

Synthesis, Characterization, and Dilute Solution Properties of pH-Responsive Polyacryloyl ethylpiperazinium Polymers

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ABSTRACT: Four different pH- and electrolyte-responsive polymers were synthesized from ethyl piperazine with four different counter ions viz., chloride, bromide, sulfate, and nitrate. IR and NMR spectroscopic techniques confirmed the structure of monomers and polymers. Thermal properties of these polymers were investigated by TGA and DSC analysis. The dilute solution properties in pure water, in inorganic simple salt solutions, and pH-responsive behav-

ior of these polymers were studied by the measurement of viscosity by Ubbelohde viscometer. Flocculation behavior of these polymers was investigated by turbidity studies with bentonite suspension. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 100: 3174–3186, 2006

Key words: polyelectrolyte; ethylpiperazinium; pH-responsive; viscosity; flocculation

INTRODUCTION

Water soluble ionic polymers have been found to be useful in many industrial processes such as waste water treatment, mineral processing, membrane filtration, virus removal, controlled release of drugs, etc.^{1–5} The polyelectrolytes have been employed for the preparation of thin films on flat surfaces and on particles by alternative deposition of cationic and anionic polyelectrolytes. These polymers have potential applications in the areas of membrane modification, humidity sensors, protein immobilization inside the capsules, etc.^{6–8} The stimuli-responsive polymers have attracted much attention in recent years because of their phase transition behavior based on external stimuli such as temperature, pH, electrolyte, magnetic field, etc.^{9–10} Most of the systems exhibiting stimuli-responsive polymers contain poly(*N*-isopropylacrylamide) and *N,N*-dimethylaminoethylmethacrylate on dilution or acrylic acid derivatives.¹¹

Piperazine derivatives are a class of materials that are easily available commercially and act as potential drug intermediates. In recent past, allyl and acryloyl piperazine derivatives have been used for the synthesis of water soluble copolymers with methylmethacrylate, water swellable crosslinked gels, dicationic polymers, etc.^{12–14} Danusso et al.¹⁵ have investigated the synthesis and characterization of polymers and copolymers of *N*-acryloyl-*N*-phenyl piperazine. Co-

polymers of *N*-acryloyl-*N*'-methyl piperazine with 2-acrylamido-2-methyl-1-propane sulfonic acid and its metal binding ability have been reported.¹⁶ Gan et al. have reported the pH-responsive behavior of acryloyl methylpiperazine copolymers and propyl piperazine crosslinked gels.^{17–18} Even though many reports are available on piperazine-containing polymers, mono-cationic piperazine polymers with a variety of counter ions have not been investigated.

In the present study, we are reporting the synthesis and characterization of four different cationic piperazinium polymers with chloride, bromide, sulfate, and nitrate as counter ions. The structure of these polymers was confirmed by IR and NMR spectral studies and their thermal properties were investigated by TGA and DSC studies. The viscometric behavior of these polymers was investigated in pure water, in salt solution, and at different pH conditions to explore the electrolyte and pH-responsive nature of the polymers. Flocculation studies were conducted for all four polymers with bentonite suspension.

EXPERIMENTAL

Materials

Piperazine derivatives were purchased from Enzal chemicals, Mumbai, India, and were used after purification. Acryloyl chloride was synthesized from acrylic acid and benzoyl chloride by the reported procedure and was used after redistillation.¹⁹ The common solvents viz., tetrahydrofuran (THF) and acetone were distilled before use and mineral acids such as hydrochloric acid, hydrobromic acid, sulfuric acid,

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and nitric acid were of LR grade and were purchased from Glaxo (India) limited.

Synthesis of *N*-acryloyl-*N'*-ethyl piperazine

N-ethyl piperazine (28.5 g, 0.25 mol) and triethylamine (27.8 g, 0.27 mol) were dissolved in 250 mL of THF in a round-bottom flask and cooled in an ice bath. Acryloyl chloride (24.5 g, 1.1 mol) was dissolved in THF (100 mL) separately in a pressure-equalizing funnel and added dropwise to the solution of ethylpiperazine and triethylamine for a period of 1 h. The reaction mixture was stirred for about 4 h and the precipitated white triethylamine hydrochloride was filtered off. Then the filtrate was concentrated in a rotary evaporator. The concentrate was distilled under high vacuum to get the desired product.

B. P. 84°C (0.15 mm Hg) Yield: 36 g (86%)

Synthesis of *N*-acryloyl-*N'*-ethyl piperazinium salts

N-acryloyl-*N'*-ethylpiperazine (3.0 g, 0.0178 mol) was dissolved in dry THF (50 mL) kept in an ice bath. The desired mineral acid (0.02 mol: HCl = 0.73 g; HBr = 1.61 g; H₂SO₄ = 2 g; HNO₃ = 1.26 g) was dissolved separately in THF (20 mL) and added slowly into the solution of *N*-acryloyl-*N'*-ethylpiperazine. The precipitated salts were filtered and dried in a vacuum desiccator and stored under vacuum to prevent from moisture.

Yield: 65–75%. [chloride (PAEPC) 2.5 g; bromide (PAEPB) 3.1 g; sulfate (PAEPS) 3.5 g, and nitrate (PAEPN) 3.0 g]

Synthesis of *N*-acryloyl-*N'*-ethylpiperazinium polymers

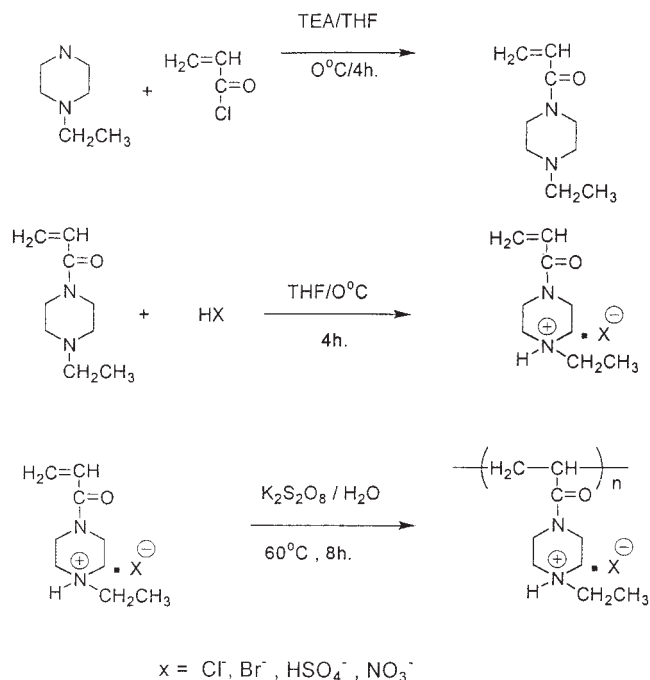
N-acryloyl-*N'*-ethylpiperazinium salt (3 g) and potassium peroxydisulfate (1 wt %) as a free radical initiator were dissolved in distilled water, kept in a polymerization tube and nitrogen was passed through the solution for about 15 min. Then the solution was kept at 60°C for 8 h and cooled to room temperature. The polymer was precipitated in cold acetone, filtered, and dried in a vacuum oven over night to get dry polymer.

