

# Dilute solution properties of poly(3-dimethyl acryloyloxyethyl ammonium propiolactone)

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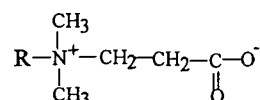
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The aqueous solution properties of an ampholytic poly(3-dimethylacryloyloxyethyl ammonium propiolactone), poly(DMAEAPL), are examined in this study by measuring reduced viscosity, intrinsic viscosity, degree of binding and dynamic light scattering. This polyampholyte's intrinsic viscosity is related to the type and concentration of the salt added. The intrinsic viscosity behaviour for the polyampholyte resulting from the associations of the polymer chains is in contrast with cationic and anionic polyelectrolyte. The polyampholyte in high concentration of NaCl has a low degree of binding, indicating that the proton ion ( $H^+$ ) has difficulty in binding to the carboxylate group ( $COO^-$ ) at the polymer end. The carboxybetaine, DMAEAPL, has a higher degree of binding than the corresponding sulfobetaine, DMAPS. Dynamic light scattering measurements indicate that the poly(carboxybetaine) diffusion coefficients decrease and the chain dimensions increase with an increasing salt concentration. The models proposed in this study can account for the poly(DMAEAPL) solution viscometrics and the degree of binding. © 1997 Elsevier Science Ltd.

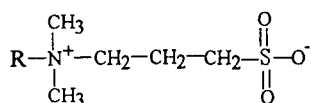
(Keywords: polyampholyte; reduced viscosity; intrinsic viscosity)

## INTRODUCTION

The internal salts of betaine substances such as carboxybetaine,



and sulfobetaine,

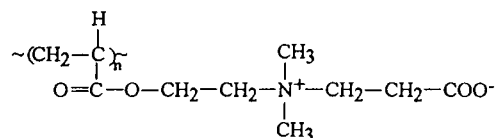


are widely used in textile, medical, and other branches of industry<sup>1-8</sup>. Sulfobetaine monomers such as acryloyl or methacryloyl ammonium propane sulfonate are the functional monomers frequently used as minor components for copolymers in dispersing agents, medical, membrane, adhesive and latex<sup>1,3-6,9-11</sup>. For instance, Szita *et al.* and Priestersbach *et al.* reported that such a monomer is polymerizable with acrylonitrile and can be applied to the dyeing processing of textiles<sup>3-5</sup>. Ishikura *et al.* also used this polymerizable monomer to enhance the physical properties of emulsions<sup>6</sup>.

Several investigators studied the aqueous solution properties of betaines<sup>12-21</sup>. Topchiev *et al.* investigated the kinetic features of the radical polymerization of an unsaturated carboxybetaine in various pH ranges<sup>13</sup>. Asonova *et al.* also reported that such a polycarboxybetaine had a varied reduced viscosity as a function of pH<sup>12</sup>. Moreover,

Salamone *et al.* thoroughly examined the solution properties of sulfobetaine homopolymers, particularly in the vinylimidazole series<sup>14-19</sup>.

Correspondingly, many workers have investigated the effects of various salt ions on the interaction of polyelectrolytes in the aqueous solution<sup>20-32</sup>. The same is true for site-binding interaction of salt ions and polymers by Huggins equation and Huggins constant  $k'$ . The counterion size has been confirmed to have militated the degree of site binding for salt ion attracting polymers<sup>20-32</sup>. A series of poly(betaine)s and corresponding cationic polyelectrolytes with different electro-drawing groups and varying the methylene units between the charge groups were researched previously<sup>33,34</sup>. Previous works have also addressed the aqueous properties of polyelectrolytes such as cationic polyelectrolyte, poly(dimethyl sulfate quaternized dimethylaminoethyl methacrylate) [poly(DMAEM.C<sub>2</sub>H<sub>6</sub>SO<sub>4</sub>)]<sup>30</sup>, and polyampholyte, poly[3-dimethyl (methacryloyloxyethyl) ammonium propane sulphonate] [poly(DMAPS)]<sup>31</sup>. Moreover, aqueous polyelectrolytes have been extensively studied and comprehensively described in numerous reviews<sup>12-35</sup>. In contrast, systematic investigations of aqueous polycarboxybetaines are relatively few<sup>12,35</sup>. Our primary interest is drawn toward the difference of solution properties among poly(carboxybetaine) and poly(sulfobetaine). Thus, this study examines the aqueous solution properties of a poly(carboxybetaine), poly(DMAEAPL),



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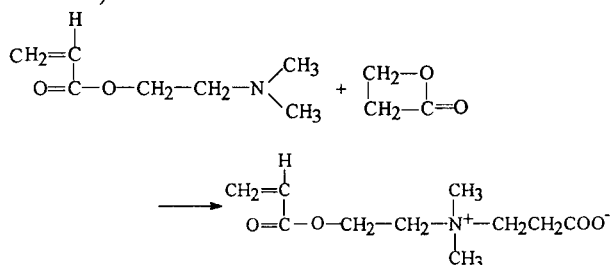
particularly in reduced viscosity, intrinsic viscosity and the degree of binding in the presence of various salts. In addition, quasielastic light scattering (QELS) was employed to obtain the entire chain dimensions and dynamics. Furthermore, the proposed schematic models were used to accurately describe their properties.

## EXPERIMENTAL

### Synthesis of monomers

3-Dimethyl (acryloyloxyethyl) ammonium propiolactone, (DMAEAPL). In a 0.25 L flask equipped with a stirrer, a cooler, and a thermometer, dimethylaminoethyl acrylate and dried acetone were charged under a  $N_2$  atmosphere and the contents were stirred at *ca.* 15°C. A mixture of  $\beta$ -propiolactone and dried acetone was added dropwise for 2 h. Following completion of the addition, the mixture was stirred for 2 h and allowed to stand at the same temperature for 4 h. The white crystals were accumulated by filtration, washed with dry ether several times, and dried under reduced pressure to obtain white crystals (DMAEAPL).

