

Dilute Solution Properties of Cationic Poly(dimethyl sulfate quaternized dimethylaminoethyl methacrylate)

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SYNOPSIS

The dilute solution properties of a cationic polyelectrolyte, poly(dimethyl sulfate quaternized dimethylaminoethyl methacrylate) [poly(DMAEM · C₂H₆SO₄)], are studied by measurements of intrinsic viscosity, degree of binding, and flocculation application. The intrinsic viscosity of this polyelectrolyte is related to the type and concentration of added salt. The intrinsic viscosity behavior for cationic polyelectrolyte resulting from the electrostatic repulsive force of the polymer chain is contrasted with polyampholyte. The polyelectrolyte in the presence of KCl has a lower degree of binding, indicating that the proton ion (H⁺) is relatively difficult to bind to the CH₃SO₄⁻ at the polymer end. The polymerization of DMAEM · C₂H₆SO₄ in 0.5M KCl aqueous solution proceeded more easily than that of DMAEM · C₂H₆SO₄ in pure water. The polymerization rate of DMAEM · C₂H₆SO₄ is found to pass through an extreme value as a function of pH. Optimum flocculation, corresponding to the complete removal of turbidity in the supernatant, is achieved. Beyond the optimum flocculation, high polymer dosages redisperse the bentonite suspensions.

INTRODUCTION

Cationic quaternary polyelectrolytes have broad industrial application in the adhesive, coating, textile, hair conditioner, flocculent, and other industries.¹⁻⁶ Amino-containing monomer/polymer systems derived from amino alkyl acrylates and methacrylates have been one of the most extensively used types of cationic polymers.⁷ Dimethyl sulfate quaternized dimethylaminoethyl methacrylate (DMAEM · C₂H₆SO₄) is one of these quaternary ammonium compounds. Several workers reported that such cationic monomers are easily polymerized and can be applied to impart antistatic effects to the textiles.^{1,2,5,6} The copolymer containing DMAEM · C₂H₆SO₄ as a monomer is widely used as a flocculent for sludge treatment.^{3,4} In addition, such a monomer copoly-

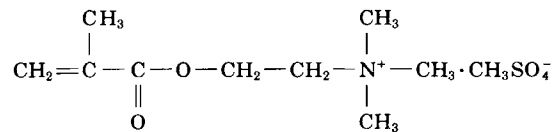
merized with vinyl pyrrolidone could be prepared to become the cosmetic compounds that exhibit excellent adhesion and holding power.^{8,9} In a previous paper,¹⁰ solution properties of the internal salts of poly[3-dimethyl(methacryloyloxyethyl)ammonium propane sulfonate] [poly(DMAPS)] were reported. We concluded that the salts, either the common anions or cations with a small charge/radius ratio, are easy to dissolve into polymer. Furthermore, the heat stability of the polyampholyte is higher than that of the cationic polyelectrolyte [poly(DMAEM · C₂H₆SO₄)].¹¹⁻¹³ However, some researchers have published only a few fundamental results for solution properties of such cationic quaternary polyelectrolytes. The difference of solution properties between cationic polyelectrolyte and polyampholyte is also interesting. The aqueous solution properties of poly(DMAEM · C₂H₆SO₄), especially in intrinsic viscosity in the presence of various salts and degree of binding in various pH ranges, were discussed. Finally, the cationic polyelectrolyte was applied in the flocculation test of a bentonite sol system.

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EXPERIMENTAL

Monomer Preparation¹³

In a 0.25 L volume flask equipped with a stirrer, a cooler, and a thermometer, *N,N*-dimethylaminoethyl methacrylate (8.00 g) and isobutyl alcohol (16.00 g) were charged and the contents stirred at ca. 15°C. A mixture of dimethyl sulfate (7.00 g) and isobutyl alcohol (7.00 g) was added dropwise for 2 h. After 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 collected by vacuum to remove the isobutyl alcohol, washed with dry ether several times, and dried under reduced pressure to obtain β -methacryloyloxy ethyl trimethyl ammonium methyl sulfate (DMAEM·C₂H₆SO₄) with the following structure:



Yield: 13.27 g (92.0%); mp: 73°C.

The procedure mentioned above for the monomer preparation is also repeated except that ether is used to replace isobutyl alcohol. The final product has almost the same yield either in ether or in isobutyl alcohol.

The monomer was characterized by elemental analysis, IR, and NMR as described before¹³ and was quite hygroscopic (mp 73°C).

Polymerization

Five grams (0.018 mol) of DMAEM·C₂H₆SO₄ monomer and 0.1 g (2.0 mol %) of 4,4-azo-bis-4-cyanovaleric acid (ACVA) were introduced into a 100 mL polymerization tube. To this, 50 mL of distilled water was added to yield a 0.36M aqueous solution. The contents of the tube were then flushed with nitrogen and sealed in vacuum after utilization of the freeze-thaw technique.