Yield: 50–75% (PAEPC 2.1 g, PAEPB 1.5 g, PAEPS 1.9 g, and PAEPN 2.25 g)

Characterization methods

Spectral studies

IR spectra were recorded on a Shimadzu FTIR 8300 spectrophotometer in the range of 4000–400 cm⁻¹ for the monomers and polymers by KBr disk method. ¹H and ¹³C-NMR spectra were recorded on a JEOL JNM GSX 400 FT NMR spectrometer. The samples were



Scheme 1 Synthesis of monomeric salts and polymers.

dissolved in D₂O and tetramethylsilane was used as a reference compound.

Thermal studies

Simultaneous TG/DTA analyses were carried out using a Seiko model SSC 5200H thermal analysis system attached to a TG 220 module. All the experiments were carried out under nitrogen atmosphere, with a gas flow rate of 100 mL/min. The thermal analyzer was calibrated using calcium sulfate as standard.

Differential Scanning Calorimetry was performed on a Seiko SSC 5200 H thermal analysis unit attached to the DSC 220 module. The experiments were carried out under nitrogen atmosphere, with a nitrogen flow rate of 50 mL/min. The temperature of the sample was varied in the range of 30–400°C, at a heating rate of 10°C/min.

Viscosity studies

Viscosity measurements were carried out using an Ubbelohde viscometer at constant temperature (30 ± 0.2)°C. Polymer stock solutions were prepared by dissolving 50 mg of the polymer in 25 mL of distilled water. The stock solutions of polymer in salt solutions were prepared by dissolving 50 mg of polymer in 25 mL of corresponding salt solutions.

Flocculation studies

Flocculation efficiency of polymers was ascertained with bentonite suspensions. The tests were carried out

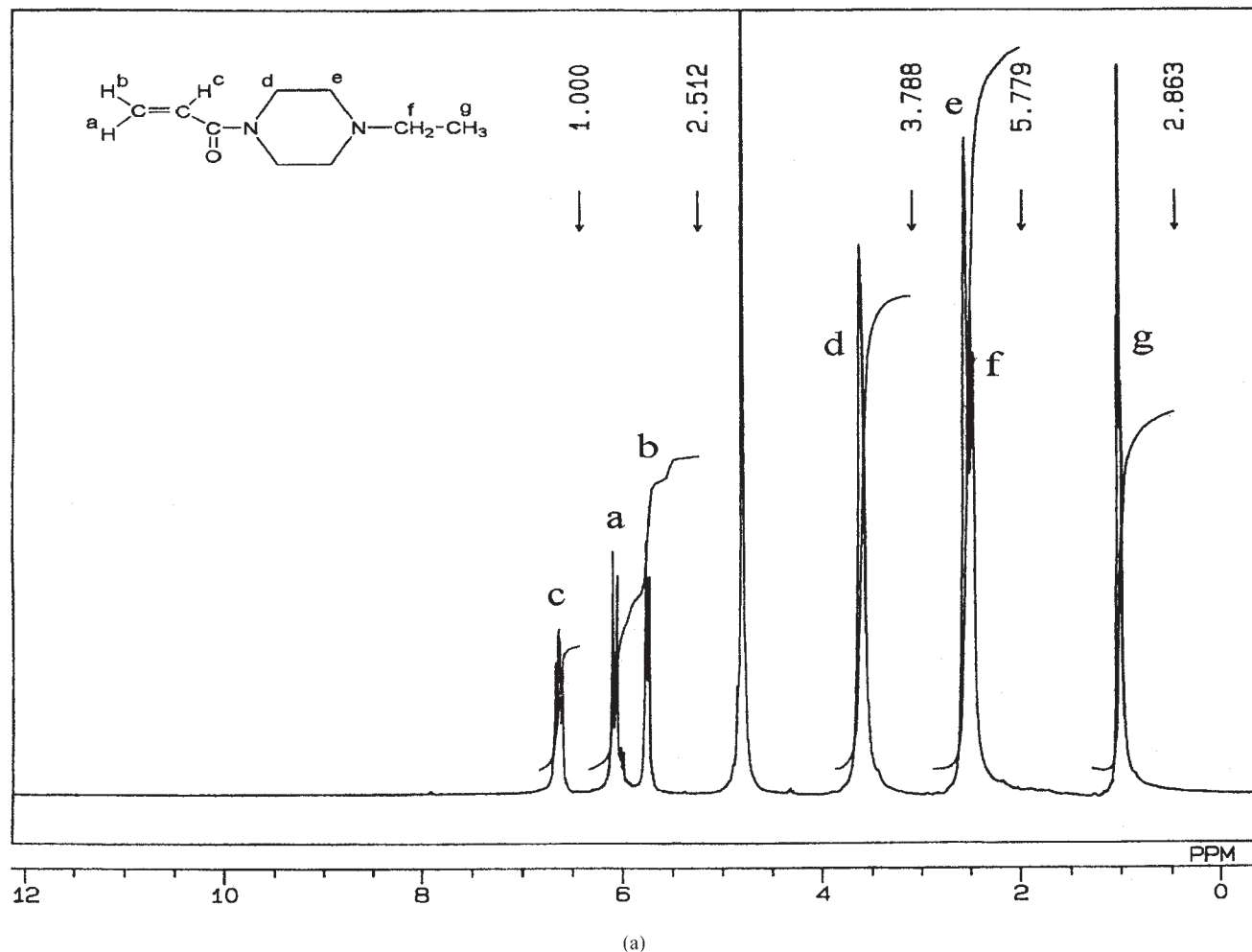


Figure 1 (a) ¹H-NMR spectrum of *N*-acryloyl-*N'*-ethylpiperazine (D₂O). (b) ¹H-NMR spectrum of *N*-acryloyl-*N'*-ethylpiperazinium bromide (D₂O).

in a 100 mL graduated cylinder with a constant height and diameter (250 mm and 35 mm respectively). Different doses of polymer were added to a bentonite suspension (1000 ppm), stirred for 2 min and kept aside for 10 min without any disturbance. The supernatant liquid was taken out by a long needle syringe for the measurement of turbidity.

RESULTS AND DISCUSSION

Synthesis and spectral studies

The ethylpiperazinium polymers were synthesized with four different counter ions viz., chloride, bromide, sulfate, and nitrate. The synthesis of monomers and polymers are depicted in Scheme 1. Quaternary piperazinium salts and polymers were all highly hygroscopic in nature and pale white in color. All are freely soluble in water and insoluble in organic solvents like benzene and toluene.

The FTIR spectral studies of acryloyl ethyl piperazine and monomeric salts confirm the presence of expected functional groups. The absorption around 1640 cm⁻¹ corresponds to stretching frequency of the carbonyl group, which confirms the incorporation of acryloyl group into the monomer. A sharp peak around 2930 cm⁻¹ in all the spectra corresponds to C—H stretching frequency.

IR spectra of polymers also show a strong absorption around 1640 cm⁻¹, which confirms the presence of carbonyl group. The NH stretching frequency merges with OH frequency and appears as a broad peak around 3400 to 3450 cm⁻¹ due to the hygroscopic nature of some of the polymers. A peak around 2930 cm⁻¹ in all the spectra corresponds to C—H stretching frequency.

