

# Dilute Solution Properties of Anionic Poly(potassium-2-sulfopropylmethacrylate)

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## SYNOPSIS

The dilute solution properties of an anionic polyelectrolyte, poly(potassium-2-sulfopropylmethacrylate) [poly(SPM)], are studied by measurements of polymerization rate, intrinsic viscosity, degree of binding, ionic strength, and critical micelle concentration. The polymerization of SPM in 0.5M NaCl aqueous solution proceeded more easily than that of SPM in pure water. The polymerization rate of SPM is found to pass through an extreme value as a function of pH. The intrinsic viscosity of this polyelectrolyte is related to the type and concentration of the salt added. The intrinsic viscosity for anionic polyelectrolyte resulting from the electrostatic repulsive force of the polymer chain is in contrast with the polyampholyte. The polyelectrolyte in a high concentration of NaCl has a low degree of binding, indicating that the proton ion ( $H^+$ ) is relatively difficult to bind to the sulfonate group ( $SO_3^-$ ) at the polymer end. An increase in ionic strength causes the pKa (dissociation constant) to decrease at the half-neutralization point. The monomer solutions exhibit a plot typical of those observed for detergents, with a break in the curve occurring at the critical micelle concentration. For the polymer solutions, no break in the equivalent conductance curve was found for the concentrations studied. The polymer is adapted for use as viscosity-controlling agents in secondary oil recovery operations by water flooding. We have the proposed models to account for the poly(SPM) solution viscometrics. © 1997 John Wiley & Sons, Inc.

## INTRODUCTION

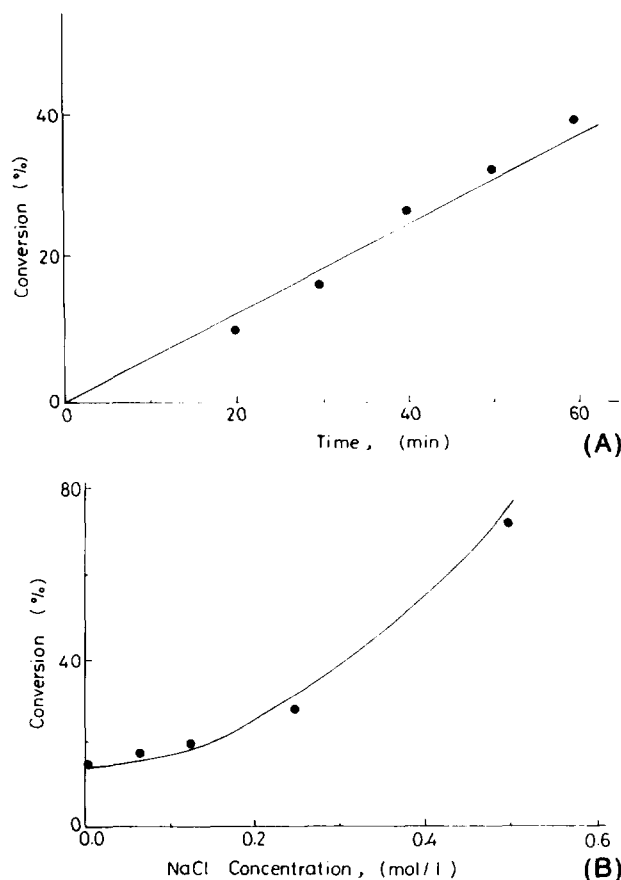
Aqueous polyelectrolytes of varying types have been extensively studied and comprehensively described in numerous reviews and books.<sup>1-18</sup> They have been widely used in the adhesive, coating, textile, hair-conditioning, flocculant, and other related industries. The functional groups on the side chain of the anionic polyelectrolytes are usually sulphonate and carboxylate groups. Anionic monomers with sulphonate group or carboxylate group, when polymerized, are usually on the polymeric side chain.

For example, McCormick and associates<sup>3,4</sup> reported the synthesis of 3-acrylamido-3-methylbutanoic acid and their polymeric aqueous properties. Aqueous polyelectrolytes with an anionic group offer

hydrogen-bonding capability and polyelectrolyte behavior in aqueous solutions.