The tube was then placed in a constant temperature bath. The heterogeneous polymer solutions were placed in spectrapor membrane tubing (molecular weight cutoff 6000–8000) for 72 h to eliminate the unreacted monomer, dried for 8 h at 80°C under vacuum, and weighted. The dried, brittle, and white polymer was obtained.

The conversion was about 81%, and intrinsic viscosity was calculated to be 0.245 dL/g in

0.50M NaCl solution with an Ubbelohde viscometer at 30°C.

Viscometric Measurements

Viscometric measurements were carried out with an Ubbelohde viscometer (the viscometer has the flow time of 127.15 s for the pure water) at 30.00 ± 0.01°C. The polymer samples were dissolved in the salt concentration to yield a stock solution of approximately 1 g/100 mL solvent.

Viscosity data were calculated by the Mark-Huggins equation:

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

pH Measurements

The Seibold-Messtechnik pH G103 instrument was used with a Mallinckrodt standard buffer solution (pH 7.00 ± 0.01 and 4.01 ± 0.01 at 25°C). The sensitivity of this instrument is of 0.01 pH unit. Experiments were performed with solutions containing monomer or polymer 0.1063 g in 50 mL salt solution at starting KCl molarities of 0.0 and 0.1.

Flocculation Test^{14,15}

The extent of flocculation was determined by measurement of the turbidity of the supernatant. The tests were carried out in 50 mL graduate cylinders. A bentonite sol 40 mL was added to the cylinder. A stirring bar was inserted vertically into the cylinder, and the solution was stirred at a constant speed of about 180 rpm. Ten milliliters of polymer aqueous solution (0.001–1.0%) was then rapidly pipetted into the cylinder and stirring was continued for 2 more minutes. (The final sol concentration was 0.6%.) The stirring bar was removed and the cylinder was allowed to stand undisturbed for 3 min. An aliquot of supernatant was removed from the cylinder with a long-needle syringe, and its turbidity was measured in Hach turbidimeter (Model 43900 RATIO/XR).

RESULTS AND DISCUSSION

Time-Conversion Curves

Time-conversion curves were obtained by carrying out the polymerization at 40–60°C in a system of 0.5 g of DMAEM·C₂H₆SO₄ and 20 mL of H₂O in

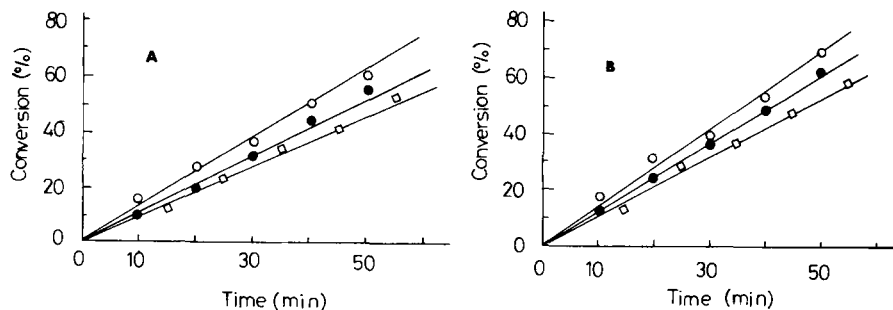


Figure 1 Monomer conversion vs. polymerization time. (A) Polymerization in H₂O; (B) polymerization in KCl (0.5M); (○) 60°C, (●) 50°C, (△) 40°C; monomer: 0.5 g; ACVA: 0.01 g; solvent: 20 mL.

the presence or absence of KCl. The results obtained are shown in Figure 1. There are good linear relationships between conversion and polymerization time. The conversion of DMAEM·C₂H₆SO₄ also increases with an increase of polymerization temperature. The figure also shows that the polymerization rate of DMAEM·C₂H₆SO₄ in pure water is

lower than that in 0.5M KCl aqueous solution. These phenomena might be due to the fact that both the cationic monomer and polymer could be neutralized by KCl aqueous solution.¹⁶ Then, the electrostatic repulsive force decreases. By applying the Arrhenius equation, the overall activation energy (E_a) was estimated to be 8.76 and 11.48 kJ/mol in the presence and absence of KCl, respectively.