(DMAEAPL).



### Preparation of poly(3-dimethylacryloyloxyethyl ammonium propiolactone), poly(DMAEAPL)

The monomer (DMAEAPL) (0.02 mol) and 0.1 g (2.0 mol%) of 4,4'-azo-bis-4-cyanovaleric acid (ACVA) were introduced into a 100 mL ampoule. To this solution, 50 mL of distilled water were added to produce a 0.4 M aqueous solution. The ampoule contents were then flushed with argon and sealed in a vacuum after utilizing of the freeze-thaw technique. Next, the ampoule was placed in a constant temperature bath for 24 h. The heterogeneous polymer solutions were then precipitated with acetone, washed with isobutanol to eliminate the unreacted monomer, and dried for 24 h at 70°C under vacuum and weighed. A dried, brittle, and white polymer was subsequently obtained: yield, 96%;  $T_g$ , 177°C (by DSC at 10°C  $cm^{-1}$ ). The intrinsic viscosity was calculated to be 1.51 dL/g in 0.5M NaCl solution with an Ubbelohde viscometer at 30°C.

### Viscometric measurements

Viscometric measurements were carried out with a Ubbelohde viscometer (the viscometer has a flow time of 79.19 sec in the pure water) at 30.00  $\pm$  0.01°C. The polymer samples were dissolved in the salt concentration to yield a stock solution of approximately 1 g/100mL solvent.

Viscosity data were calculated by the Huggins equation<sup>24,26</sup>:

$$\frac{\eta - \eta_0}{\eta_0 C} = \frac{\eta_{sp}}{C} = [\eta] + k'[\eta]^2 C. \quad (1)$$

### pH measurements

The pH measurements were used with the KYOTO ELECTRONICS AT-210 instrument with a Mallinckrodt standard buffer solution (pH 7.00  $\pm$  0.01 and 4.01  $\pm$  0.01 at 25°C). The instrument's sensitivity was of 0.01 pH unit. Experiments were performed with solutions containing monomer or polymer 0.10 g in 50 mL.

### Quasielastic light scattering (QELS) measurements

The polymer solutions used in the QELS measurements were carefully filtered prior to placing into the light scattering apparatus.

The quasielastic light scattering instrument used in these experiments was the OTSUKA DLS7000. All QELS measurements were performed at room temperature in the dilute solution regime, i.e. polymer concentration was 1000 ppm.

## RESULTS AND DISCUSSION

### Hygroscopic monomer

The monomer 3-dimethyl (acryloyloxyethyl) ammonium

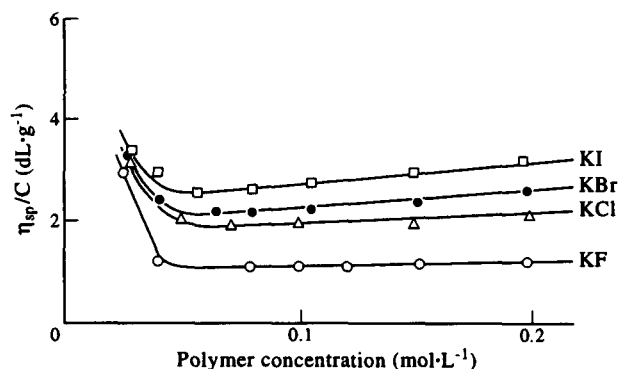
propiolactone (DMAEAPL) was quite hygroscopic (M.P. 126°C). Elemental analysis ( $C_{10}H_{17}N_1O_4$ ): calcd.: C, 55.80%; H, 7.90%; N 6.50%. Found: C, 55.50%, H, 8.17%, N, 6.34%. The monomer's hygroscopicity hindered the analysis. This phenomenon was also observed in other literature<sup>30,31,36</sup>.

The monomer's structure was further characterized by i.r. and n.m.r. The i.r. spectra of the DMAEAPL obtained confirms the proposed structure. The stretching vibrations of C = O and C-O bonds in the ester group are located at 1724 and 1175  $cm^{-1}$ , respectively. The stretching vibration of the C = C double bond is represented by a strong band in the 1600  $cm^{-1}$  region. In this region, there is a superposition of the bands of the stretching vibrations of the C = C double bond and the asymmetric stretching vibrations of the  $\begin{array}{c} \text{---C---O}^+ \\ | \\ \text{O} \end{array}$

group. The symmetrical stretching vibrations of this group are represented by the band at 1380  $cm^{-1}$ . A medium intensity band in the 820  $cm^{-1}$  region corresponds to the C-H deformation vibrations of the vinyl group, and the deformation vibrations appear in the 1480  $cm^{-1}$  region. N.m.r. ( $D_2O$ , 4.63ppm),  $\delta$  6.5-5.8 (m, 3H,  $CH_2 = CH$ ); 4.51 (m, 2H,  $COOCH_2$ ); 3.65(m 2H,  $COOCH_2CH_2$ ); 3.10 (s, 6H,  $^+N(CH_3)_2$ ); 3.55 (m, 2H,  $^+NCH_2$ ); 2.52 (m, 2H,  $CH_2COO^-$ ).