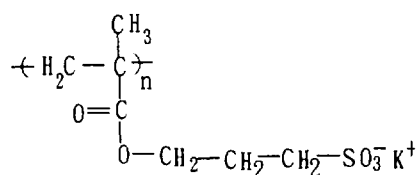
The effect of various salt ions on the interaction of polyelectrolytes in the aqueous solution has therefore been investigated by several scholars.<sup>5-18</sup> The same is true for the site-binding interaction of salt ions and polymers by Huggins equation and Huggins constant  $k'$ . The counterion size has been confirmed to have militated the degree of site binding for salt ion-attracting polymers. Previous works have dealt with the aqueous properties of polyelectrolytes such as cationic polyelectrolyte, poly[3-dimethyl(methacryloyloxyethyl) ammonium propane sulfonate] [poly(DMAEM·C<sub>2</sub>H<sub>6</sub>SO<sub>4</sub>)],<sup>19</sup> and polyampholyte, poly(dimethylsulfate quaternized dimethylaminoethyl methacrylate) [poly(DMAPS)].<sup>20</sup> In contrast, systematic examinations of the anionic polyelectrolyte are few. Our interest is drawn on the difference among amphoteric, cationic, and anionic polyelectrolytes. Thus, this article describes the aqueous solution properties of an anionic polyelec-

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**Figure 1** (A) Monomer conversion of SPM vs. polymerization time in  $H_2O$ . (B) Monomer conversion of SPM vs. NaCl added.

trolyte, poly(potassium-2-sulfopropylmethacrylate) [poly(SPM)],

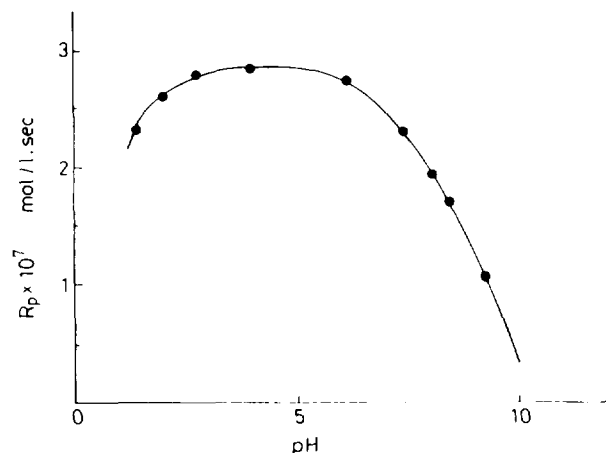


especially in intrinsic viscosity and the degree of binding in the presence of various salts. In addition, the critical micelle concentration (CMC) is discussed. The application of viscosity-controlling agents was also studied. We have proposed schematic models to describe their properties.

## EXPERIMENTAL

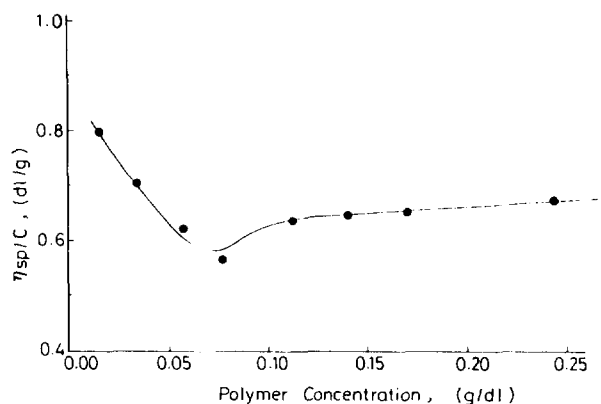
### Preparation of Poly(SPM)

Four grams (0.02 mol) of SPM (Rasching Co.) monomer and 0.1 g (2.0 mol %) of 4,4'-azo-bis-4-

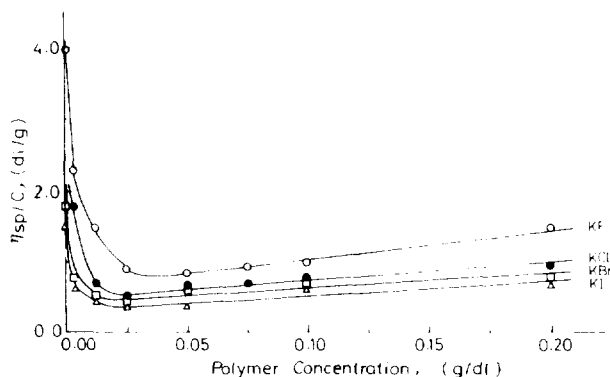


**Figure 2** Polymerization rate of SPM vs. pH of the aqueous solution. Monomer, 0.5 g; ACVA, 0.01 g; buffer solution, 20 mL; polymerization time, 2 h; polymerization temperature,  $60^\circ\text{C}$ ; buffer solutions were prepared with following systems: pH 3 ~ 5, 0.1M sodium citrate-0.1M HCl; pH 6, 0.1M sodium citrate-0.1M NaOH; pH 7 ~ 8, 0.1M  $\text{KH}_2\text{PO}_4$ -0.5M  $\text{Na}_2\text{B}_4\text{O}_7$ ; pH 10-12, 0.2M  $\text{Na}_2\text{B}_4\text{O}_7$ -0.1M NaOH.