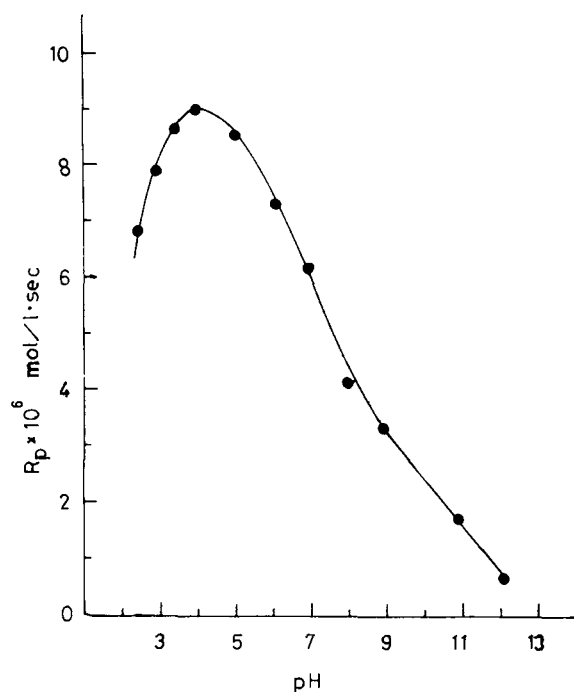


Figure 2 Polymerization rate of DMAEM·C₂H₆SO₄ vs. pH of the aqueous solution. Monomer: 0.5 g; ACVA: 0.01 g; buffer solution: 20 mL; polymerization time: 2 h; polymerization temperature: 60°C; buffer solutions were prepared with following systems: pH 3–5, 0.1M sodium citrate–0.1M HCl; pH 6, 0.1M sodium citrate–0.1M NaOH; pH 7–8, 0.1M KH₂PO₄–0.5M Na₂B₄O₇; pH 10–12, 0.2M Na₂B₄O₇–0.1M NaOH.

Effect of pH on the Polymerization Rate of DMAEM·C₂H₆SO₄

The polymerization rate of DMAEM·C₂H₆SO₄ as a function of the pH of the reaction solutions, the pH being set by the addition of buffer solution, passes through an extreme value and the maximum polymerization rate corresponds a pH of 4 as shown in Figure 2. This phenomenon could be explained as follows: The electrostatic repulsive force was decreased to a minimum value between the polymer

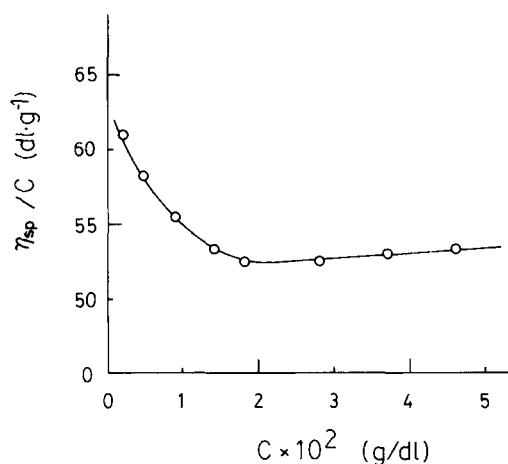


Figure 3 Reduced viscosities of poly(DMAEM·C₂H₆SO₄) in H₂O.

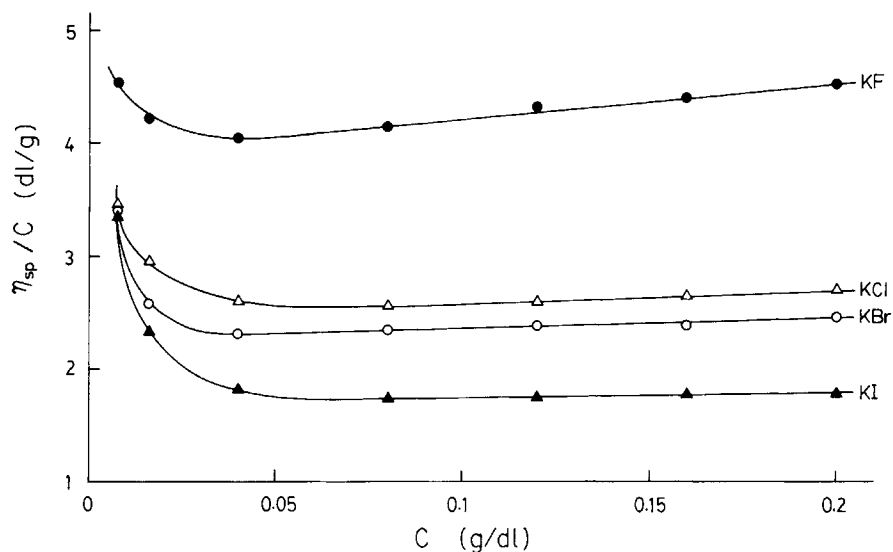


Figure 4 Reduced viscosities of poly(DMAEM · C₂H₆SO₄) as a function of concentration for salts containing a common cation. (●) 0.1M KF; (Δ) 0.1M KCl; (○) 0.1M KBr; (\blacktriangle) 0.1M KI.

and salt interaction to around pH 4. Thus, the maximum polymerization rate was obtained.

