' vs. α curves in figure 6.18 for various concentration of KCl demonstrate a flatter profile for higher concentration of KCl than in water or at lower concentration of KCl due to removal of charge-charge effects in the salt solutions.

CONDUCTOMETRIC MEASUREMENTS

To gain insight on the concepts of counterion condensation, which have been used to attribute the results of viscometric and potentiometric measurements, conductometric measurements were also performed. Manning theory has played a leading role in developing experimental researches on solution properties of polyelectrolytes. According to this theory the equivalent conductivity (Λ) of a polyelectrolyte solution in the absence of added salt is given by[41-47]

$$\Lambda = f (\lambda_c^0 + \lambda_p) \qquad\qquad 5$$

where f is the free fraction of counter ion, λ_c^0 is the equivalent conductance of the counter ion in pure solvent and λ_p is the equivalent conductance of the polyion

species in the solution. In the above equation free fraction of counterion, f is defined as

$$f = 0.866/\xi \qquad\qquad 6$$

where ξ is the charge density parameter of the polyion and is defined by

$$\xi = e^2/bDk_BT \qquad\qquad 7$$

(where e is the protonic charge, D is the relative permittivity of the medium, b is the spacing between charged groups along the axis of the polyion chain, k_B is the Boltzman constant and T is the temperature).

λ_p has been derived theoretically for the cylinder model of polyelectrolytes and it follows for counterions with a charge of z_c that :

$$\lambda_p = 279|z_c|^{-1}|\ln ka|/[1+43.2A(|z_c| \lambda_c^0)^{-1}|\ln ka] \qquad\qquad 8$$

where the parameter a is the radius of the polymer chain, while

$$A = Dk_BT/3\pi \eta_0 e \qquad\qquad 9$$

with η_0 being the coefficient of the viscosity of the solvent. In the above equation k is the Debye screening constant, which is defined by

$$k^2 = 4 \pi \eta^2 \xi^{-1} n_e |z_c|/Dk_BT \qquad\qquad 10$$

To calculate the charge density parameter ξ, segment length of 3.8 angstrom[46] and a cylindrical radius of 3 angstrom are used for the present analysis [47]. Experimental data and theoretical predictions of equivalent conductivity of HPAM are shown in figure 6.19. The charge density parameter of LPAM is found to be 0.312 in the present case which is much lower than 1 and equation 7 is valid only for $\xi > 1$. Therefore, it is not possible to determine the equivalent conductivities of LPAM with the help of the above equations. For HPAM, experimentally obtained equivalent conductivities are found to be considerably lower than the theoretically predicted values. Concentration dependence of equivalent conductivity is also found to deviate from the theoretically predicted trends. In the case of flexible polyelectrolytes like HPAM, effective charge density parameter should be higher than the value obtained from structural data because of locally curved or coiled conformation of the polyion.[48] The counter ions then see an effective charge being more highly charged than in fully stretched chain. Hence their mobility is lowered concomitantly. Another important
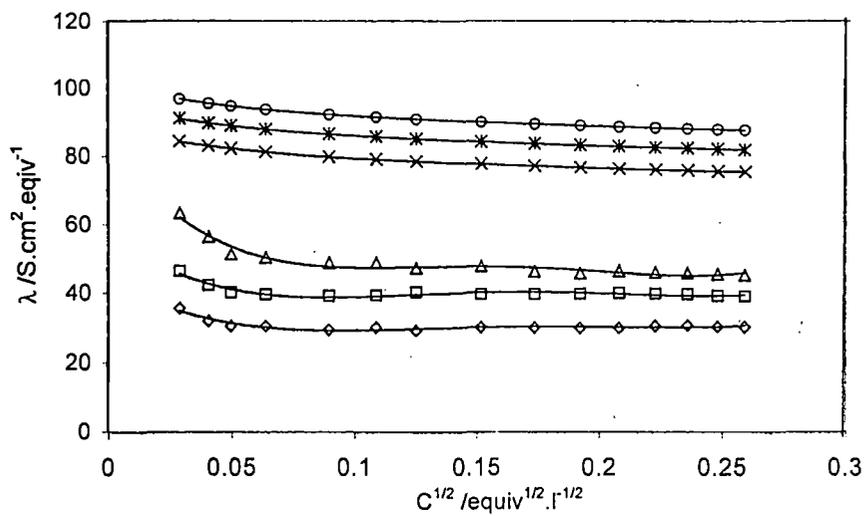
Figure 6.19:Comparision of the experimental values of the equivalent conductivity of solutions of HPAM with those predicted the Manning theory at different temperatures.

◇ 303K,EXP.   □ 313K,EXP.   △ 323K,EXP.   ✕ 303K,THE.
✳ 313K,THE.   ○ 323K,THE.

EXP and THE stand for experimental and theoretical respectively.

reason for the observed differences between the theoretical and experimental values includes deviation from the rod like model because of kinking in the structure of the polyelectrolyte. In this context it may be noted that viscosity measurement of present polymer system also predicted more or less spherical shape of the polymer molecules (shape factor 2.5) in aqueous solution as well as in aqueous-nonaqueous mixtures (discussed in chapter 6 and chapter 5 respectively), which also support deviation from rod like structure.

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