### Measurement of the viscosity of poly(DMAEAPL)

The intrinsic viscosity is generally accepted to be an effective measure of the hydrodynamic volume of the polymer containing the same molecular weight. Therefore, determining the intrinsic viscosity of poly(DMAEAPL) in the presence of different electrolytes should reflect the



**Figure 1** Reduced viscosities of poly(DMAEAPL) as a function of concentration for salts containing a common cation in 0.1 M salt aqueous solution

**Table 1** Effect of various salt solutions on the viscosity behaviour of poly(DMAEAPL) at 30°C

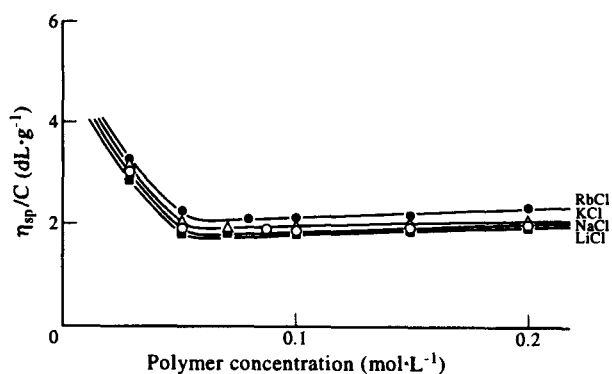
Salt solution (0.1 M)	Common cation [ $\eta$ ] (dL/g)	$k'$
KF	1.01	0.75
KCl	1.73	0.65
KBr	1.94	0.58
KI	2.25	0.45

influence of these salts on the polymer chain's hydrodynamic volume.

The intrinsic viscosity of poly(DMAEAPL) in the presence of different electrolytes is discussed as follows: (1) common cations (KF, KCl, KBr and KI); (2) common anions (LiCl, NaCl, KCl and RbCl); and (3) divalent cations ( $MgCl_2$ ,  $CaCl_2$ ,  $SrCl_2$  and  $BaCl_2$ ). Figure 1 shows the influence of different electrolytes with a common cation,  $K^+$ , on the intrinsic viscosities of poly(DMAEAPL).

The intrinsic viscosity [ $\eta$ ] and Huggins constant  $k'$  can be calculated according to Figure 1 and equation (1). Table 1 summarizes those results. The data reveal an increase in the intrinsic viscosity of poly(DMAEAPL) in 0.5 M aqueous salt solution in the order  $KF < KCl < KBr < KI$ . These phenomena are the same as polysulfobetaine behaviours.<sup>31</sup> These results coincide with the Pearson principle, which states that hard acid species prefer binding with a hard base species and soft acid species prefer binding with a soft base species (the hard species, both acids and bases, tend to be smaller and slightly polarizable species; soft acids and bases tend to be larger and polarizable species)<sup>32,37</sup>. The hard acid species, e.g. potassium ion ( $K^+$ ), are easily bound to a small radius hard base, e.g. fluoride ion ( $F^-$ ). Hence, the fluoride ion ( $F^-$ ) is more easily attracted to potassium ion than chloride ion ( $Cl^-$ ), bromide ion ( $Br^-$ ) or iodide ion ( $I^-$ ). This result would reduce the site-binding degree of potassium ion ( $K^+$ ) on the carboxylate group ( $COO^-$ ), but also decreases the degree of the potassium ion ( $K^+$ ) rupturing the polymer network. The result yields to a lower intrinsic viscosity of the polyampholyte in KF salt aqueous solution. The polyampholyte's ionic condition was neutralized and the intrinsic viscosity started to increase. As indicated in Table 1, the value for the Huggins constant,  $k'$ , decreases as the intrinsic viscosity increases. This decrease in the Huggins constant may be associated with an increase of polymer-solvent interaction<sup>30,31</sup>.

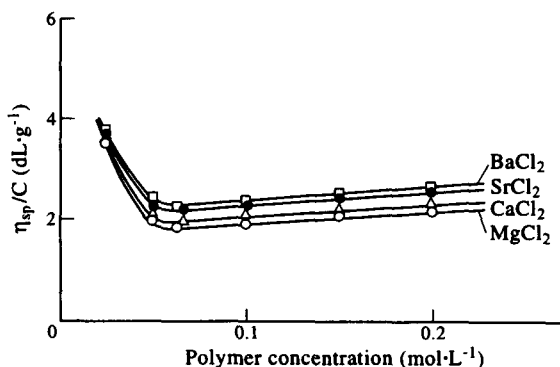
Figure 2 presents the influence of different electrolytes with a common anion,  $Cl^-$ , on the intrinsic viscosity of



**Figure 2** Reduced viscosity of poly(DMAEAPL) as a function of concentration for salts containing a common anion in 0.1 M salt aqueous solution

**Table 2** Effect of various salt solutions on the viscosity behaviour of poly(DMAEAPL) at 30°C

Salt solution (0.1 M)	Common anion [ $\eta$ ] (dL/g)	$k'$
LiCl	1.47	0.73
NaCl	1.51	0.70
KCl	1.73	0.65
RbCl	1.86	0.62