Measurement the Viscosity of Poly(DMAEM · C₂H₆SO₄)

The polyelectrolyte, either zwitterionic and cationic polymer, has special viscosity behavior in comparison with antipolyelectrolyte^{17,18}; that is, antipolyelectrolyte, such as styrene and methyl methacrylate, has the property that reduced viscosity (η_{sp}/C) increases with the increase of polymer concentration. Furthermore, the reduced viscosity of polyelectrolyte in a dilute aqueous solution was more than tens of times as large as the antipolyelectrolyte. The data in Figure 3 show that in the dilute solution

regime, there is an upturn in reduced viscosity that in a typical polyelectrolyte would be attributed to the ionization and subsequent repulsion of the ionic groups attached to the chain backbone.¹⁹ These phenomena were also observed by Thu et al.,¹⁷ Wiley et al.,^{20,21} and Salamone et al.^{22,23} for various polyelectrolytes.

The intrinsic viscosity of poly(DMAEM · C₂H₆SO₄) in the presence of different electrolytes should be discussed as follows: (1) common cations (KF, KCl, KBr, and KI); (2) common anions (LiCl, NaCl, KCl, and CsCl); and (3) divalent cations (MgCl₂, CaCl₂, SrCl₂, and BaCl₂). The influence of different electrolytes with a common cation, K⁺, on the intrinsic viscosities of poly(DMAEM · C₂H₆SO₄) is shown in Figure 4.

Table I Effect of Various Salt Solutions on the Viscosity Behavior of Poly(DMAEM · C₂H₆SO₄) at 30°C

Salt Solution (0.1M)	Common Cation	
	$[\eta]$ (dL/g)	k'
KF	3.86	0.21
KCl	2.43	0.23
KBr	2.24	0.25
KI	1.70	0.28

Table II Effect of Various Salt Solutions on the Viscosity Behavior of Poly(DMAEM · C₂H₆SO₄) at 30°C

Salt Solution (0.1M)	Common Anion	
	$[\eta]$ (dL/g)	k'
LiCl	2.80	0.11
NaCl	2.53	0.21
KCl	2.43	0.23
CsCl	2.47	0.50

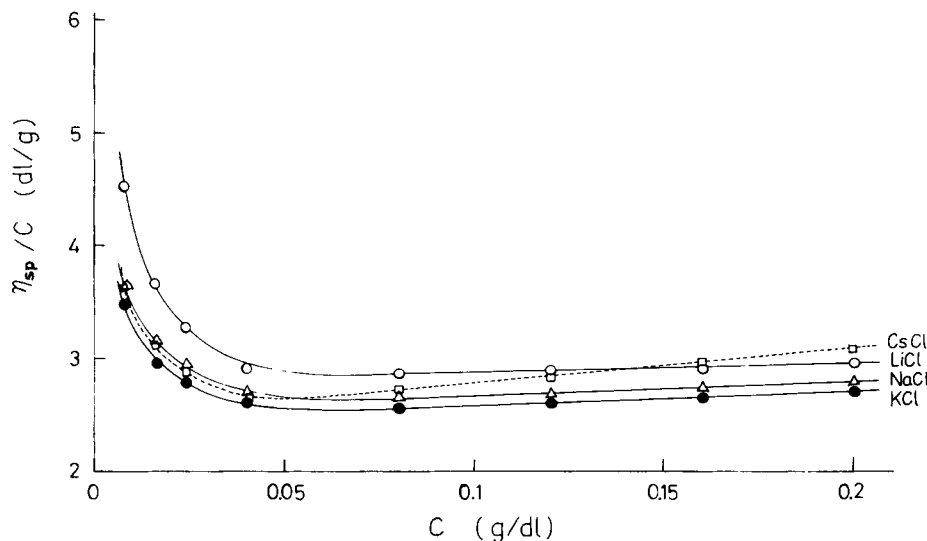


Figure 5 Reduced viscosities of poly(DMAEM·C₂H₆SO₄) as a function of concentration for salts containing a common anion. (●) 0.1M KCl; (△) 0.1M NaCl; (○) 0.1M LiCl; (□) 0.1M CsCl.

From Figure 4 and eq. (1), the intrinsic viscosity $[\eta]$ and Huggins constant k' could be calculated. The results are shown in Table I. The data show an increase in the intrinsic viscosity of poly(DMAEM·C₂H₆SO₄) in 0.1M aqueous salt solution in the order KF > KCl > KBr > KI. These phenomena might be due to the fact that the interaction between salt and poly(DMAEM·C₂H₆SO₄) increases with an increase of charge density of salts. This phenomenon is contrasted with polyampholyte behavior.¹⁰ In fact,

the charge density for common cations is in the order KF > KCl > KBr > KI. Furthermore, from Figure 3, the intrinsic viscosity of the polyelectrolyte solution has a high value that resulted from the electrostatic repulsive force of the polymer chain. While the salt was added, the electrostatic repulsive force began to drop. The ionic condition of the polyelectrolyte was neutralized and the intrinsic viscosity started to decrease. From Table I, the value for the Huggins constant decreases as the intrinsic viscosity