In the proton NMR spectrum of *N*-acryloyl-*N'*-ethylpiperazine, methyl protons appear as a triplet at 1.01 δ because of the presence of a methylene group adjacent to the methyl group. Similarly methylene pro-

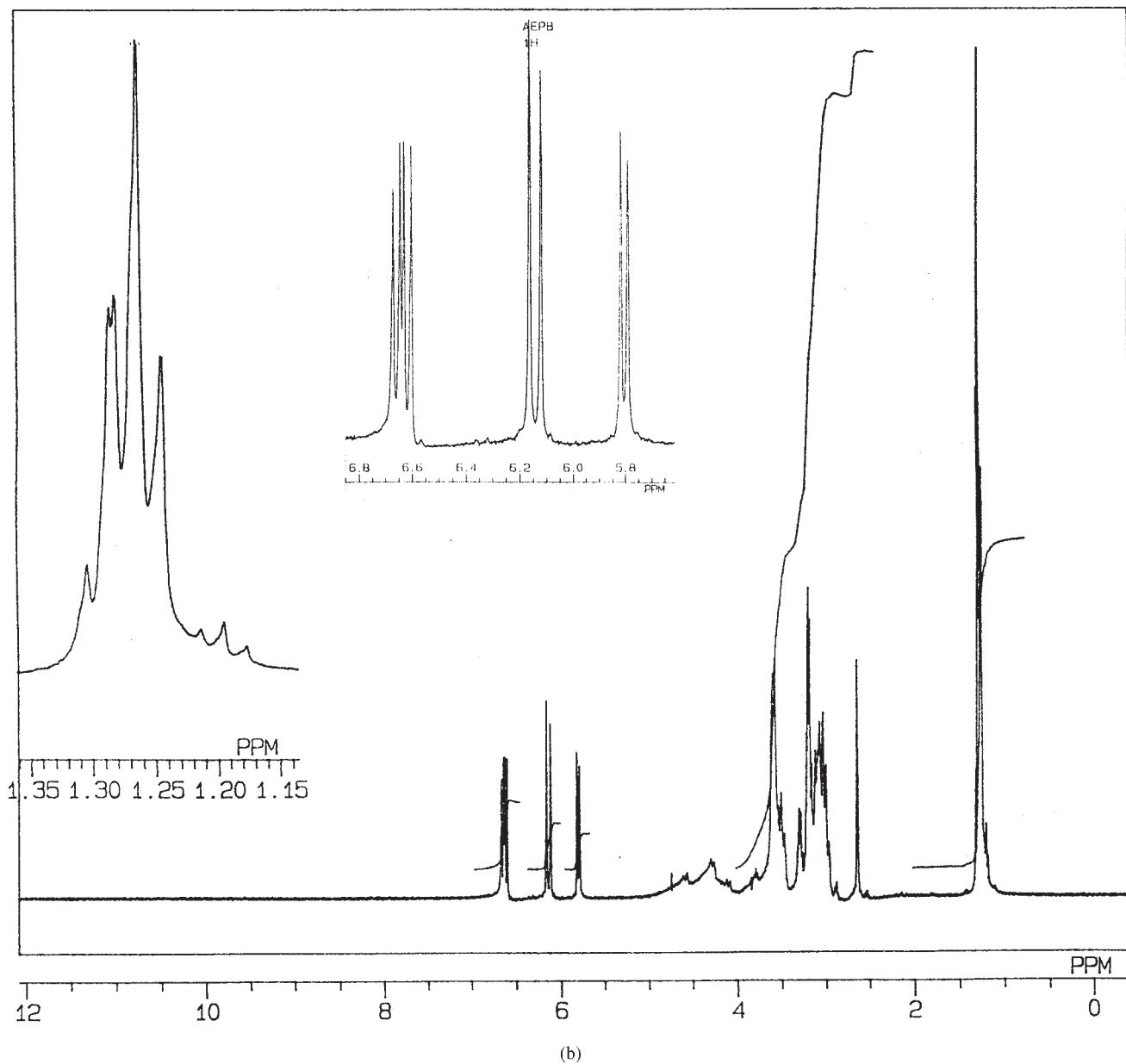


Figure 1 (Continued)

tons, which should appear as quartet, exhibit a multiplet around 2.47–2.55 δ due to the ring methylene protons interference. The ring methylene protons attached to $-\text{N}-\text{CO}$ appear as a singlet around 3.6 δ . The allylic protons exhibit a quartet around 6.59–6.66 δ (1H) for $-\text{CH}$ proton and two doublets around 5.75–6.09 δ for $-\text{CH}_2$ protons [Fig. 1(a)]

The proton NMR spectra of the piperazinium salts resemble very closely to that of the parent compound. The methyl protons appear at 1.3 δ while the ring methylene protons are observed in between 3 and 4 δ . The vinylic protons are observed at 5.8 (d), 6.2 (d), and 6.7 (q) δ [(Fig. 1(b)).

Thermal studies

The TGA curves of the polymers clearly indicate that the degradation of the polymer occurs in two stages except in the case of chloride system, which undergoes degradation in three stages (Table I). The experiment was conducted under nitrogen atmosphere and all the samples leave a definite amount of residue after the completion of the degradation process (Fig. 2).

The observed IDT in the case of the polymers range from 265°C to 290°C. The residue obtained in all these cases is quite appreciable and the percentage char yield ranges from 8 to 23. The percentage char yield was higher in the case of PAEPS and PAEPN (20 and

TABLE I
TGA Data for Polymers

Sl. no.	Polymer	Initial decomposition temperature (°C)	Temperature range for each stage (°C)			Char yield (%)
			I stage	II stage	III stage	
1	PAEPC	290	50–160	260–380	380–470	8
2	PAEPB	280	270–290	300–440	—	15
3	PAEPS	273	80–300	300–600	—	20
4	PAEPN	265	80–330	330–520	—	23

23% respectively), compared with other two polymers viz. PAEPC and PAEPN (8 and 15% respectively). The IDT as well as the decomposition observed in the present series is generally higher than that of the acryloylmethyl piperazinium polymers. The DSC studies of these systems indicate that only two polymers (PAEPB and PAEPS) exhibit sharp melting points compared with the other two polymers (PAEPC and PAEPN), which may be attributed to the crystalline nature of these two polymers (Table II).

Viscosity studies

The intrinsic viscosity of the polymers was calculated by three different methods viz. Huggins, Fuoss, and Fedors methods and the corresponding equations are given below:

$$\text{Huggins equation: } (\eta_{sp}/c) = [\eta] + k'[\eta]^2c \quad (1)$$

$$\text{Fuoss equation: } (\eta_{sp}/c)^{-1} = 1/A + B/A\sqrt{c} \quad (2)$$

$$\text{Fedors equation: } 1/[2(\eta_r^{1.2}-1)] = 1C/[\eta] - 1C_m/[\eta] \quad (3)$$

The polymers investigated in the present study exhibit polyelectrolytic behavior i.e., the reduced viscosity of the system increases with dilution. Some of the polymers showed very high reduced viscosity values

because of their high molecular weight. The data have been analyzed based on Huggins, Fuoss, and Fedors equations. The reduced viscosity as well as the intrinsic viscosity of these polymers were investigated in three different conditions viz. (a) polymers in pure water, (b) polymers in salt solution at varying concentration of salts, and (c) polymers in salt solutions having common cation and different anions.

Viscosity behavior of polymers in pure water

The intrinsic viscosity in aqueous solution was calculated at different concentrations of polymers ranging from 0.05 to 0.2 dL/g. The intrinsic viscosity is very high for all polymers at lower concentration region (0.05–0.12 g/dL) compared with higher concentration regions (0.15–0.25 g/dL). This behavior may be attributed to the higher ionization of the polymer at the lower concentration region i.e., because of higher ionization of the polymers, the counter ions present in the polymer chain are separated farther apart from the polymer chain. Hence charge repulsion along the polymer chain is higher in dilute solutions compared with concentrated solutions. Higher charge repulsion favors rod-like conformation of polymers, which results in higher intrinsic viscosity of solutions.