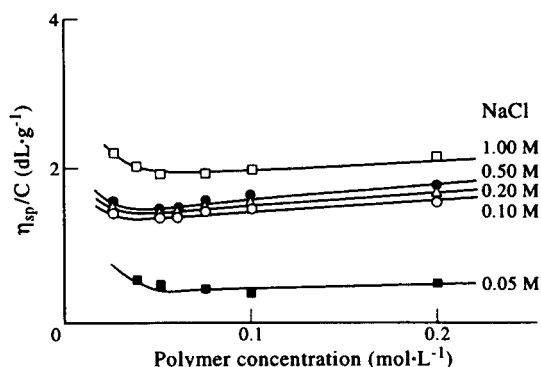
**Figure 3** Reduced viscosity of poly(DMAEAPL) as a function of concentration for salts containing a divalent cation in 0.1 M aqueous solution

poly(DMAEAPL). This figure reveals an increase in the intrinsic viscosity of poly(DMAEAPL) in 0.5 M aqueous solution in the order  $LiCl < NaCl < KCl < RbCl$ . These results also coincide with the Pearson principle, the hard base species, e.g. chloride ion ( $Cl^-$ ) are easily bound to a small radius hard acid, e.g. lithium ion ( $Li^+$ ). Hence, the lithium ion ( $Li^+$ ) is more easily attracted to chloride ion ( $Cl^-$ ) than ( $Na^+$ ), potassium ion ( $K^+$ ) or rubidium ion ( $Rb^+$ ). This result would not only reduce the site-binding degree of chloride ion ( $Cl^-$ ) on the quaternary ammonium group ( $R_4N^+$ ) but also decrease the degree of the chloride ion ( $Cl^-$ ) rupturing the polymer network. This event subsequently yields a lower intrinsic viscosity of the polycarboxybetaine in LiCl salt aqueous solution. Furthermore, Table 2 displays the Huggins constant in a common anion solution to be in the order  $LiCl > NaCl > KCl > RbCl$ . This tendency is the same as for the common cations.

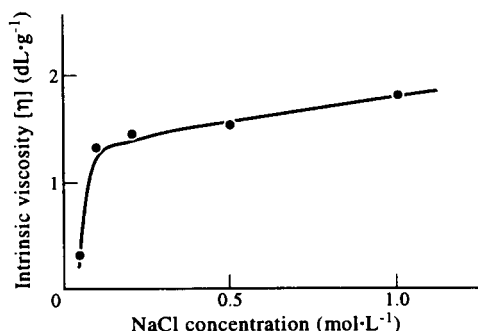
Figure 3 and Table 3 present the intrinsic viscosity and Huggins constant of poly(DMAEAPL) influenced by divalent cations. The data indicate an increase in the

**Table 3** Effect of various salt solutions on the viscosity behaviour of poly(DMAEAPL) at 30°C

Salt solution (0.1 M)	Divalent cation [η] (dL/g)	k'
MgCl <sub>2</sub>	1.70	0.74
CaCl <sub>2</sub>	1.88	0.65
SrCl <sub>2</sub>	2.06	0.53
BaCl <sub>2</sub>	2.13	0.49



**Figure 4** Reduced viscosities of poly(DMAEAPL) as a function of concentration for NaCl



**Figure 5** Intrinsic viscosity of poly(DMAEAPL) as a function of NaCl concentration

**Table 4** Effect of NaCl concentration on the intrinsic viscosity and Huggins constant of poly(DMAEAPL) at 30°C

Concentration of NaCl	[η] (dL/g)	k'
0.05 M	0.31	9.06
0.1 M	1.35	0.88
0.2 M	1.43	0.77
0.5 M	1.51	0.70
1.0 M	1.84	0.56

intrinsic viscosity of poly(DMAEAPL) in 0.5 M aqueous salt solution in the order MgCl<sub>2</sub> < CaCl<sub>2</sub> < SrCl<sub>2</sub> < BaCl<sub>2</sub>. This trend is similar to that of monovalent common anions (Table 1); that is, as the radius of the cation decreases, the intrinsic viscosity begins to decrease and the Huggins constant starts to increase. Furthermore, Figure 3 shows low intrinsic viscosities of the polycarboxybetaine solution resulting from the inter- and intra-associations of the polymer chains. While the salt was added, the associations began to drop. The ionic condition of the polycarboxybetaine was neutralized and the intrinsic viscosity started to increase.

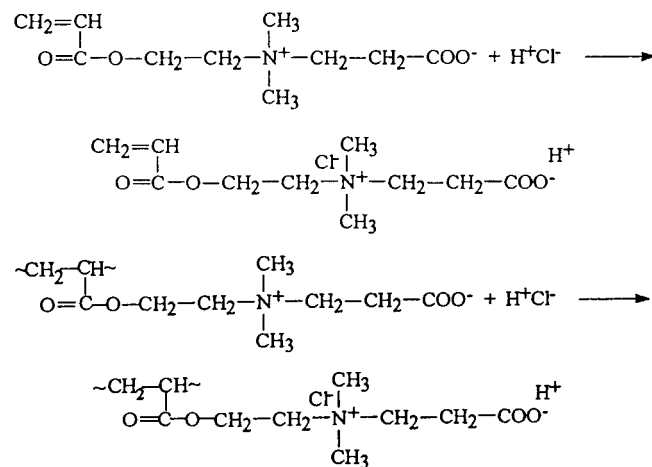
The intrinsic viscosities and Huggins constant of solutions of NaCl of different concentrations containing fixed poly(DMAEAPL) were determined. Figure 4 and Table 4 summarize those results. As the concentration of the salt was increased, the intrinsic viscosity began to increase and the Huggins constant started to decrease. These phenomena might be due to the addition of salt, which can loosen the compact structure caused by the inter- and intra-molecular ionic conditions; thus, the polymer can behave more freely in the salt solution<sup>31</sup>. Restated, the higher the salt concentration implies the lower the inter- and intra-associations and, subsequently, the higher the intrinsic viscosity. This result was also observed by Schulz<sup>38</sup> and Liaw<sup>31</sup>. Figure 5 plots the intrinsic viscosities [η], obtained by extrapolating the curves of Huggins plot (Figure 4) at constant simple electrolyte concentration [NaCl] to zero concentration of the polymer as a function of the medium's ionic strength. Results of the various salts for poly(DMAEAPL) are the same as those obtained for polysulfobetaine<sup>31</sup>, but are reversed from those for cationic polyelectrolyte<sup>30</sup>.

