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Water soluble polymers: 70. Effects of methylene *versus* propylene spacers in the pH and electrolyte responsiveness of zwitterionic copolymers incorporating carboxybetaine monomers

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Water soluble polyzwitterions have been synthesized by free radical copolymerization of acrylamide with the novel carboxybetaine monomer, 2-(2-acrylamido-2-methylpropyldimethylammonio) ethanoate (AMPDAE). Feed ratios of 10 to 100 mol% AMPDAE were employed to give the polyzwitterion series, DAEAM. Copolymer compositions of low conversion samples were determined from ^{13}C n.m.r. by integration of the carbonyl resonances. Reactivity ratios were determined yielding an r_1r_2 value of 0.6. Molecular weights range from 6.3 to 10.4 × 10^6 g mol^{-1} as determined by low angle laser light scattering. Dilute solution properties of the copolymers have been studied as a function of added electrolytes and pH. Intrinsic viscosity behaviour in NaCl solutions is dependent on the mol% of AMPDAE incorporated into the copolymers. Reduced viscosities were also examined as a function of the nature of added electrolytes, displaying higher viscosity values in accord with the Hoffmiester lyotropic series. The copolymers exhibit an enhancement in viscosity as pH is lowered due to protonation of the carboxylate groups which renders the polymer coil cationic due to the presence of quaternary ammonium groups. The solution behaviour of the copolymer containing 25 mol% AMPDAE, which possesses one methylene unit between the quaternary ammonium group and the carboxylate group, is compared to that of a copolymer containing 25 mol% 4-(2-acrylamido-2-methylpropyldimethylammonio) butanoate, which possesses three methylene units between the charged centres. © 1997 Elsevier Science Ltd. All rights reserved.

(Keywords: polyampholytes; water soluble polymers; zwitterionic polymers; carboxybetaines; sulfobetaines; acrylamide copolymers)

INTRODUCTION

Polyampholytes based on zwitterionic or dipolar ions have recently become the subject of synthetic and theoretical investigations due to their unique behaviour. Typically, the cationic species is based on an ammonium group while the anionic species has been comprised of several different anionic moieties[1–22]. The majority of the studies involve the aqueous solution behaviour of poly(sulfobetaines)[1–16]. These systems were first prepared by Hart and Timmerman by polymerizing the product of the reaction of 2- and 4-vinylpyridine with 1,4-butanesultone[1]. The polymer derived from 4-vinylpyridine was insoluble in deionized water and required the addition of a critical concentration of salt to achieve solubility in aqueous solution. The insolubility of other poly(sulfobetaines) in deionized water and subsequent solubilization in the presence of added electrolytes has been the typical behaviour; however, a few systems have been reported which are soluble in deionized water[1,8,9]. Unlike poly(sulfobetaines), systems in which the anionic species is a carboxylate group (poly(carboxybetaines)) have received far less attention[17–22]. Topchiev *et al.* reported kinetic studies of the free radical polymerization of 2-(*N*,*N*-dimethyl-*N*-(2-methacryloyloxyethylene))propiobetaine as well as solution behaviour[19]. Wielma *et al.* have investigated poly(carboxybetaines) based on vinylimidazole with varying numbers of methylene units between the charged centres[20]. Solubility behaviour of these systems was complex and dependent on the ionic strength, pH, and nature of the added electrolyte.

Recently we initiated studies of polyampholytes prepared from zwitterionic monomers which are structurally identical except for the nature of the anionic group[13,14]. Copolymers of acrylamide with 3-(2-acrylamido-2-methylpropanedimethylammonio)-1-propanesulfonate (DAPSAM series) were prepared and the solution behaviour found to be dependent on the mol% of sulfobetaine incorporated into the copolymers[13]. By comparison, copolymers of acrylamide with 4-(2-acrylamido-2-methylpropanedimethylammonio)butanoate (DABAM series) in which the anionic species is a carboxylate group were similarly prepared and studied[22]. It was found that changes in the nature of the anionic

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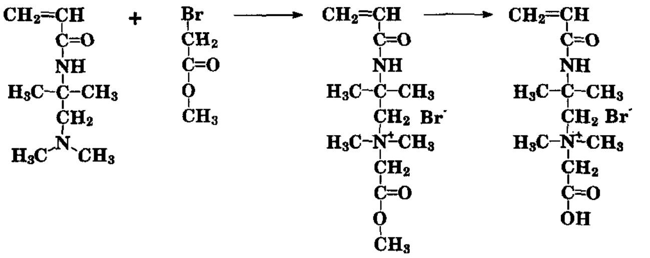


Scheme 1 Synthetic pathway for preparation of 2-(2-acrylamido-2-methylpropyldimethylammonio) ethanoate (AMPDAE)

group can lead to substantially different solution behaviour. The carboxylate group was found to increase solubility and viscosity at low pH.