The plots of reduced viscosity versus concentration for the cationic ethylpiperazinium polymers with four

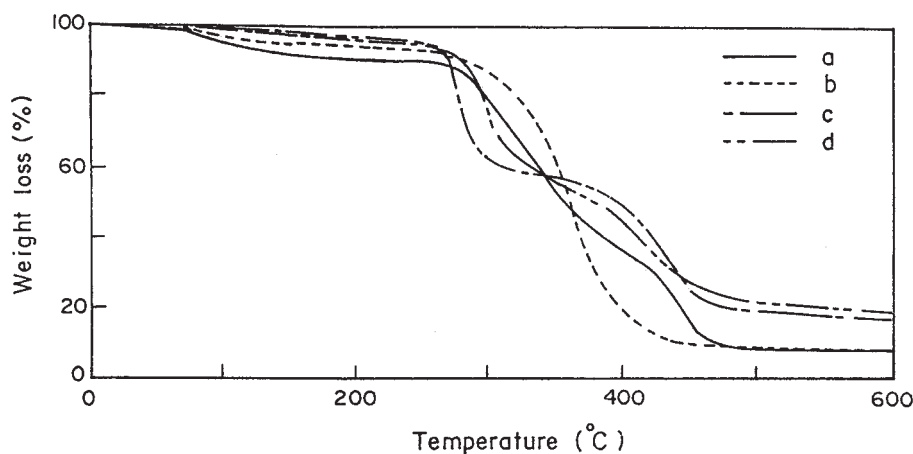


Figure 2 TGA traces of *N*-acryloyl-*N'*-ethylpiperazinium polymers (a) PAEPC, (b) PAEPB, (c) PAEPS, and (d) PAEPN.

TABLE II
DSC Data for Polymers

Sl. no.	Polymer	T_g (°C)	T_m (°C)
1	PAEPC	70	—
2	PAEPB	75	270
3	PAEPS	—	264
4	PAEPN	—	—

different counter ions (Cl^- , Br^- , HSO_4^- , and NO_3^-) in pure water are shown in Figure 3. It has been observed that when the concentration of the polymer increases, the reduced viscosity decreases due to the microstructure of the polymer chain in the aqueous solution.

The intrinsic viscosity (Fig. 3) of PAEPC is found to be higher compared with other three polymers viz. PAEPB, PAMPS, and PAEPN, which may be due to the higher molecular weight of the PAEPC. Rod-like conformation occurs in dilute regimes because of the mutual repulsion of the positive charges, which results in higher reduced viscosity. When the molecular weight of the polymer increases, the length of straight extended chains of the polymer also increases. Also, the high molecular weight polymers exhibit higher intrinsic viscosity values compared with low molecular weight polymers. The intrinsic viscosity values are provided in Table III, which shows that PAEPC has much higher value (Huggins method: 8.92 dL/g) compared with other three polymers (PAEPB 0.3448, PAEPS 0.3748 and PAEPN 5.018 dL/g).

Effect of different concentrations of KCl on the reduced viscosity

The polymer solutions were prepared in three different concentrations of salt solution viz. 0.025, 0.05, and 0.1M KCl. The resultant solution viscosity was measured to investigate the effect of different concentrations of the salt on the reduced viscosity behavior of polymers.

The addition of 0.025M KCl to the polymer solution of PAEPC lowers the reduced viscosity at all concentrations of polymer to a large extent (Fig. 3). This lowers intrinsic viscosity value from 6.87 dL/g to 1.26 dL/g, i.e., a fivefold reduction. Further addition of salt to the system, 0.05M and 0.1M KCl, decreases the intrinsic viscosity value to 0.96 dL/g and 0.46 dL/g, respectively. The remaining polymers also show similar reduction in intrinsic viscosity values when KCl is added to polymer solution. The addition of 0.025M KCl decreases the intrinsic viscosity to the extent of twofold to fivefold in all polymer solutions. Further increase in the concentration of salt, i.e., 0.05M KCl and 0.01M KCl, changes the intrinsic viscosity to a lower value but not significantly as in the case of 0.025M KCl addition (Table IV). The addition of KCl to

polymer solution completely reverses the reduced viscosity behavior of all polyelectrolytes, except in the case of PAEPS where reduced viscosity decreases on dilution, which is similar to the case of normal polymers²⁰ (Figs. 4–7).

The above results which indicate polyelectrolyte behavior due to the addition of KCl salt at various con-

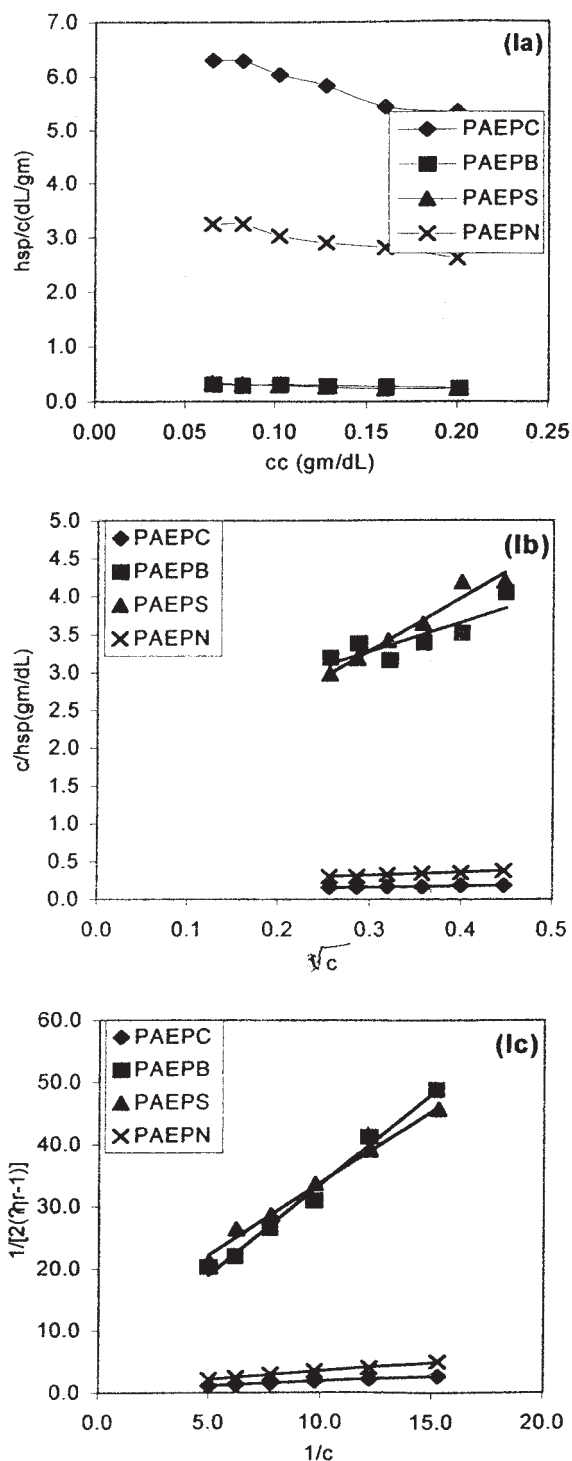


Figure 3 Huggins, Fuoss, and Fedors plots of polymers in pure water.