cyanovaleic acid (ACVA) were introduced into a 100 mL polymerization tube. To this, 50 mL of distilled water was added to make a 0.4M aqueous solution. The contents of the tube were then flushed with argon and sealed in a vacuum by the use of the freeze-thaw technique. The tube was then placed in a constant temperature bath for 24 h. The homogeneous polymer solutions were then precipitated with methanol, washed with methanol to eliminate the unreacted monomer, dried for 24 h at  $70^\circ\text{C}$  under a vacuum and weighed. A dried, brittle, white polymer was obtained. The yield is 96%, and  $T_g = 106.22^\circ\text{C}$  by differential scanning calorimetry (DSC). The intrinsic viscosity was calculated to be  $0.38 \text{ dL g}^{-1}$  in 0.5M NaCl solution with an Ubbel-



**Figure 3** Reduced viscosities of poly(SPM) in  $H_2O$ .



**Figure 4** Reduced viscosities of poly(SPM) as a function of concentration for salts containing a common cation in 0.1M salt aqueous solution.

lohde viscometer at 30°C. Poly(SPM) was soluble in pure water but insoluble in aliphatic hydrocarbons such as hexane; alcoholic solvents such as CH<sub>3</sub>OH, isopropanol, and isobutanol; chlorinated aliphatic hydrocarbons such as CHCl<sub>3</sub> and CH<sub>2</sub>Cl<sub>2</sub>; and aprotic solvents such as dimethyl sulfoxide (DMSO) and dimethyl formamide (DMF).

#### Viscometric Measurements

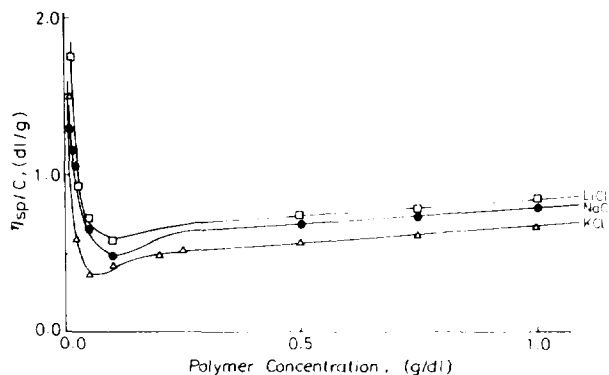
Viscometric measurements were carried out with a Ubbelohde viscometer (the viscometer has the flow rate of 79.19 sec for pure water) at 30.00 ± 0.01°C. The polymer samples were dissolved in the salt concentration to make a stock solution of approximately 1 g/100 mL of solvent.

Viscosity data were calculated by the Mark-Huggins equation:

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

**Table I** Effect of Various Salt Solutions on the Viscosity Behavior of Poly(SPM) at 30°C

Salt Solution (0.1M)	Common Cation	
	[η] (dL/g)	k'
KF	0.83	2.35
KCl	0.57	5.10
KBr	0.51	5.52
KI	0.36	13.28



**Figure 5** Reduced viscosity of poly(SPM) as a function of concentration for salts containing a common anion in 0.1M salt aqueous solution.

#### pH Measurements

A Kyoto Electronics At-210 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 0.01 pH unit. Experiments were performed with solutions containing 0.1 g of monomer or polymer in 50 mL of salt solution.