In this paper we report the synthesis and characterization of copolymers of acrylamide with the novel carboxybetaine monomer 2-(2-acrylamido-2-methylpropyldimethylammonio) ethanoate (DAEAM series). The impetus behind this study is to further investigate structure–property relationships of polyzwitterions composed of structurally similar zwitterionic monomers. The zwitterionic monomer of the DAEAM series differs from that of the DABAM series by the number of methylene units between the quaternary ammonium group and the carboxylate group (one vs three). The solution behaviour of the DAEAM series has been investigated as a function of added electrolytes and pH and compared to that of copolymers of the DABAM series. In this paper it is shown that the spatial proximity of the quaternary ammonium and carboxylate groups has a significant effect on the basicity of the latter, greatly affecting solution behaviour.

EXPERIMENTAL

Materials

Acrylamide (AM) from Aldrich was recrystallized twice from acetone and vacuum dried at room temperature. Potassium persulfate from J. T. Baker was recrystallized twice from deionized water. Methyl bromoacetate from Aldrich Chemical Co. was used as received.

Monomer synthesis (2-carboxyethyl)-2-acrylamido-2-methylpropanedimethylammonium bromide (Scheme 1)

The synthesis of (2-carboxyethyl)-2-acrylamido-2-methylpropanedimethylammonium bromide (AMPDAE) involved a procedure employed by Laughlin and others for synthesis of various carboxybetaine surfactants[25–27]. 2-Acrylamido-2-methylpropanedimethylamine, AMPDA[23,24] (0.5 mol) was dissolved in 200 ml of acetonitrile followed by the addition of an excess of methyl bromoacetate (0.75 mol). The reaction was allowed to proceed for 72 h at 45°C under a nitrogen atmosphere. The solid product that formed was washed twice with 700 ml of acetone. The precipitate was filtered and thoroughly dried (yield: 75%). Once dried, the product was dissolved in water and passed over Amberlite IRA-400(OH) ion-exchange resin. The water was removed under reduced pressure at 50°C to yield the zwitterionic product in an oily state. The oil was dissolved in water, chilled on an ice bath, and one equivalent of HBr was added. The water was once again removed under reduced pressure at 50°C to yield the cationic monomer as a white, cakey powder. The monomer was washed with acetone, dried, and subsequently recrystallized from ethanol to yield pure AMPDAE (yield: 80%). M.p. 120–122°C (dec). Analysis for $C_{11}H_{21}N_2O_3Br \cdot H_2O$: Calculated—C, 40.37%; H, 7.03%; N, 8.56%. Found—C, 40.81%; H, 6.78%; N, 8.78%.*FT*i.r. (KBr pellet) acid O–H, 3600–2600 cm^{-1}; aliphatic C–H, 2970 cm^{-1}; acid C=O, 1724 cm^{-1}; amide C=O, 1664 cm^{-1} and 1537 cm^{-1}; acid C–O, 1260 cm^{-1}. ^{13}C n.m.r. (D_2O with 3-(trimethylsilyl)-1-propane-sulfonic acid, sodium salt (DSS as the reference): 29.52, 55.83, 56.38, 64.92, 69.94, 130.36, 132.61, 168.70, and 170.54 ppm. Peak assignments are given in *Figure 1*.

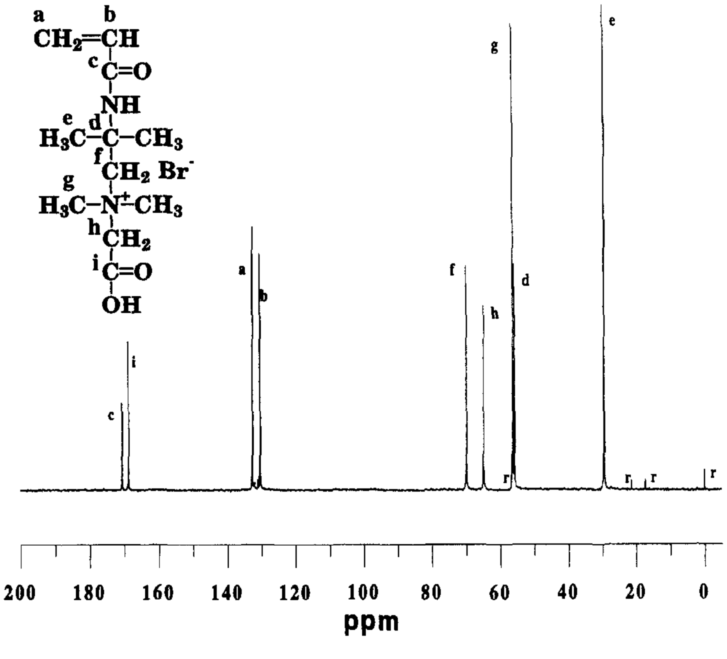
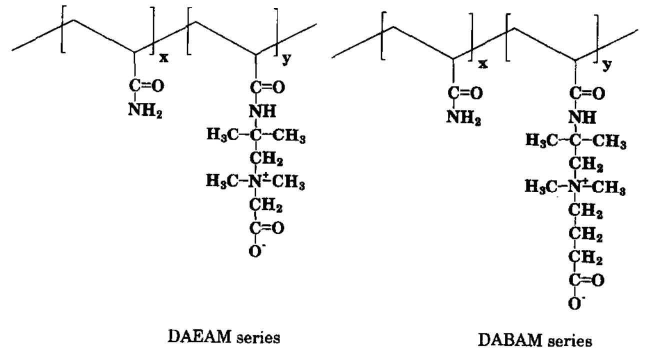