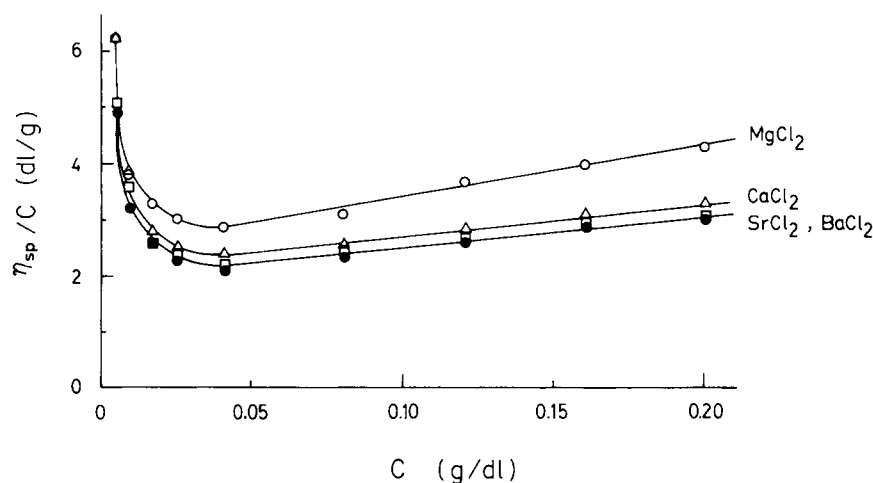


Figure 6 Reduced viscosities of poly(DMAEM·C₂H₆SO₄) as a function of concentration for salts containing a divalent cation. (○) 0.1M MgCl₂; (△) 0.1M CaCl₂; (□) 0.1M SrCl₂; (●) 0.1M BaCl₂.

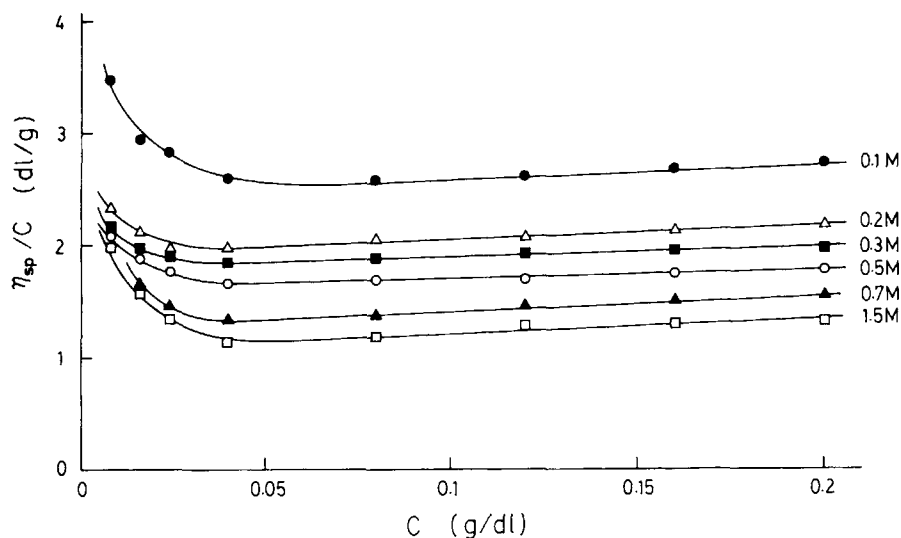


Figure 7 Reduced viscosities of poly(DMAEM·C₂H₆SO₄) as a function of concentration for KCl. (●) 0.1M; (△) 0.2M; (■) 0.3M; (○) 0.5M; (▲) 0.7M; (□) 1.5M.

increases. This decrease in the Huggins constant may be associated with an increase of polymer-solvent interaction.¹⁰

The influence of different electrolytes with a common anion, Cl⁻, on the intrinsic viscosity of poly(DMAEM·C₂H₆SO₄) is shown in Figure 5. The data show an increase in the intrinsic viscosity of poly(DMAEM·C₂H₆SO₄) in 0.1M aqueous solution in the order LiCl > NaCl > KCl ≅ CsCl. These phenomena were the same as for the common cations; that is, the interaction between salt and poly(DMAEM·C₂H₆SO₄) increases with the increase of charge density of salt. Furthermore, from Table II, the data show the Huggins constant in a common anion solution in the order LiCl < NaCl < KCl < CsCl. This tendency is the same as for the common cations.