TABLE III
Viscosity Data for Polymers in Pure Water

Sl. no.	Polymer	Huggins method (dL/gm)	Fuoss method (dL/gm)	Fedors method (dL/gm)
1	PAEPC	6.8766	8.9285	6.9589
2	PAEPB	0.3448	0.4655	0.3924
3	PAEPS	0.3748	0.8216	0.2347
4	PAEPN	3.5873	5.0150	3.7313

centrations may be interpreted as follows: When the salt concentration is increased, a partial amount of negative charge of salt would become site-bound on the quaternary ammonium group of the polyelectrolyte. The charges on the polymer back bone would be neutralized by the counter ions in the aqueous solution. Hence, this affects the repulsion of polymeric side chains in the absence of both decreasing the extent of tightly stretched chains and also coiling of the polymeric main chains.²¹ The chloride ion binding on quaternary ammonium group of polyelectrolyte was more in high salt concentration, which forms regions of high local charge density. This may also be due to the fact that addition of salt can loosen the compact structure that results from the inter- and intra-molecular ionic interactions, thereby facilitating the free movement of polymer in the salt solution. In other words, the higher the salt concentration, the lower is the electrostatic repulsive force and hence lower is the intrinsic viscosity.²²

The addition of salt to the polymer solution reverses the trend of reduced viscosity in the case of PAEPS, i.e., the reduced viscosity decreases on dilution like in the case normal polymer. This behavior may be attributed to the complete neutralization of the charges of the polymer backbone by the addition of even very low concentration of (0.025M) KCl. Further addition of salt to the system increases the intrinsic viscosity values because of the higher chloride ion binding onto the ammonium group, which may result in the formation of high local charge density.

Effect of common cation

The dilute solution viscosity of the polymers was determined in the presence of simple salts (KCl, KBr, and KI) to demonstrate their influence on the reduced viscosity. Three salts with similar cation were investigated for the effect of common cation on intrinsic viscosity. The addition of inorganic salts to the polyelectrolyte solution drastically decreases the reduced viscosity and intrinsic viscosity. In the present study, four polymers have been tested for their viscosity-dependence on salt addition and all of them show considerable decrease in reduced viscosity. The intrinsic viscosity values are also low compared with the viscosity of polymers in pure water. For example, the reduction in intrinsic viscosity value on addition of 0.05M KCl to PAEPC is about fivefold, i.e., from 6.87 dL/g to 0.961 dL/g. while the addition of 0.05M KBr and 0.05M KI lowers the value from 6.87 dL/g to 0.33 dL/g and 6.87 dL/g to 0.25 dL/g, respectively, (Table IV). In all cases, the magnitude of reduction in the intrinsic viscosity is almost similar, when the salts were added to the polymer solution (Figs. 4–7). The lowering of reduced viscosity as well as intrinsic viscosity value is attributed to the charge neutralization mechanism. The following trend has been observed while comparing the extent of intrinsic viscosity change among these polymers. Liaw and coworkers have observed similar trend for methylsulfate quaternized dimethylaminoethyl polymer.²²



This behavior may be due to the fact that larger anions with common cation, which have higher charge density, are readily polarizable compared with the smaller anions. Hence the more polarized larger anions are readily bound to polyelectrolyte charges than are smaller anions. The positive charges of piperazinium group therefore get effectively neutralized by the larger anions and results in lower intrinsic viscosity values. Iodide (I^-) being the largest anion, compared with other anions (viz., Cl^- , Br^-), exhibits the lowest intrinsic viscosity values.

TABLE IV
Viscosity Data for Polymers in Salt Solutions

Salt	Salt concn (M)	Intrinsic viscosity (dL/gm)											
		PAEPC			PAEPB			PAEPS			PAEPN		
		Huggins	Fuoss	Fedors	Huggins	Fuoss	Fedors	Huggins	Fuoss	Fedors	Huggins	Fuoss	Fedors
KCl	0.025	1.2647	1.2086	1.271	0.1126	0.1036	0.1129	0.3309	1.2526	0.3279	0.7106	0.7441	0.7375
KCl	0.05	0.9610	0.8916	0.9222	0.0597	0.0532	0.0637	0.3097	1.973	0.4000	0.4923	0.4806	0.4998
KCl	0.1	0.4674	0.4000	0.4492	0.0566	0.0508	0.0618	0.2882	0.6520	0.3187	0.3518	0.3360	0.3487
KCl	0.05	0.9610	0.8916	0.9222	0.0597	0.0532	0.0637	0.3097	1.973	0.4000	0.4923	0.4806	0.4998
KBr	0.05	0.3290	0.3878	0.3376	0.1262	0.0881	0.0081	0.2482	0.3004	0.2457	0.4077	0.3499	0.3898
KI	0.05	0.2574	0.2646	0.27920	0.0164	0.0195	0.0261	0.1035	0.0869	0.0997	0.3477	0.3448	0.3716