Figure 1 ^{13}C n.m.r. of 2-(2-acrylamido-2-methylpropyldimethylammonio) ethanoate (AMPDAE)



Scheme 2 Structural composition of copolymers of acrylamide with 2-(2-acrylamido-2-methylpropyldimethylammonio) ethanoate (the DAEMA series) and with 4-(2-acrylamido-2-methylpropyldimethylammonio) butanoate (the DABAM series)

Table 1 Reaction parameters for the copolymerization of acrylamide (M_1) with 2-(2-acrylamido-2-methylpropyldimethylammonio) ethanoate (M_2)

Sample	Feed ratio (mol%) (AM/AMPDAE)	Rxn. time (h)	% Conv.	AMPDAE found[a] (mol%)
DAEAM-10	90.0/ 10.0	3.1	4.0	11.0
DAEAM-25	75.0/ 25.0	1.5	9.5	26.0
DAEAM-40	60.0/ 40.0	1.4	18	38.0
DAEAM-60	40.0/ 60.0	1.4	15	58.0
DAEAM-80	20.0/ 80.0	2	17	75.0
DAEAM-100	0.0/100.0	—	—	100.0[b]

[a] Determined from ^{13}C n.m.r.
[b] Theoretical value

Synthesis of copolymers of 2-(2-acrylamido-2-methylpropanedimethylammonio)ethanoate with acrylamide (Scheme 2)

The homopolymer of AMPDAE and the copolymers of AMPDAE with AM (the DAEAM series) were synthesized by free radical polymerization in a 0.5 M aqueous NaBr solution under nitrogen at 30°C using 0.1 mol% potassium persulfate as the initiator. The feed ratio of AM/AMPDAE was varied from 90/10 to 0/100 mol% with the total monomer concentration held constant at 0.45 M. 0.5 M NaBr in the reaction medium was used as a precaution to ensure homogeneity during polymerization.

In a typical synthesis, specified quantities of each monomer were dissolved in small volumes of deionized water. The separate solutions were then combined and one equivalent of sodium hydroxide per equivalent of AMBDAE was added and the pH adjusted to 8. The necessary quantity of NaBr was then added to achieve a 0.5 M NaBr solution. The reaction mixture was sparged with nitrogen and initiated with 0.1 mol% potassium persulfate. A low conversion sample was acquired to allow reactivity ratio studies. The reaction was terminated around 50% conversion due to the high viscosity of the reaction medium and as a precaution against copolymer drift. DABAM-25 was synthesized in a similar manner previously described[22]. The polymers were precipitated in acetone, redissolved in deionized water, then dialysed using Spectra/Por 4 dialysis bags with molecular-weight cutoffs of 12 000 to 14 000 g mol^{-1}. After dialysis, the polymers were isolated by lyophilization.

Synthesis of the copolymer of 4-(2-acrylamido-2-methylpropanedimethylammonio)butanoate with acrylamide (Scheme 2)

The polymerization procedure for DABAM-25 was conducted in a similar manner as previously reported[22].

Copolymer characterization

^{13}C n.m.r. spectra of the copolymers were obtained at 50.3 MHz on a Bruker AC200 spectrometer using 15–20 wt% aqueous (D_2O) polymer solutions with DSS as a reference. A recycle delay of 8 s, 90° pulse length, and gated decoupling to remove all NOE were employed for quantitative spectral analysis. Molecular weight studies were performed with a Chromatix KMX-6 low angle laser light scattering instrument. Refractive index increments were obtained using a Chromatix KMX-16 laser differential refractometer.

Viscosity measurements

Polymer solutions were made by dissolving designated amounts of polymer in the stock electrolyte solutions. The solutions were then diluted to appropriate concentrations and allowed to age for seven to ten days before being analysed with a Contraves LS-30 rheometer. Duplicate runs were conducted and reproducibility found to be within ±3–7% dependent on the magnitude of the viscosity values. Intrinsic viscosities were evaluated using the Huggins equation.

RESULTS AND DISCUSSION

Monomer synthesis

2-(2-Acrylamido-2-methylpropyldimethylammonio) ethanoate (*Scheme 1*) was synthesized utilizing a method commonly used to prepare small molecule surfactants with carboxybetaine head groups. The advantages of the method vs typical basic hydrolysis procedures (using alkali hydroxides) are the relatively mild conditions and the absence of inorganic electrolyte by-products which, due to the limited solubility of zwitterions in organic solvents, may be difficult to remove. Briefly, the monomeric tertiary amine was quaternerized by the reaction with methylbromoacetate and, after isolation, was percolated through an anionic exchange resin of the hydroxide form (OH^-). The associated hydroxide ion promotes hydrolysis of the ester functionality with methanol as the by-product to yield the zwitterionic product. Due to the hygroscopic nature of the product, the monomer was isolated as a bromide salt by addition of one equivalent of HBr[20,22]. A ^{13}C n.m.r. spectrum of the monomer is shown in *Figure 1*.