**Determination of QELS**

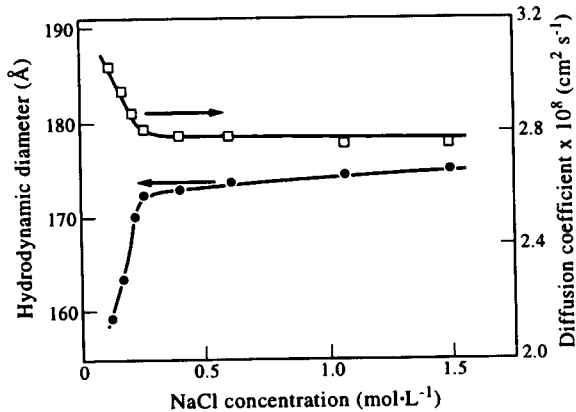
Figure 6 shows a plot of both average hydrodynamic diameter and diffusion coefficient of a poly(DMAEAPL) as a function of the increasing salt concentration. In general (i.e. > 0.5% NaCl), the hydrodynamic diameter rises with increasing salt levels, going from about 159 Å in 0.1 M NaCl(aq) to about 173 Å in 1.5 M NaCl(aq). Moreover, the largest increases in the hydrodynamic diameter occur in the low salt region which corresponds to the dilute solution rheology (Figure 5). The diffusion coefficient response is the mirror image of size response. The entire chain dimensions and dynamics were obtained. These phenomena are the same as for poly(sulfobetaine)<sup>38</sup>.

**Determination of degree of binding**

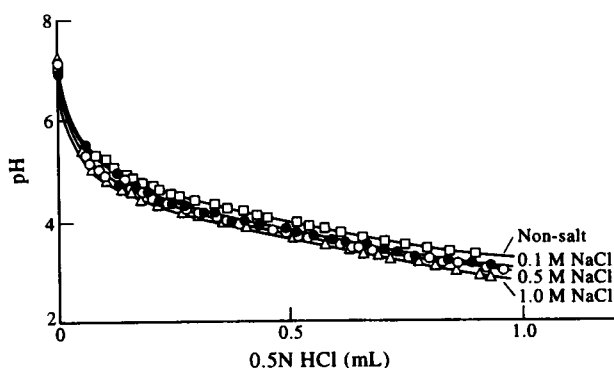
The nature of the potentiometric titration curve resembles that of the titration of a salt of a weak and a strong base with a strong acid (HCl). This permits the assumption that in neutral solutions, a carboxybetaine exists in the form of a bipolar ion and that the reaction with the acid takes place according to the following scheme for monomer and polymer carboxybetaines:



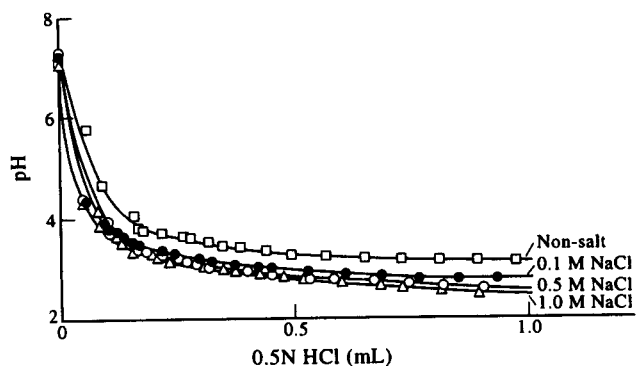
Potentiometric titration of the poly(DMAEAPL) and DMAEAPL with hydrochloric acid in aqueous solution was carried out both in the presence and absence of salt. Figure 7 summarizes the results for the DMAEAPL. As indicated in above figures, DMAEAPL monomer in the presence of



**Figure 6** QELS measurements on poly(DMAEAPL) solution: [polymer] = 0.1 g/dl, temperature = 30°C

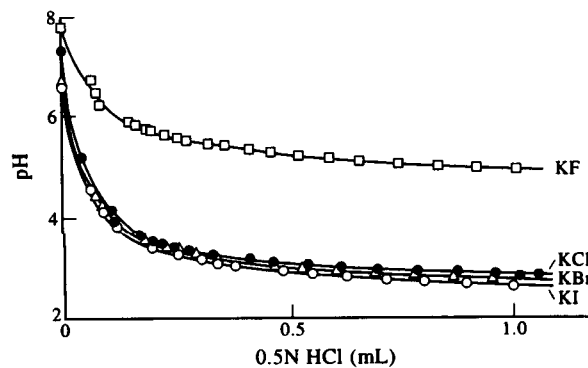


**Figure 7** Relationships of pH versus 0.5 N HCl: (□) DMAEAPL 0.1 g in H<sub>2</sub>O; (●) DMAEAPL 0.1 g in 0.1 M NaCl<sub>(aq)</sub>; (○) DMAEAPL 0.1 g in 0.5 M NaCl<sub>(aq)</sub>; (△) DMAEAPL 0.1 g in 1.0 M NaCl<sub>(aq)</sub>