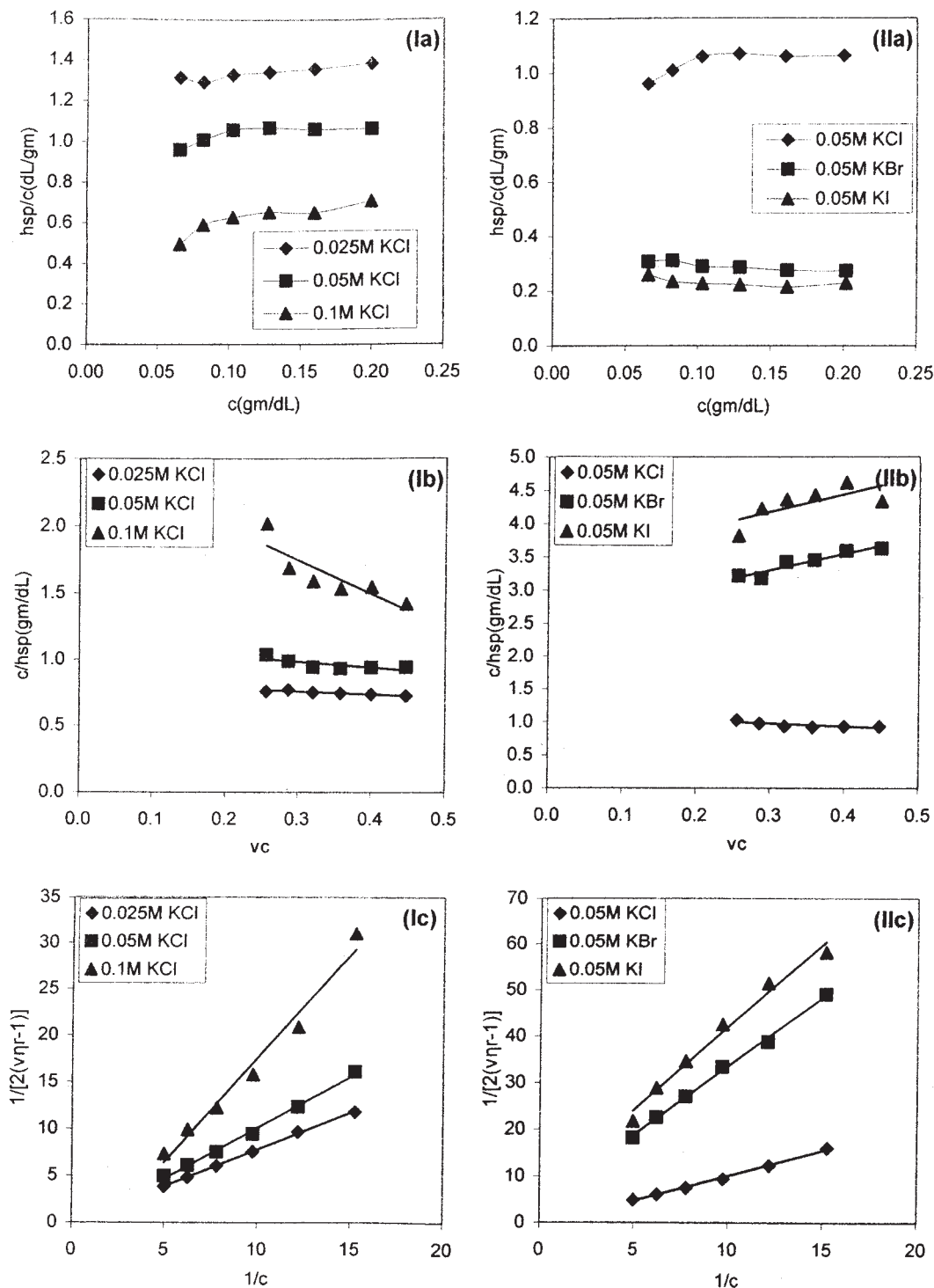


Figure 4 Huggins, Fuoss, and Fedors plots of PAEPC in salt solutions.

Flocculation studies

In the present investigation, all the four polymers are found to be highly soluble in water. They exhibit typical viscosity behavior of polyelectrolytes and are likely to exhibit efficient flocculation behavior. The polymers were tested for their flocculation ability with bentonite suspension. Different dosages of polymers

were added (2–100ppm) to bentonite suspension (1000 ppm) and the turbidity was measured for supernatant solution to determine the extent of flocculation.

The polyelectrolytes investigated in the present study exhibit good flocculating ability around 40 ppm to 60 ppm dosage. The polyelectrolytes PAEPC and

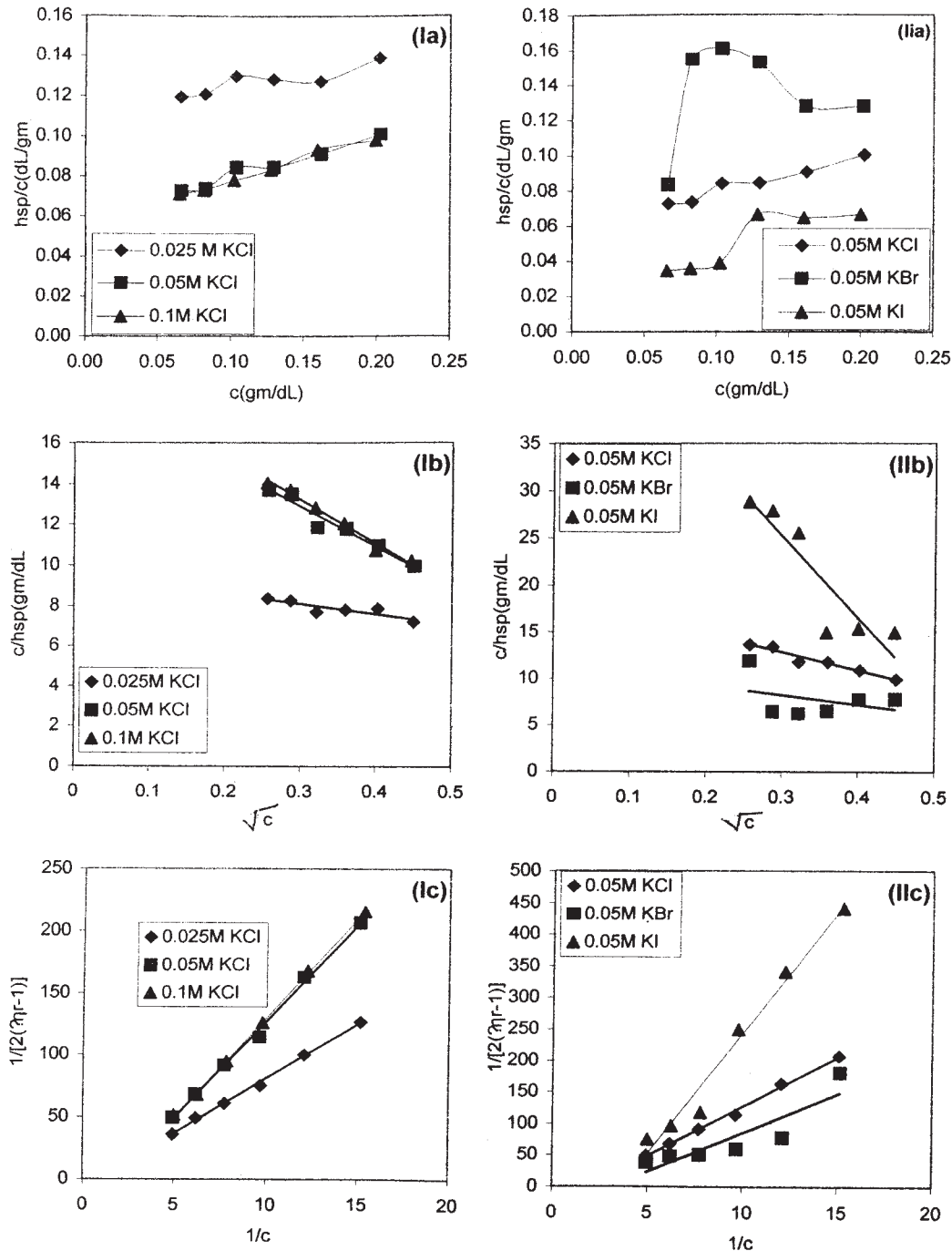


Figure 5 Huggins, Fuoss, and Fedors plots of PAEPB in salt solutions.

PAEPN show better flocculating efficiency at 40 ppm concentration compared with other two polymers. The flocculating ability is significant between 2 and 40 ppm concentration of the polyelectrolytes (Table V). However, further increase in the concentration of polyelectrolyte did not result in the reduction of turbidity values to a greater extent. On the contrary, the turbidity values showed a marginal increase when the concentration of the polyelectrolyte exceeded 40 ppm. This behavior can be attributed to the deflocculation of

the settled particles due to increase in the cationic charge density. It has been observed that the reversal in the flocculation trend is not uniform in all cases (Fig. 8).