Compositional and reactivity ratio analysis

The concentrations of charged groups incorporated into polyampholytic systems affect the solution behaviour of the resulting polymers. Inter- and intramolecular associations as well as solubility have been shown to be directly related to the charge density of the systems[13,22,32,33]. To investigate this issue for poly(vinylcarboxybetaine), a series of copolymers were synthesized and reactivity ratios determined. The reaction parameters and compositions of low conversion copolymer samples, determined from ^{13}C n.m.r. by integration of the carbonyl peaks, are presented in *Table 1*. From the experimental compositions, reactivity ratios for the AM(M_1)/AMPDAE(M_2)

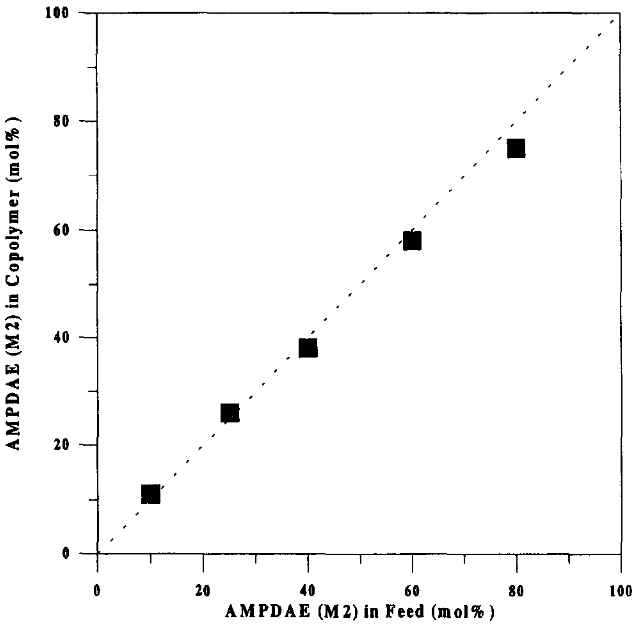


Figure 2 Mole percent AMPDAE incorporated into the copolymers as a function of comonomer ratio

Table 2 Structural data for the copolymers of acrylamide (M_1) with 2-(2-acrylamido-2-methylpropyldimethylammonio) ethanoate (M_2)

Sample number	M_1 in copolymer (mol%)	Blockiness mol% M_1–M_1	M_2–M_2	Alternation mol% M_1–M_2	Mean seq. length M_1	M_2
DAEAM-10	89.0	78.78	0.78	20.00	8.67	1.08
DAEAM-25	74.0	52.93	4.93	42.14	3.56	1.23
DAEAM-40	62.0	35.56	11.56	52.88	2.28	1.46
DAEAM-60	42.0	14.53	30.53	54.94	1.57	2.03
DAEAM-80	25.0	4.52	54.52	40.96	1.21	3.76

Table 3 Classical light scattering data for the copolymers of acrylamide (M_1) with 2-(2-acrylamido-2-methylpropyldimethylammonio) ethanoate (M_2)

Sample	AMPDAE found[a] (mol %)	$M_w \times 10^{-6}$ (g mol^{-1})	$A_2 \times 10^4$ (ml mol g^{-2})	$DP \times 10^{-4}$
DAEAM-10	11.0	7.4	2.7	8.5
DAEAM-25	26.0	10.4	2.4	9.4
DAEAM-40	38.0	7.5	1.3	5.6
DAEAM-60	58.0	6.3	1.4	3.8
DAEAM-80	75.0	10.2	0.8	5.2
DAEAM-100	100[b]	7.3	0.7	3.2
DABAM-25[c]	22.4	10.2	0.8	8.7

[a] Determined from ^{13}n.m.r.
[b] Theoretical value
[c] mol% AMPDAB found

copolymers were determined by the methods of Fineman–Ross[29], Kelen–Tudos[30], and nonlinear least squares (NLS)[31]. The methods yielded values (±0.05) of $r_1 = 0.86$, $r_2 = 0.70$; $r_1 = 0.85$, $r_2 = 0.69$; and $r_1 = 0.86$, $r_2 = 0.70$, respectively. The experimentally measured copolymer composition as a function of feed composition is shown in *Figure 2*; the dashed line represents ideal incorporation. The random comonomer incorporation is in accord with the behaviour of other acrylamido type monomers previously studied in our laboratories[13,14,22]. The methods of Igarashi[31] were employed to determine the microstructural composition (*Table 2*) using the reactivity ratios from the Kelen–Tudos method.

Low angle laser light scattering

Table 3 shows the weight-averaged molecular weights determined by low-angle laser light scattering at 25°C in 1 M NaCl. The molecular weight for the DAEAM series varies from 6.3 to 10.4×10^6 g mol^{-1}. These values demonstrate the high reactivity of acrylamido monomers. The second virial coefficients (A_2) for the DAEAM series have values between 2.7 to 0.8×10^{-4} ml · mol g^{-2}. The trend suggests that as more of the zwitterionic comonomer is incorporated into the copolymer, the lesser the extent of polymer/solvent interaction. This behaviour is representative of polyampholytic systems in aqueous solutions which typically have low A_2 values.