The intrinsic viscosity and Huggins constant of poly(DMAEM·C₂H₆SO₄) influenced by divalent cations are shown in Figure 6 and Table III. The data show an increase in the intrinsic viscosity of poly(DMAEM·C₂H₆SO₄) in 0.1M aqueous salt solution in the order MgCl₂ > CaCl₂ > SrCl₂ ≅ BaCl₂. This tendency is similar to that of the monovalent common cations (Table I) and anions (Table II); that is, as the electrolyte charge density increases, the intrinsic viscosity begins to increase and the Huggins constant starts to decrease.

The intrinsic viscosities and Huggins constant of solutions of KCl of several different concentrations containing fixed poly(DMAEM·C₂H₆SO₄) were determined. The results are shown in Figure 7 and Table IV. As the concentration of the salt was increased, the intrinsic viscosity began to decrease and

Table III Effect of Various Salt Solutions on the Viscosity Behavior of Poly(DMAEM·C₂H₆SO₄) at 30°C

Salt Solution (0.1M)	Divalent Cation	
	[η] (dL/g)	k'
MgCl ₂	2.60	1.02
CaCl ₂	2.23	1.05
SrCl ₂	2.00	1.19
BaCl ₂	2.00	1.19

Table IV Effect of KCl Concentration on the Intrinsic Viscosity and Huggins Constant of Poly(DMAEM·C₂H₆SO₄) at 30°C

KCl Concentration	[η] (dL/g)	k'
0.1M	2.43	0.23
0.2M	1.91	0.29
0.3M	1.81	0.31
0.5M	1.63	0.34
0.7M	1.27	0.82
1.5M	1.08	1.14

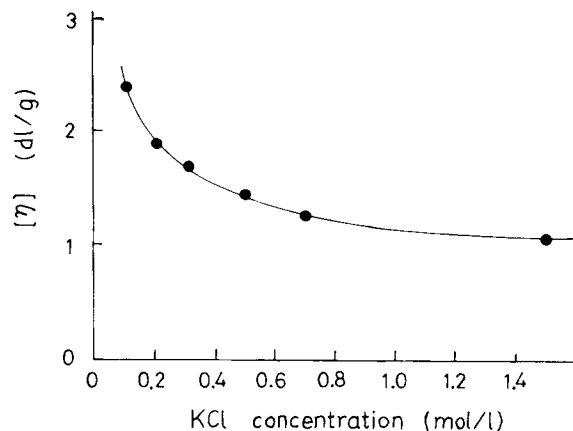


Figure 8 Intrinsic viscosity of poly(DMAEM·C₂H₆SO₄) as a function of KCl concentration.

the Huggins constant started to increase. These phenomena might be due to the fact that the addition of salt can loosen the compact structure that resulted from the inter- and intramolecular ionic interactions, and, thus, the polymer can behave more freely in the salt solution.²⁴ In other words, the higher the salt concentration is, the lower is the electrostatic repulsive force and, thus, the lower the intrinsic viscosity. This result was also observed by Conway²⁵ and Eisenberg and Pouyet.²⁶ The intrinsic viscosity $[\eta]$, obtained by extrapolating the curves of Figure 7 at constant simple electrolyte concentration $[KCl]$ to zero concentration of the polymer, are plotted in Figure 8 as a function of the ionic strength of the medium.

Determination of Degree of Binding

The potentiometric titration of the cationic polyelectrolyte with hydrochloric acid in aqueous solution was carried out in the presence and absence of KCl salt. The result is shown in Figure 9 for the poly(DMAEM·C₂H₆SO₄). From Figure 9, it is seen that polymer in the presence of salt has a lower pH value at the same amount of added HCl solution. Similar behavior was also observed for the DMAEM·C₂H₆SO₄ monomer. This means that poly(DMAEM·C₂H₆SO₄) and/or DMAEM·C₂H₆SO₄ monomer has a certain degree of site binding with KCl. The salt KCl hinders the binding ability of the cationic poly(DMAEM·C₂H₆SO₄) and/or DMAEM·C₂H₆SO₄ monomer with HCl solution. Consequently, the concentration of free HCl solution increases, resulting in the lower pH value in the presence of KCl salt.

The pK_a can be calculated from the modified Henderson-Hasselbach equation:

$$pH = pK_a + n \log(1 - \alpha)/\alpha \quad (2)$$

where α is the degree of binding for the cationic polyelectrolyte and/or DMAEM·C₂H₆SO₄ monomer with HCl solution and K_a is the constant of binding. From Figure 9 and eq. (2), the relationship between pH and α can be calculated. The results are shown in Figure 10. It is clear that the polyelectrolyte in the presence of KCl has a lower degree of binding at the same pH value in comparison to the absence of KCl. A similar tendency was also observed for monomeric electrolyte. These phenomena could be explained by the argument that the proton ion (H⁺) is relatively difficult to bind to the CH₃SO₄⁻ at the polymer end and results in the lower degree of binding in the presence of KCl. From the plot of pH vs. $\log[(1 - \alpha)/\alpha]$, the pK_a could be calculated; that is, the pK_a is equal to the pH as α is equal to 0.5. The results are shown in Figures 11 and 12 for the monomer and polymer, respectively. From Table V, both the monomer and polymer elec-