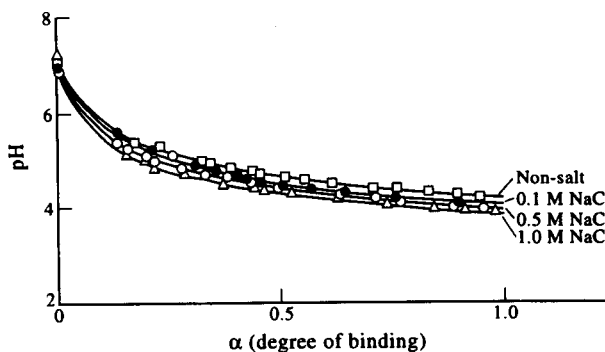


**Figure 8** Relationships of pH versus 0.5 N HCl: (□) poly(DMAEAPL) 0.1 g in H<sub>2</sub>O; (●) poly(DMAEAPL) 0.1 g in 0.1 M NaCl<sub>(aq)</sub>; (○) poly(DMAEAPL) 0.1 g in 0.5 M NaCl<sub>(aq)</sub>; (△) poly(DMAEAPL) 0.1 g in 1.0 M NaCl<sub>(aq)</sub>

NaCl salt has a lower pH value for the same amount of added HCl solution. The more salt added in solution implies the lower the pH value. A similar behaviour was also observed for the poly(DMAEAPL) in NaCl salt solution (Figure 8), implying that poly(DMAEAPL) and/or DMAEAPL monomer has a certain degree of sites binding with NaCl salt. The salt hinders the binding capability of the ampholytic poly(DMAEAPL) and/or DMAEAPL monomer with HCl solution. Consequently, the concentration of free HCl solution increases resulting in the lower pH value in the presence of salt. Figure 9 shows that the poly(DMAEAPL) in the various salt aqueous solutions with



**Figure 9** Relationships of pH versus 0.5 N HCl: (□) poly(DMAEAPL) 0.1 g in 0.1 M KF<sub>(aq)</sub>; (●) poly(DMAEAPL) 0.1 g in 0.1 M KCl<sub>(aq)</sub>; (△) poly(DMAEAPL) 0.1 g in 0.1 M KBr<sub>(aq)</sub>; (○) poly(DMAEAPL) 0.1 g in 0.1 M KI<sub>(aq)</sub>



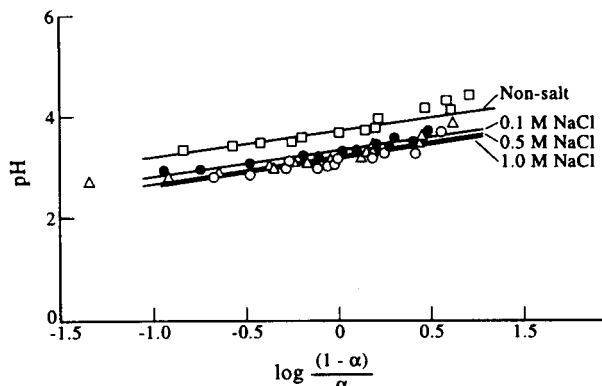
**Figure 10** Relationships of pH versus degree of binding ( $\alpha$ ): (□) DMAEAPL 0.1 g in H<sub>2</sub>O; (●) (DMAEAPL) 0.1 g in 0.1 M NaCl<sub>(aq)</sub>; (○) DMAEAPL 0.1 g in 0.5 M NaCl<sub>(aq)</sub>; (△) DMAEAPL 0.1 g in 1.0 M NaCl<sub>(aq)</sub>

a common cation (K<sup>+</sup>) has pH values in the following order KF > KCl > KBr > KI. This phenomenon is due to the decrease in site-binding degree of potassium ion (K<sup>+</sup>) on the carboxylate group (COO<sup>-</sup>) and the increase in proton ion bonded to it. Consequently, the ion radius increases, resulting in the lower pH value and degree of binding. A similar behaviour was also observed for the monomer DMAEAPL.

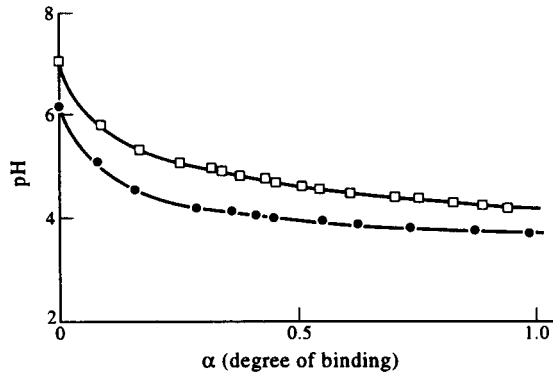
The pKa can be calculated from the modified Henderson-Hasselbach equation<sup>30,31,39</sup>

$$\text{pH} = \text{pKa} + n \log \frac{(1 - \alpha)}{\alpha}, \quad (2)$$

where  $\alpha$  is the degree of binding for the ampholytic poly-electrolyte poly(DMAEAPL) and/or DMAEAPL monomer with HCl solution and  $K_a$  is the constant of binding. The relationship between pH and  $\alpha$  can be calculated according to Figure 7 and equation (2). Figure 10 summarizes those results. This figure clearly indicates that the polyampholyte in the more presence of NaCl has a lower degree of binding ( $\alpha$ ) at the same pH value. A similar tendency was also observed for the monomeric amphoteric (DMAEAPL). This phenomenon could be accounted for by the difficulty of the proton ion (H<sup>+</sup>) to bind to the carboxylate group (COO<sup>-</sup>) at the polymer end, thereby resulting in the lower degree of binding in the larger presence of NaCl. Moreover, the pKa could be calculated according to the plot of pH versus  $\log \left[ \frac{1-\alpha}{\alpha} \right]$ , where pKa is equal to the pH as  $\alpha$  is equal to 0.5. Figure 11 presents the results for the poly(DMAEAPL) in various concentrations of NaCl salt