SOLUTION BEHAVIOUR

Solubility of DAEAM series

AMPDAE was copolymerized with AM in varying molar ratios to yield water soluble ionic copolymer systems. Since these polymers can behave as polyelectrolytes or polyampholytes depending on the pH of the solution, the viscosity behaviour of the above copolymers was studied as a function of pH and added electrolytes at 25°C and a shear rate of 6 s^{-1} utilizing a Contraves LS-30 rheometer.

The numbers to the right of DAEAM in the following discussion indicate the mol% of AMPDAE present in the polymerization. Copolymers of DAEAM series are soluble in deionized water at all pH values. Even DAEAM-100, a homopolymer of AMPDAE, is soluble. Most polyzwitterions require the addition of electrolytes to screen attractive charge–charge interactions to achieve solubility. The solubility of DAEAM-100 and other examples referenced in the Introduction indicate that structural features of the monomer units as well as the polymer backbone are important in determining solubility in aqueous media.

Effects of added electrolytes

The effect of sodium chloride on the intrinsic viscosities of the DAEAM copolymers at pH 8 are shown in *Figure 3*. Complex solution behaviour is observed and is related to the amount of AMPDAE incorporated into the copolymers. For DAEAM-10, -25 and -40 a decrease in the intrinsic viscosity upon the addition of sodium chloride is observed. As more sodium chloride is added, the intrinsic viscosity increases. The concentration of sodium chloride required to induce this increase is dependent on the number of zwitterionic comonomers incorporated into the copolymer. The decrease in intrinsic viscosity at low concentration may be explained by the elimination of intermolecular coulombic interactions. Further addition of the electrolyte enhances the solvent quality as charge–charge interactions are screened and the hydrodynamic volume of the polymer increases. This behaviour has been observed previously for low charge density polyampholytic systems[13,22,32,33]. At incorporations of AMPDAE of 60 mol% or greater (DAEAM-60, -80, -100), this behaviour is no longer observed. Instead, the intrinsic viscosity increases with addition of sodium chloride. This suggests that the coulombic interactions between the oppositely

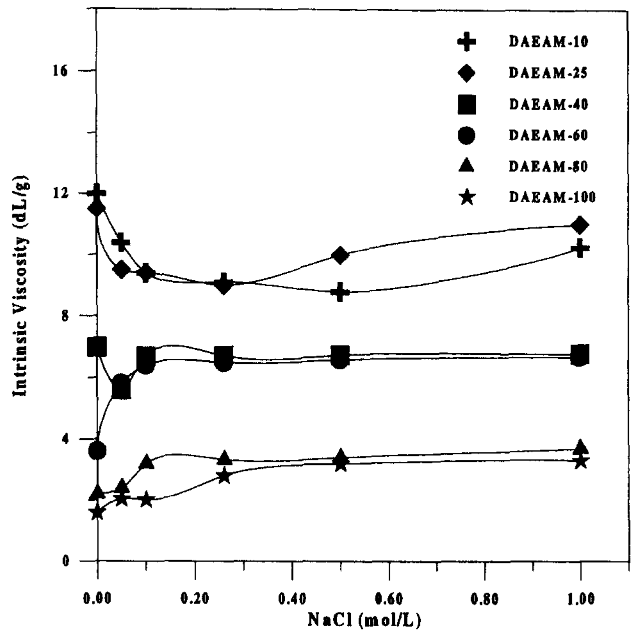


Figure 3 Intrinsic viscosities of DAEAM copolymers as a function of NaCl concentration

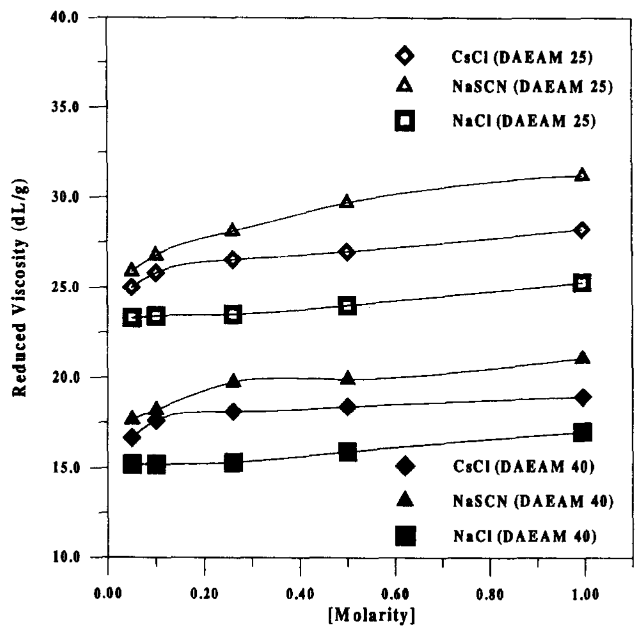


Figure 4 Reduced viscosities for DAEAM 25 and DAEAM 40 as a function of increasing ionic strength of various salts ($C_p = 0.3\,g\,dl^{-1}$)

charged species are intramolecular in deionized water. Therefore, addition of sodium chloride acts to disrupt or shield these interactions and solvation of the polymer is enhanced.