#### Conductance Measurements

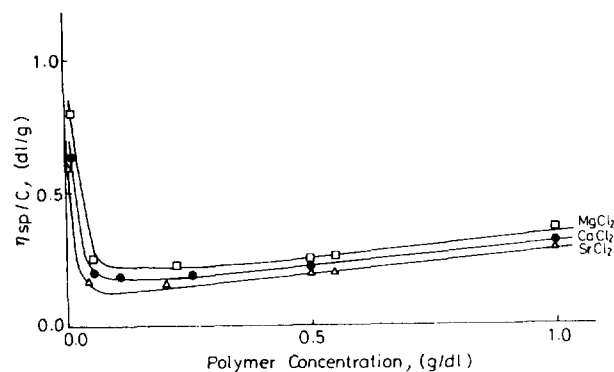
All conductivity measurements were done with a Wissenschaftlich Technische Werkstätten LF 95. The conductivity water was used to prepare a stock solution of monomer or polymer from which a series of solutions were then prepared by successive dilution. The solutions were allowed to remain in the constant temperature bath for 24 h before conductance measurements were recorded.

#### Brookfield Viscosity Measurements

SPM, acrylamide (AAm), and initiator ACVA were dissolved in water and placed in a 100 mL ampule. The solutions were degassed by nitrogen bubbling and a freeze-thaw technique. The reaction was po-

**Table II** Effect of Various Salt Solutions on the Viscosity Behavior of Poly(SPM) at 30°C

Salt Solution (0.1M)	Common Anion	
	[η] (dL/g)	k'
LiCl	0.68	0.49
NaCl	0.56	0.80
KCl	0.42	1.58



**Figure 6** Reduced viscosity ( $\eta_{sp}/C$ ) of poly(SPM) as a function of concentration for salts containing a divalent cation in 0.1M aqueous solution.

lymerized in a shaking water bath at 60°C for 24 h. The polymer solutions were then precipitated with acetone, washed with methanol to eliminate the unreacted monomer, and dried for 24 h at 70°C under a vacuum.

All of the copolymer samples were prepared in water and 500 ppm NaCl<sub>(aq)</sub>. The samples were analyzed after 7 days at 25°C in a water bath.

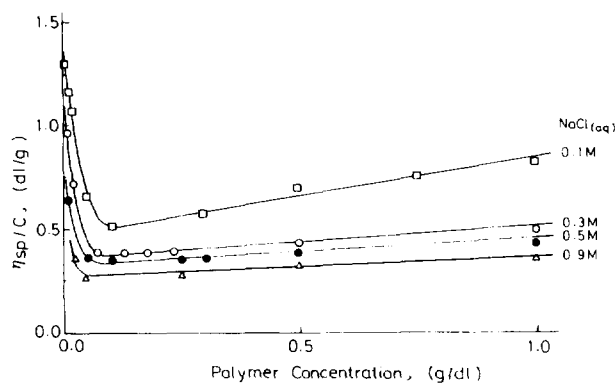
## RESULTS AND DISCUSSION

### Polymerization Curves

The data curves were obtained by carrying out the polymerization at 60°C in a system of 0.5 g of SPM and 20 mL of H<sub>2</sub>O in the presence or absence of NaCl. The results obtained are shown in Figure 1. Figure 1(A) shows the conversion of SPM increases with an increase of polymerization time. There are good linear relationships between conversion and polymerization time. Figure 1(B) shows that the polymerization rate of SPM in pure water is lower than that in a 0.5 M NaCl aqueous solution.<sup>19</sup> These phenomena might result from the fact that both the anionic monomer and polymer could be neutralized

**Table III** Effect of Various Salt Solutions on the Viscosity Behavior of Poly(SPM) at 30°C

Salt Solution (0.1M)	Divalent Cation	
	$[\eta]$ (dL/g)	$k'$
MgCl <sub>2</sub>	0.20	3.19
CaCl <sub>2</sub>	0.18	3.58
SrCl <sub>2</sub>	0.15	6.00



**Figure 7** Reduced viscosities ( $\eta_{sp}/C$ ) of poly(SPM) as a function of concentration for NaCl.

by the NaCl aqueous solution. Then, the electrostatic repulsive force decreases and the polymerization rate of SPM increases.