**Figure 11** Relationships of pH versus  $\log \frac{1-\alpha}{\alpha}$ : (□) poly(DMAEAPL) 0.1 g in H<sub>2</sub>O; (●) poly(DMAEAPL) 0.1 g in 0.1 M NaCl<sub>(aq)</sub>; (Δ) poly(DMAEAPL) 0.1 g in 0.5 M NaCl<sub>(aq)</sub>; (○) poly(DMAEAPL) 0.1 g in 1.0 M NaCl<sub>(aq)</sub>



**Figure 12** Relationships of pH versus degree of binding (α): (□) DMAEAPL 0.1 g in H<sub>2</sub>O; (●) DMAPS 0.1 g in H<sub>2</sub>O

**Table 5** Effect of the NaCl<sub>(aq)</sub> concentration on the Ka of DMAEAPL and poly(DMAEAPL) titrated with HCl<sub>(aq)</sub>

Sample	K <sub>a</sub> × 10 <sup>-4</sup>			
	in H <sub>2</sub> O	0.1 M NaCl <sub>(aq)</sub>	0.5 M NaCl <sub>(aq)</sub>	1.0 M NaCl <sub>(aq)</sub>
DMAEAPL	4.70	4.42	4.40	4.38
Poly(-DMAEAPL)	3.72	3.38	3.24	3.22

**Table 6** Effect of the various salt solutions with common cation (K<sup>+</sup>) on the Ka of DMAEAPL and poly(DMAEAPL) titrated with HCl<sub>(aq)</sub>

Sample	K <sub>a</sub> × 10 <sup>-4</sup>			
	0.1 M KF <sub>(aq)</sub>	0.1 M KCl <sub>(aq)</sub>	0.1 M KBr <sub>(aq)</sub>	0.1 M KI <sub>(aq)</sub>
DMAEAPL	5.76	4.45	3.64	3.22
Poly(DMAEAPL)	4.62	3.37	3.13	2.84

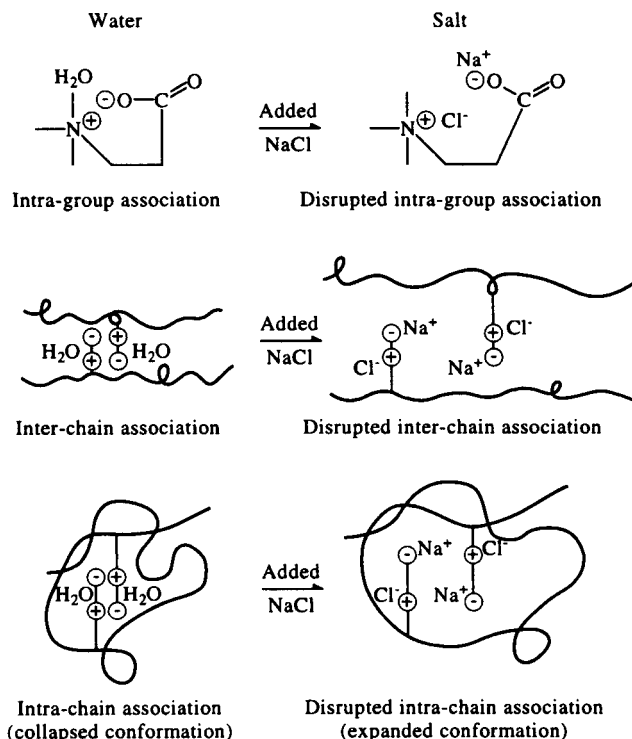
aqueous solution. From Table 5, both the monomer and polymer electrolyte in the K<sub>a</sub> value increase with an addition of NaCl. These phenomena were the same as those mentioned above; that is, more free proton ions caused the increase of K<sub>a</sub> value in the increasing NaCl. The same results have also been observed in previous works<sup>30,31</sup>. Similarly, the pK<sub>a</sub> value of the other salt aqueous solution can also be obtained. Table 6 summarizes those results.

A smaller radius hard base species easily binds with hard acid species; thus, the proton ion (H<sup>+</sup>) binds with the carboxylate group (COO<sup>-</sup>), decreasing the free proton ions in solution. The following trend can thus be drawn: KF > KCl > KBr > KI. Therefore, the concentration of free proton ion (H<sup>+</sup>) increases and then pK<sub>a</sub> value decreases.

Figure 12 shows the different degrees of binding of betaines. Comparing the degree of binding of DMAEAPL and the corresponding DMAPS reveals that carboxybetaine (DMAEAPL) has a higher degree of binding than sulfobetaine (DMAPS). This is owing to the fact that the anionic sulfonate group of DMAPS is more difficult to protonate than the anionic carboxylate group of DMAEAPL.

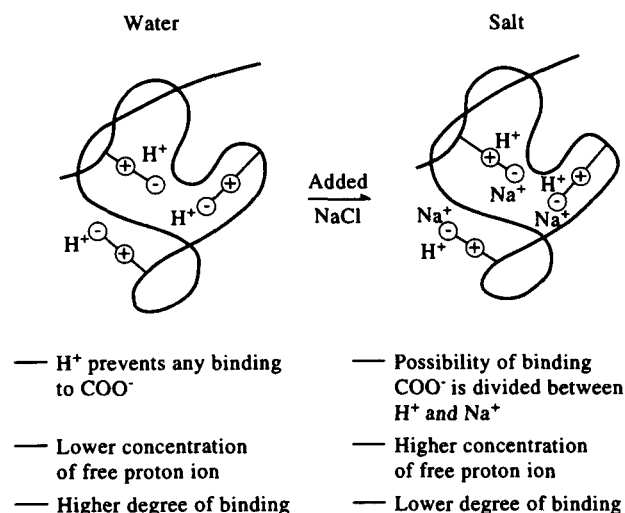
*Proposed model for poly(DMAEAPL) in NaCl<sub>(aq)</sub> and H<sub>2</sub>O*