The nature of the counterions of the added electrolyte has also been investigated. *Figure 4* shows the reduced viscosity of DAEAM-25 and DAEAM-40 as a function of increasing ionic strength utilizing NaCl, NaSCN, and CsCl. The order of the electrolytes in terms of increasing reduced viscosity is NaSCN > CsCl > NaCl in accord with the Hoffmiester lytropic series[35]. This behaviour has been attributed to a stronger interaction of the larger, more polarizable counterions with the charged moieties of the zwitterionic comonomer[7]. In addition, effects of the electrolyte species on the water structure and, therefore, polymer/solvent interactions must be considered.

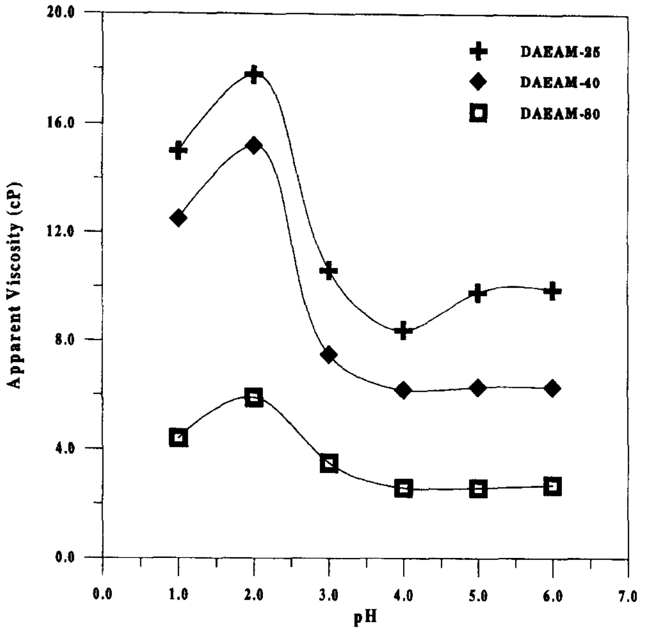


Figure 5 Apparent viscosities of DAEAM copolymers at various pH values ($C_p = 0.3\,g\,dl^{-1}$)

Effects of pH

The zwitterionic comonomer in the DAEAM series possesses a carboxylate moiety and thus should be sensitive to changes in the pH of the aqueous medium. Therefore studies were conducted on the copolymers as function of pH in deionized water and in the presence of added electrolytes.

Shown in *Figure 5* are the effects of pH on the apparent viscosity of DAEAM-25, -40 and -80. All of the copolymers display maxima. This behaviour demonstrates the transition of the copolymers from polyzwitterions to polycations. As the pH is lowered, the carboxylate moieties are progressively protonated into the carboxylic acid moiety. The polymer coil acquires an overall positive charge due to the quaternary ammonium species and charge repulsions force the coil to expand. Larger hydrodynamic volumes and therefore enhanced viscosities are observed. Further lowering of the pH increases the concentration of hydronium and chloride ions which act to shield the charge repulsions between the ammonium moieties and, therefore, a reduction in the viscosity is observed. Hydrophobic effects may also be operative.

DAEAM-25 and -40 show a greater enhancement in viscosity as the pH is lowered compared to DAAAM-80. The weight average molecular weights of DAEAM-25 and DAEAM-80 are similar (around 10 million) while the degree of polymerization of DAEAM-40 and DAEAM-80 are similar ($\approx 50\,000$). One would intuitively expect that the copolymer possessing the greatest number of charged groups would experience the greatest charge–charge repulsions and therefore attain the largest hydrodynamic volume leading to higher viscosity values. This behaviour is not observed. The inherent bulkiness of the AMPDAE comonomer may cause hindered rotation, thus restricting the degrees of freedom along the polymer backbone. Hydration of the polymer coil

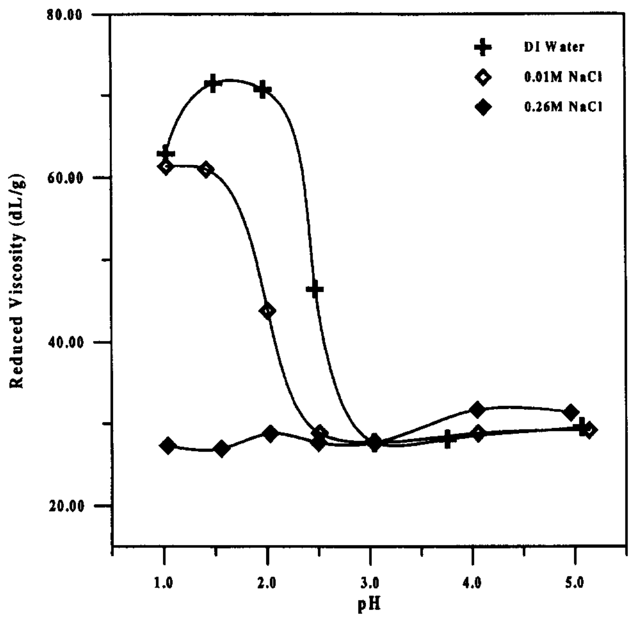


Figure 6 Reduced viscosities of DAEAM 25 in deionized water and NaCl solutions as a function of pH(C_p = 0.3 g dl^{-1})