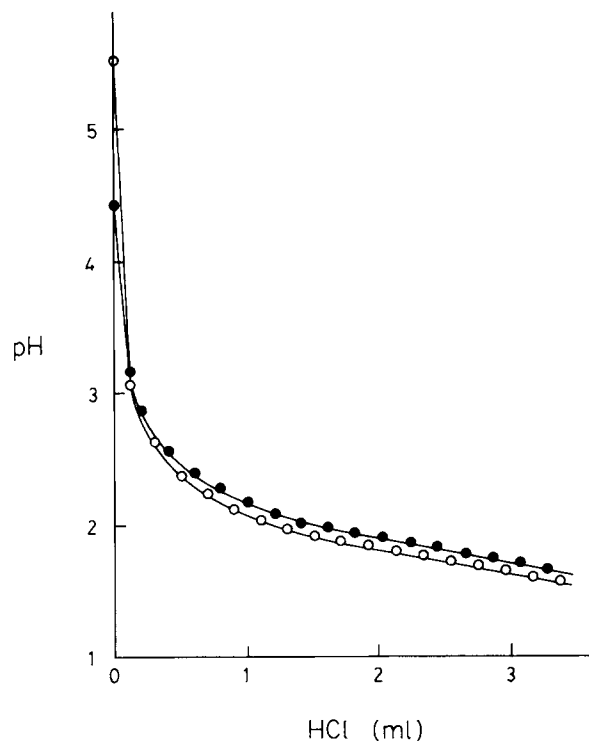


Figure 9 Relationships of pH vs. 0.5N HCl. (●) poly(DMAEM·C₂H₆SO₄) 0.1063 g in H₂O; (○) poly(DMAEM·C₂H₆SO₄) 0.1063 g in KCl (0.1M).

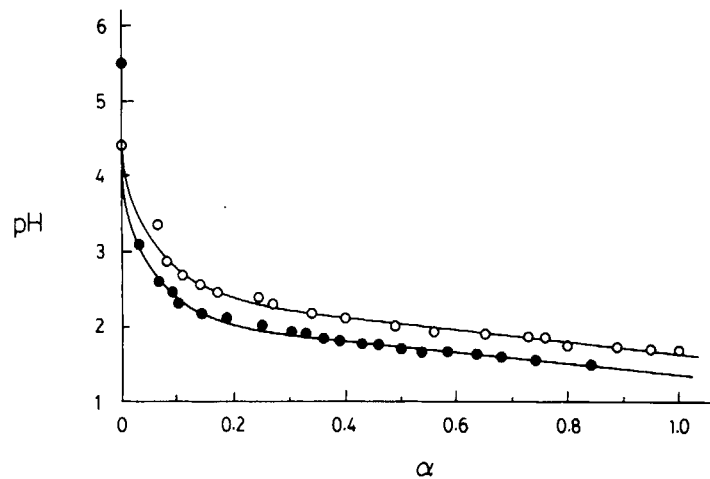


Figure 10 Relationships of pH vs. α . (O) poly(DMAEM · C₂H₆SO₄) 0.1063 g in H₂O; (●) poly(DMAEM · C₂H₆SO₄) 0.1063 g in KCl (0.1M).

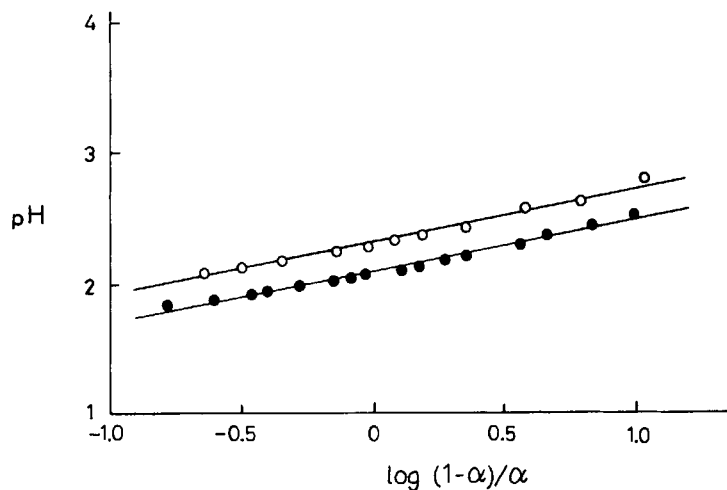


Figure 11 The dependence of pH on $\log(1 - \alpha)/\alpha$. (O) DMAEM · C₂H₆SO₄ in 50 mL H₂O; (●) DMAEM · C₂H₆SO₄ in 50 mL KCl (0.1M).