Figure 13 presents our proposed schematic model to rationalize changes in the solution viscometrics of poly(DMAEAPL) in NaCl<sub>(aq)</sub> and H<sub>2</sub>O. In H<sub>2</sub>O,



**Figure 13** The proposed model for effect of salt concentration on poly(DMAEAPL) solution viscometrics

poly(DMAEAPL) has extensive inter- and intra-associations. The intra-chain association results from interactions between the quaternary ammonium group ion and the carboxylate group ion of the same poly(DMAEAPL) side chains. Meanwhile, the inter-chain association derives from interactions between the quaternary ammonium group (R<sub>4</sub>N<sup>+</sup>) and the carboxylate group (COO<sup>-</sup>) of the different poly(DMAEAPL) side chain. Schultz *et al.* reported that the intensive intra-associations are both of the intra-chain and intra-group type. The intra-chain association results from zwitterionic and H-bonded attractions on the same chain. The intra-group associations derive from intra-group ion pairs<sup>38</sup>. The net effect of among these types of associations is to vitiate the water solubilizing effect of the ionic functionalities and render the polymer insoluble. In NaCl<sub>(aq)</sub>, adding more NaCl would neutralize the negative and positive charges of poly(DMAEAPL) and decrease the associations between the quaternary ammonium group ions and the carboxylate group ions. This event disrupts the intra-



**Figure 14** The proposed model for effect of salt concentration on the degree of binding of poly(DMAEAPL) solution

and inter-associations; thus, conformation expands in the solution system.

A proposed model is used to rationalize the effects of NaCl<sub>(aq)</sub> concentration on the viscosity behaviour of poly(DMAEAPL). At the low concentrations of NaCl<sub>(aq)</sub>, a slight increase in NaCl<sub>(aq)</sub> concentration would result in a rapid disruption of the conformation of poly(DMAEAPL). This is because ions neutralize the charges of poly(DMAEAPL), thereby decreasing the inter- and intra-associations. Those associations are what hold together the collapsed conformation of the polymers. As more NaCl is added, not only does it neutralize the charge, but the accumulated ions begin to repel each other. This accumulated ion charge repulsion slows down the disintegration of the conformation of poly(DMAEAPL). Thus, *Figure 5* indicates that at high concentrations of NaCl<sub>(aq)</sub>, the increase in intrinsic viscosity of the poly(DMAEAPL) is slower. The polymer's collapsed conformation is what produces a low intrinsic viscosity to the polyampholyte's aqueous solution. When the conformation disintegrates, intrinsic viscosity increases. At this point, for any type of salt that can neutralize the quaternary ammonium group (R<sub>4</sub>N<sup>+</sup>) and the carboxylate group (COO<sup>-</sup>), it can disrupt associations, and eventually increase intrinsic viscosity of the polyampholyte.

*Figure 14* presents our proposed schematic model to rationalize changes in the degree of binding of poly(DMAEAPL). Zwitterionic poly(DMAEAPL) has many carboxylate groups (COO<sup>-</sup>) at the end of its side chain. An aqueous solution of this polymer when titrated with HCl<sub>(aq)</sub> would easily allow binding between them. Restated, in water, the proton ion (H<sup>+</sup>) prevents any binding to the carboxylate groups (COO<sup>-</sup>). Thus, the free proton ion concentration decreases. Consequently, pH and the degree of binding increase. On the other hand, in salt solution systems, adding NaCl would cause the sodium ion to compete with the proton ion for binding with the carboxylate groups (COO<sup>-</sup>). Thus, free proton ion concentration increases, resulting in a decrease in both pH and the degree of binding.

High concentrations in aqueous poly(DMAEAPL) solution would imply that the polymer chains have a more closely knit and 'entangled' situation than those in low concentrations of poly(DMAEAPL). When it is titrated with HCl<sub>(aq)</sub>, the proton

ion (H<sup>+</sup>) not only binds to the carboxylate groups (COO<sup>-</sup>), but can also form hydrogen-bonding with the neighbouring ( )

in the polymer chain. Consequently, it would be difficult for H<sup>+</sup> to be released as free proton ions in solution. Thus, although adding HCl<sub>(aq)</sub> would theoretically imply an increase in the free proton ion in solution, this does not actually occur.

## CONCLUSIONS

The behaviour of aqueous solution properties of a polyampholytic, poly(DMAEAPL), would be evidently transferred as salts were added in a polymeric aqueous solution. In this study, as the radius of salt ion became large, the degree of attracting poly(DMAEAPL) for salt was decreased and intrinsic viscosity was increased. As the salt concentration was increased, the intrinsic viscosity was increased and Huggins constant *k'* was decreased (Huggins constant *k'* was affected from polymer-solvent and polymer-polymer interaction). Also, the polyampholyte in high concentration of NaCl has a low degree of binding, indicating that the proton ion (H<sup>+</sup>) is relatively difficult to bind to the carboxylate group (COO<sup>-</sup>) at the polymer's end. Smaller anions such as F<sup>-</sup> with a common cation (K<sup>+</sup>) are found to be the most difficult bound to the carboxylate group (COO<sup>-</sup>), indicating that the proton ion (H<sup>+</sup>) can easily bind to the carboxylate group (COO<sup>-</sup>) at the polymer end of polycarboxybetaine and resulting in a high pH values. The carboxybetaine has a higher degree of binding than the corresponding sulfobetaine. Dynamic light scattering measurements indicate that the poly(carboxybetaine) diffusion coefficients decrease and the chain dimensions increase with an increasing salt concentration. The models proposed in this study account for the poly(DMAEAPL) solution viscometrics and degree of binding.

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