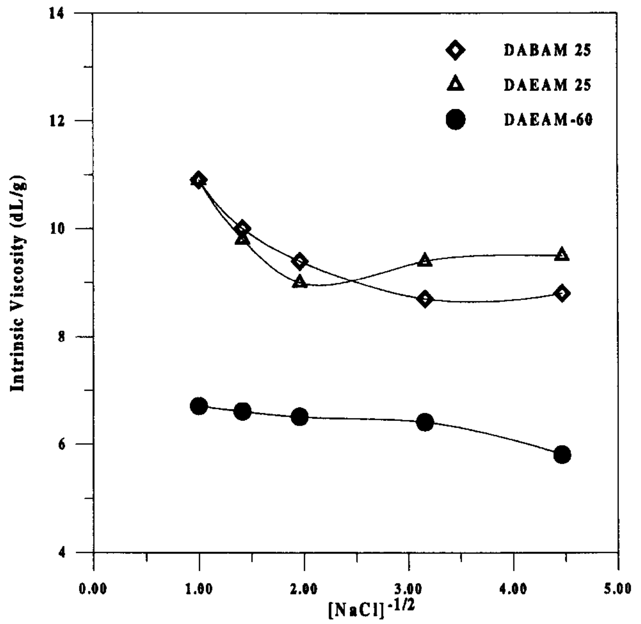


Figure 7 Intrinsic viscosities of DAEAM 25, DABAM 25, and DAEAM-60 as a function of the inverse square root of ionic strength for NaCl

must also be considered since the acrylamide mer units are well solvated in aqueous media.

The pH value required to protonate the carboxylate moiety is obviously influenced by the neighbouring ammonium moiety. Potentiometric studies by Laughlin and others[26,27,34,36] and ^{13}C n.m.r. measurements by Chevalier and Le Perchec[37] on small molecule carboxybetaines have clearly demonstrated this behaviour. Carboxybetaines with one methylene unit between the carboxylate and the quaternary ammonium groups have pK_a values near 2.0. This is considerably lower than the normal value of carboxylic acids which typically have pK_a values around 4.5.

The effects of pH on the reduced viscosity for DAEAM-25 were also examined in the presence of added electrolytes and are shown in *Figure 6*. At pH values above 3, the copolymer has a slightly higher viscosity in the presence of 0.26 M NaCl than in deionized water or in 0.017 M NaCl. The copolymer above pH 3 is zwitterionic in nature and thus charge–charge interactions are shielded in the presence of added electrolytes, leading to an enhancement in viscosity. At pH values below 3, the polymer becomes polycationic in nature for reasons discussed above. In 0.26 M NaCl, these charges are sufficiently shielded and no enhancement in viscosity is observed as the pH is lowered. In 0.017 M NaCl, lower pH values are required before an increase in viscosity is observed. This may be explained by a shielding of the initial cationic charges which are formed as a result of lowering the pH. Further lowering of the pH neutralizes more carboxylate anions yielding quaternary ammonium groups which are closer in proximity than the Debye shielding length. Thus, charge–charge repulsions arise leading to an expansion of the polymer coil. Similar viscosities are observed at pH = 1 in deionized water and in 0.017 M NaCl. Furthermore, no maximum is observed in 0.017 M NaCl. This supports the observation that the increase in ionic strength at low pH values is responsible for the decrease in viscosity in deionized water.

Effect of the number of methylene units between charges on the zwitterionic comonomer

In an effort to gain further understanding of polyzwitterions possessing carboxybetaine mer units, solution behaviour has been studied for two polymeric systems that have different spacer lengths between the quaternary ammonium group and the carboxylate group. DAEAM-25 contains one methylene group between charges while DABAM-25 has three methylene groups (*Scheme 2*). Both copolymers have similar molecular weights with DAEAM-25 having a molecular weight of 10.4 × 10^6 g mol^{-1} and DABAM-25 a molecular weight of 10.2× 10^6 g mol^{-1} (*Table 3*). Thus, a structural comparison may tentatively be drawn between the two systems.

In *Figure 7*, the intrinsic viscosity of DAEAM-25, DABAM-25, and DAEAM-60 as a function of the inverse square root of ionic strength of sodium chloride is shown. The intrinsic viscosities of polyelectrolytes normally display a linear relationship with a positive slope when plotted in this manner. In this case, no linearity in the graph is observed except possibly at the higher ionic strengths where the slope is negative. The deviation at the lower ionic strengths may be a result of the intermolecular associations discussed earlier. The curve for DAEAM-60, which does not exhibit intermolecular associations, deflects downward at the lowest ionic strength measured, while those for DAEAM-25 and DABAM-25 deflect upwards. The negative slope at the higher ionic strengths is opposite of that observed for polyelectrolytes and indicates an increase in hydrodynamic volume as the ionic strength is increased. This 'anti-polyelectrolyte' effect is normally observed for polyampholytes. At the higher electrolyte concentrations, both DAEAM-25 and DABAM-25 display essentially the same intrinsic viscosity. Therefore, at pH 8.5, no major differences in the hydrodynamic volume of the two copolymers in sodium chloride solutions are apparent. Although one might expect that increasing the number of methylene groups would