### Effect of pH on the Polymerization Rate of SPM

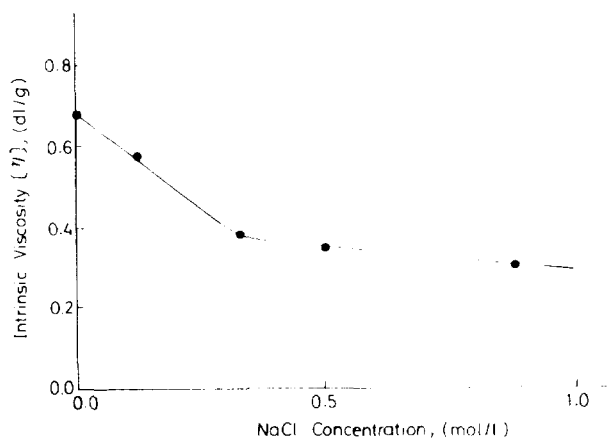
The polymerization rate of SPM as a function of the pH of the reaction solutions (the pH being set by the addition of buffer solution), passes through an extreme value, and the maximum polymerization rate corresponds to the pH range of 3 ~ 5, as shown in Figure 2. This phenomenon could be explained as follows. The electrostatic repulsive force was decreased to a minimum value between the polymer and salt interaction to the pH range of approximately 3 ~ 5. Thus, the maximum polymerization rate was obtained.

### Measurement of the Viscosity of Poly(SPM)

Polyelectrolytes normally exhibit properties in solution that are quite different from those of general polymers. They are ionized in aqueous solution; the mutual repulsion of their charges causes expansions of the polymer chain. The reduced viscosity of poly-

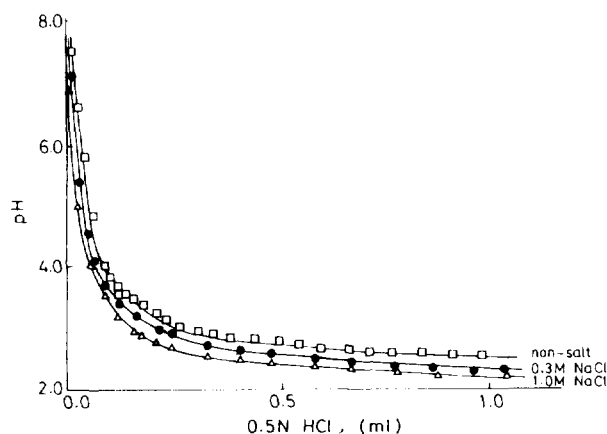
**Table IV** Effect of NaCl Concentration on the Intrinsic Viscosity and Huggin's Constant of Poly(SPM) at 30°C

NaCl Concentration (M)	$[\eta]$ (dL/g)	$k'$
0.1	0.56	0.79
0.3	0.36	0.80
0.5	0.33	0.81
0.9	0.29	1.35

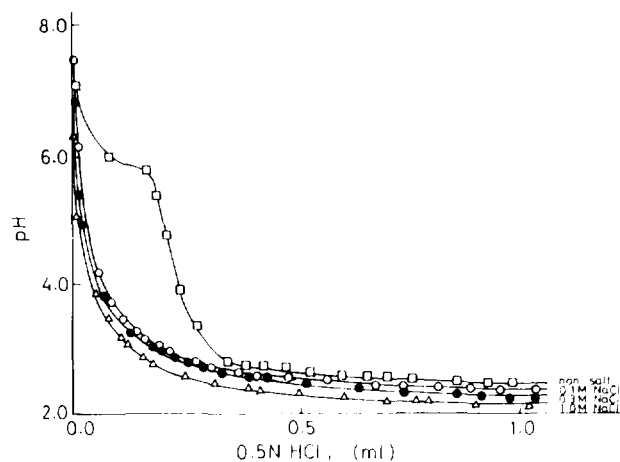


**Figure 8** Intrinsic viscosity of poly(SPM) as a function of NaCl concentration.

electrolyte in a dilute aqueous solution was many times larger than that of the antipolyelectrolyte. An antipolyelectrolyte, such as styrene and methylmethacrylate, has the property that reduced viscosity ( $\eta_{sp}/C$ ) increases with the increase of polymer concentration. The data in Figure 3 show that the reduced viscosity ( $\eta_{sp}/C$ ) in a lower concentration region increases with a decrease in polymer concentration, while the reduced viscosity ( $\eta_{sp}/C$ ) in a higher concentration region increases with an increase in polymer concentration. The phenomenon in the lower concentration region would be the result of the smaller ionization and smaller subsequent repulsion of the ionic groups attached to the polymer chain backbone, while in the higher concentration region, it would be the result of the interaction of the polymer chain, producing greater repulsion. These were also observed by Thu et al.,<sup>21</sup> Wiley et



**Figure 9** Relationships of pH vs. 0.5N HCl. ( $\square$ ) 0.1 g of SPM in  $H_2O$ , ( $\bullet$ ) 0.1 g of SPM in 0.3M  $NaCl_{(aq)}$ , ( $\Delta$ ) 0.1 g of SPM in 1.0M  $NaCl_{(aq)}$ .