The bentonite particles are reported to have net negative charge and the cationic polyelectrolytes are adsorbed on their surface. The various interactions found among these species may either be attractive or repulsive. These interactions can be classified into three different categories: (a) an attractive force of

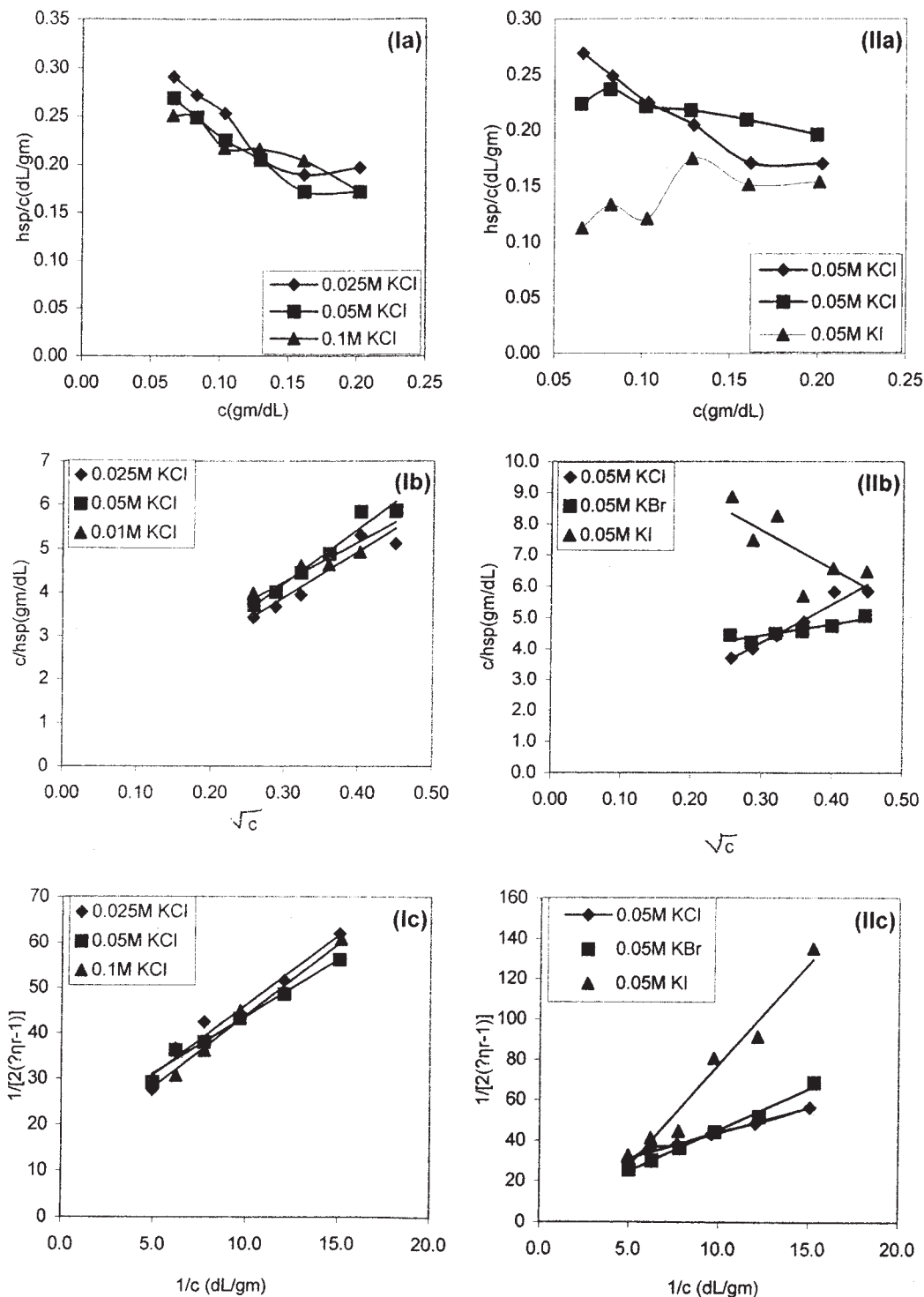


Figure 6 Huggins, Fuoss, and Fedors plots of PAEPS in salt solutions.

London–Van der Waals type; (b) a repulsive force due to electrostatic interaction; and (c) Born–Haber type for very short distances. When the number of macromolecular units adsorbed onto the bentonite surface increases, the effective charge becomes positive as a result of which the next macromolecular moiety approaches this domain, which will be repulsed and

adsorbed in a different domain. This effect will be determinant, when the surface area covered by each macromolecule exceeds certain percentage. When the charges are neutralized, the only force operative is attractive, resulting in the aggregation of the particles. The sedimentation rate is governed by the floc size, which in turn depends on the magnitude of attraction

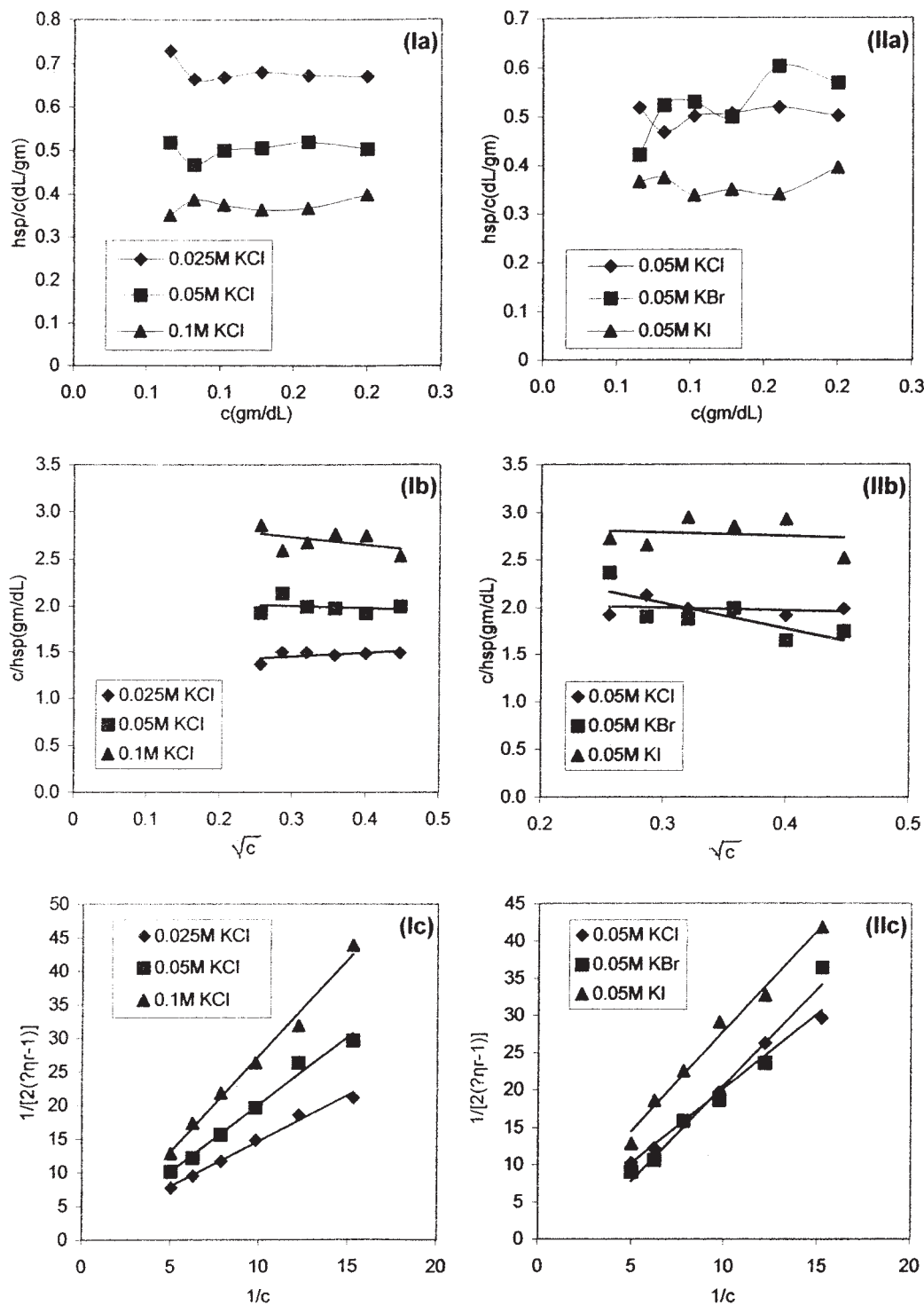


Figure 7 Huggins, Fuoss, and Fedors plots of PAEPN in salt solutions.