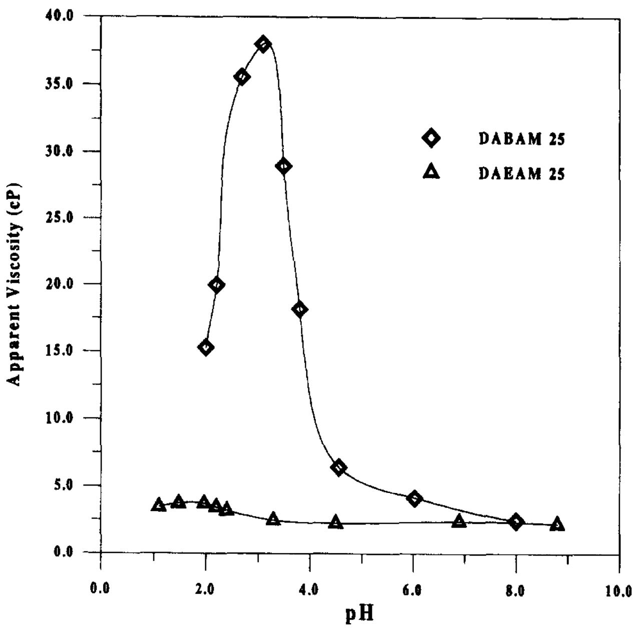


Figure 8 Apparent viscosities of DAEAM 25 and DABAM 25 in deionized water as a function of pH ($C_p = 0.1\,\mathrm{g\,dl^{-1}}$)

enhance the hydrophobicity, small molecule studies of surfactants containing carboxybetaine head groups suggest that a spacer length of three methylene units results in a more hydrophilic head group than a one methylene spacer unit[26,27]. Chevalier and Le Perchec have attributed this behaviour to an increase in the dipole moment of the head group as the charged centres are moved farther apart[37]. As the number of methylene groups increases to five or greater, however, hydrophobic effects dominate and the head group becomes less hydrophilic. Therefore a balance between the magnitude of the dipole moment, which enhances hydrophilicity, and the number of methylene groups in the spacer unit, which enhances hydrophobicity, influences the solution behaviour of zwitterionic compounds.

Solution behaviour as a function of pH has also been determined for DAEAM-25 and DABAM-25 at a polymer concentration of 0.1 g dl^{-1} (*Figure 8*). At pH 8, both copolymers have essentially the same viscosity; however, as the pH of the solution is lowered, differences between the two copolymers become evident. DABAM-25 acquires a measurable positive charge at pH 6, as evidenced by an increase in viscosity, and displays a viscosity maximum around pH 3. The viscosity of DAEAM-25 remains relatively constant until the pH falls below 3, the viscosity maximum occurring around a pH of 1.5–2. The differences in the viscosity maxima can be attributed to the differences in basicity of the two distinct carboxylate groups. As discussed earlier, small molecule studies report a pK_a value near 2 for a carboxybetaine with one methylene unit between charge centres. For a carboxybetaine with three methylene units between charge centres, this value increases to 4[26,27,37]. This effect arises through induction from the positive field generated by the quaternary ammonium group which acts to lower the basicity of the carboxylate group, the closer the two spatially become. In addition, the differences in the viscosity value between the observed maxima is almost an order of magnitude greater for DABAM-25. This behaviour may be attributed to the low pH values required to protonate the carboxylate functionality of the DAEAM copolymers. As the pH is lowered, the higher concentrations of hydronium and chloride ions increase the ionic strength and effectively screen the cationic charge centres. This effect is also observed for DABAM-25 which exhibits a decrease in viscosity below pH 3. Other factors, such as hydrophobic and nearest neighbour effects, are also likely operative.

CONCLUSIONS

Copolymers of acrylamide with 2-(2-acrylamido-2-methylpropyldimethylammonio) ethanoate have been prepared by free radical polymerization in an aqueous NaBr solution. Reactivity ratios and copolymer microstructures were determined and indicate random incorporation of both comonomers. Weight average molecular weights in the range of 6.3–10.4 × 10^6 g mol^{-1} have been determined for the copolymer series. Second virial coefficients were found to decrease as the mol% of AMPDAE incorporated into the copolymers increased. All of the polymers in the DAEAM series are soluble in deionized water. Intrinsic viscosity studies as a function of NaCl concentration suggest a decrease in intermolecular associations and an increase in intramolecular associations as the mol% of AMPDAE incorporated into the copolymers increases. Copolymers containing 60 mol% or more show an enhancement in viscosity as the concentration of added electrolytes is increased as a result of the shielding of intramolecular associations between the zwitterionic groups. The nature of added electrolytes also influences the solution behaviour; the larger, more polarizable ions enhance viscosity more than smaller ions and trend with the Hoffmiester series. The presence of carboxylate groups renders the copolymers responsive to changes in pH of the aqueous environment. As pH is lowered, the carboxylate groups are progressively protonated, resulting in an enhancement in viscosity; however, the addition of electrolytes negates the increase in viscosity due to shielding effects. Solution properties of DAEAM-25 and DABAM-25 are similar at high pH values. As pH is lowered, DABAM-25 displays a much more dramatic increase in viscosity. This behaviour is likely a result of the much lower pH required to protonate the carboxylate group of the AMPDAE mer unit.

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