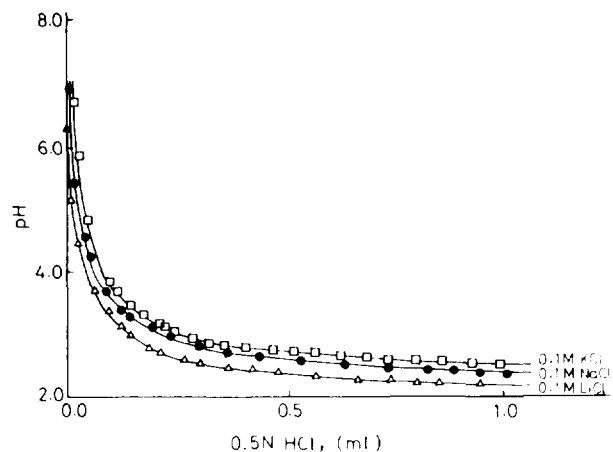


**Figure 10** Relationships of pH vs. 0.5N HCl. ( $\square$ ) 0.1 g of poly(SPM) in  $H_2O$ , ( $\circ$ ) 0.1 g of poly(SPM) in 0.1M  $NaCl_{(aq)}$ , ( $\bullet$ ) 0.1 g of poly(SPM) in 0.3M  $NaCl_{(aq)}$ , ( $\Delta$ ) 0.1 g of poly(SPM) in 1.0M  $NaCl_{(aq)}$ .

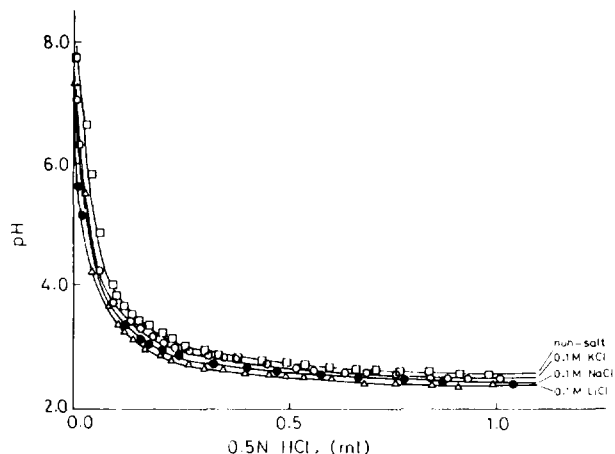
al.,<sup>22,23</sup> Salamone et al.,<sup>24</sup> Schulz et al.,<sup>25</sup> and Liaw et al.<sup>19</sup> for various polyelectrolytes.

The intrinsic viscosity of poly(SPM) in the presence of different electrolytes would be discussed as follows: 1) common cations (KF, KCl, KBr, and KI); 2) common anions (LiCl, NaCl, and KCl); and 3) divalent cations ( $MgCl_2$ ,  $CaCl_2$ , and  $SrCl_2$ ). The influence of different electrolytes with a common cation,  $K^+$ , on the intrinsic viscosities of poly(SPM) is shown in Figure 4.

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(SPM) in 0.1M aqueous salt solution in the order  $KF > KCl$

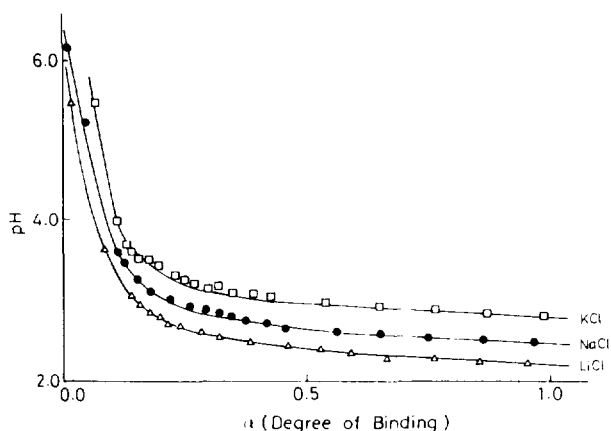


**Figure 11** Relationships of pH vs. 0.5N HCl. ( $\Delta$ ) 0.1 g of poly(SPM) in 0.1M  $LiCl_{(aq)}$ , ( $\bullet$ ) 0.1 g of poly(SPM) in 0.1M  $NaCl_{(aq)}$ , ( $\square$ ) 0.1 g of poly(SPM) in 0.3M  $NaCl_{(aq)}$ , ( $\circ$ ) 0.1 g of poly(SPM) in 1.0M  $NaCl_{(aq)}$ .