between the particles. After optimum dosage, addition of polyelectrolyte increases the turbidity value, which is an indication of redispersion of the settled particles due to the excess positive charge accumulation on the surface of the particles.

pH-responsive studies

The polyelectrolytes synthesized in the present study exhibit good electrolyte- and pH-responsive behavior. The electrolyte-responsiveness of these polymers with

TABLE V
Turbidity Values of Polymers with Bentonite Suspension

Sl no.	Conc. (ppm)	Turbidity value (NTU)			
		PAEPC	PAEPB	PAEPS	PAEPN
1	2	378	427	419	381
2	4	368	386	358	349
3	6	308	354	326	309
4	8	284	335	314	295
5	10	257	234	276	252
6	20	86.5	119	221	172
7	40	8.7	15	49.2	5
8	60	64.2	35.9	55.4	20
9	80	49.1	51.9	88.4	45
10	100	73	52.5	79.8	56

KCl, KBr, and KI has been discussed in previous sections. The degree of dissociation of ions in solution mainly depends on the pH of the medium. The polymer dissociates in different manner in acidic and basic regions. It has been reported that polyelectrolytes undergo conformational transition as a function of the degree of dissociation of polyelectrolytes.²³ The reduced viscosity measurements of polymers were made in a wide range of pH from 3 to 13. The plot of pH versus reduced viscosity is shown in Figure 9. It has been observed that when the pH of the polymer increases by the addition of sodium hydroxide to the polymer solution, the reduced viscosity of the solution decreases. This indicates that expanded rod-like structure of the polymer chains turns into smaller collapsed coils. The neutralization of positive centers of the polymer backbone by the negative hydroxyl ions causes chain contraction and decreases the reduced

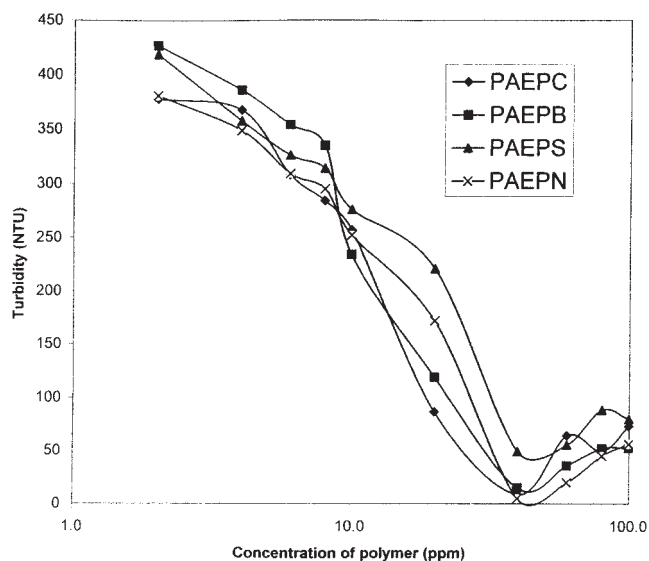


Figure 8 Plot of concentration of polymers versus turbidity values.

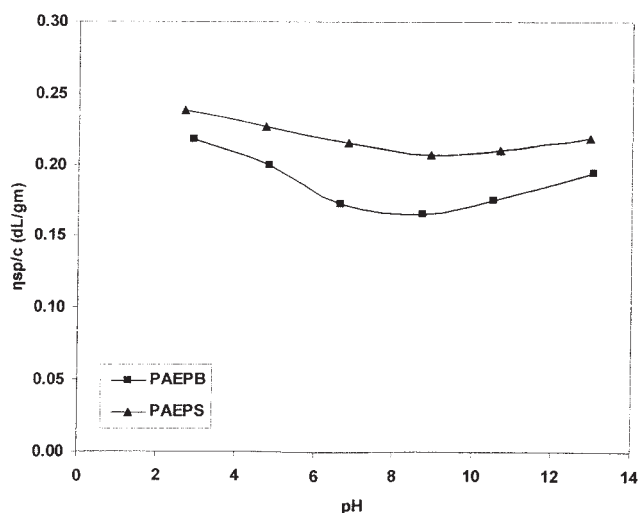
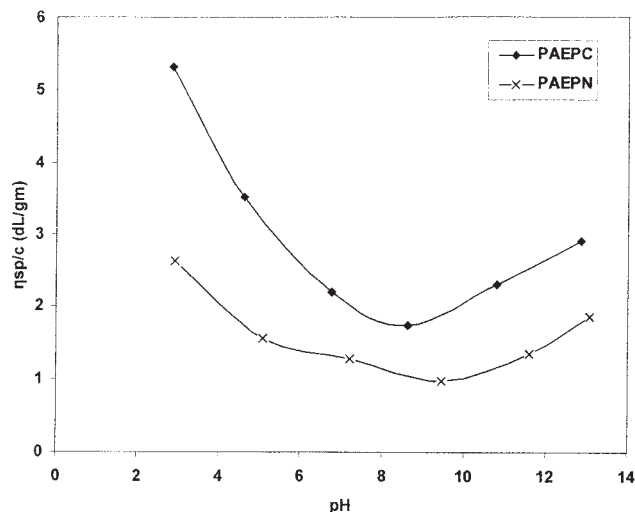


Figure 9 pH-dependence of reduced viscosity.

viscosity values. On complete neutralization of the positive centers, the polymer solution reaches minimum reduced viscosity. The addition of more sodium hydroxide increases the value of reduced viscosity to smaller extent compared with the initial reduced viscosity value of polymer. This is attributed to the interionic repulsion caused by excess hydroxyl ions.

All of the four polymers reported in the present study show considerable pH-responsive behavior in the pH range of 3–13.5 (Fig. 9). The polymers PAEPC and PAEPN exhibit larger viscosity changes with the addition of hydroxyl ions while the other two polymers viz. PAEPB and PAEPS show only minor variation because of the lower molecular weight of these polymers. All of the four polymers show viscosity increase around pH 8–9 (Fig. 9a).

CONCLUSIONS

Four new acyloylethylpiperazinium cationic polyelectrolytes were synthesized with Cl^- , Br^- , NO_3^- ,

and HSO_4^- counter ions. IR, NMR spectral techniques were employed to characterize these systems. Thermal behavior of polymers was investigated by TGA and DSC studies. The dilute solution viscometric studies of these polymers was investigated by reduced viscosity measurements and was found that the polymer viscosity increases on dilution, which is a unique property of polyelectrolyte. The addition of simple inorganic salts like KCl, KBr, and KI reduces the intrinsic viscosity values to a greater extent, which proves the electrolyte-responsive character of these polymers. The pH-responsive studies indicate that all the polymers show good response to pH changes while PAEPC and PAEPN show appreciable variation in reduced viscosity. The flocculation ability of these polymers was investigated with bentonite suspensions. PAEPC and PAEPN polymers exhibit good flocculation property compared with other two polymers.

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