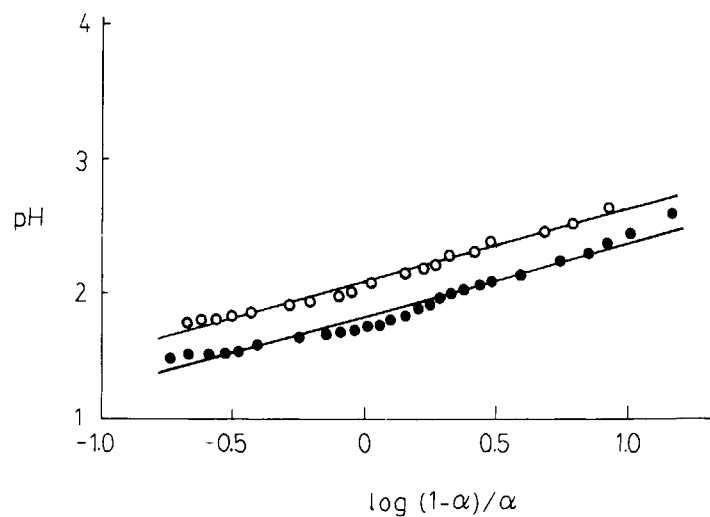


Figure 12 The dependence of pH on $\log(1 - \alpha)/\alpha$. (O) poly(DMAEM · C₂H₆SO₄) in 50 mL H₂O; (●) poly(DMAEM · C₂H₆SO₄) in 50 mL KCl (0.1M).

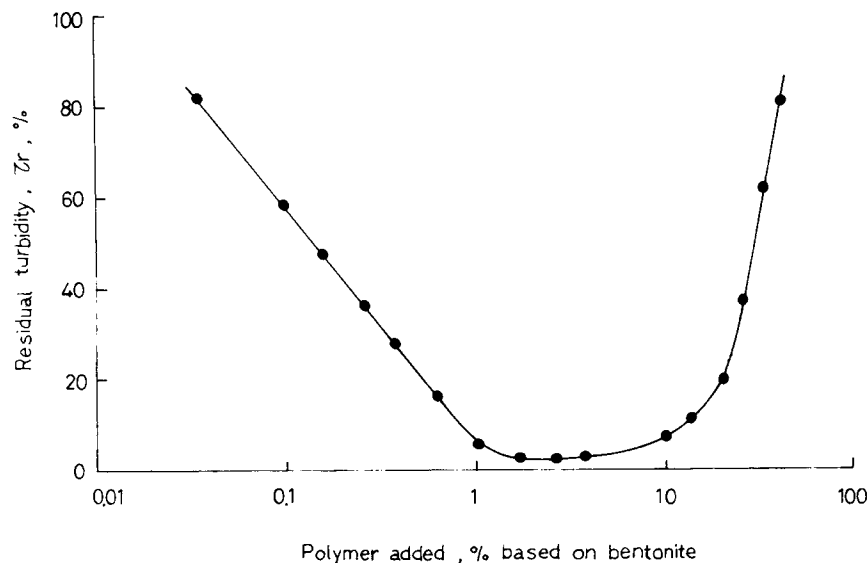


Figure 13 The residual turbidity vs. cationic polymer concentration.

trolyte in the absence of KCl have the K_a value increase with addition of KCl. These phenomena were the same as those mentioned above; that is, more free proton ions resulted in the increase of K_a value in the presence of KCl.

Flocculation Application

Residual turbidity is plotted as functions of the cationic polymer concentration in Figure 13. The polymer-bentonite system showed flocculation characteristics similar to those reported for other polymers in inorganic suspensions.^{14,15,27} As shown in Figure 13, residual turbidity decreases with increasing polymer concentration below the saturation level of adsorption. Optimum flocculation, corresponding to the complete removal of turbidity in the supernatant, is then achieved. Beyond the optimum flocculation, high polymer dosages redisperse the bentonite suspensions. The results indicate that the poly(DMAEM·C₂H₆SO₄) is a more efficient flocculant for bentonite suspension.

The equivalency of the cationic polymer on a charge-for-charge basis and the coincidence of the optimum flocculation point with neutralization of the particle charge indicate that flocculation in these systems is due entirely to a charge neutralization mechanism. This result was also observed by Gregory²⁸ and Sandell and Luner.¹⁴

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Table V Effect of Salt on the K_a of DMAEM·C₂H₆SO₄ and Poly(DMAEM·C₂H₆SO₄) Titrated with HCl

Sample	$K_a \times 10^{-3}$	
	In H ₂ O	In KCl (0.1M)
DMAEM·C ₂ H ₆ SO ₄	5.01	7.94
Poly(DMAEM·C ₂ H ₆ SO ₄)	7.94	15.13

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