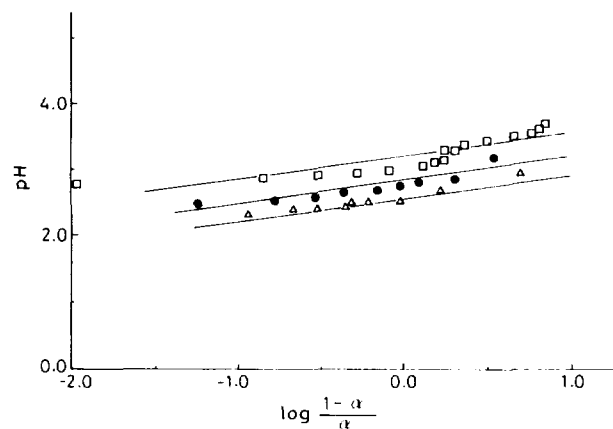


**Figure 12** Relationships of pH versus 0.5N HCl. (□) 0.1 g of SPM in  $H_2O$ , ( $\Delta$ ) 0.1 g of SPM in 0.1M  $LiCl_{(aq)}$ , ( $\bullet$ ) 0.1 g of SPM in 0.1M  $NaCl_{(aq)}$ , ( $\circ$ ) 0.1 g of SPM in 0.1M  $KCl_{(aq)}$ .

$> KBr > KI$ . These phenomena are in contrast with those of polyampholyte behavior.<sup>20</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 more polarizable species).<sup>26</sup> The hard acid species, e.g., potassium ion ( $K^+$ ), are easily bound to small-radius hard base, such as fluoride ion ( $F^-$ ). Hence, the fluoride ion ( $F^-$ ) is more easily attracted to the potassium ion than the chloride ion ( $Cl^-$ ), the bromide ion ( $Br^-$ ), or the iodide ion ( $I^-$ ). This result would reduce the site-binding degree of the potassium ion ( $K^+$ ) on the sulfonate group ( $SO_3^-$ ) and

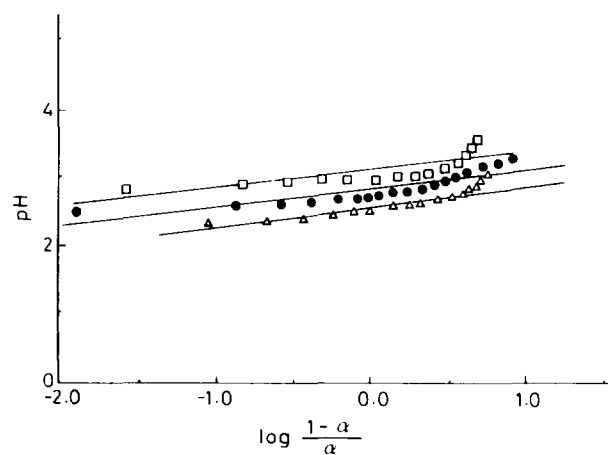


**Figure 13** Relationships of pH versus  $\alpha$ . ( $\Delta$ ) 0.1 g of SPM in 0.1M  $LiCl_{(aq)}$ , ( $\bullet$ ) 0.1 g of SPM in 0.1M  $NaCl_{(aq)}$ , ( $\square$ ) 0.1 g of SPM in 0.1M  $KCl_{(aq)}$ .



**Figure 14** Relationships of pH versus  $\log\left(\frac{1-\alpha}{\alpha}\right)$ . (□) 0.1 g of SPM in  $H_2O$ , ( $\bullet$ ) 0.1 g of SPM in 0.3M  $NaCl_{(aq)}$ , ( $\Delta$ ) 0.1 g of SPM in 1.0M  $NaCl_{(aq)}$ .

would decrease the degree of the potassium ion ( $K^+$ ) neutralizing the negative charge on polymeric side chains for poly(SPM). The result yields to a higher intrinsic viscosity of the polyelectrolyte in an aqueous salt solution. Furthermore, Figure 3 shows high intrinsic viscosities of the polyelectrolyte solution resulting 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,  $k'$ , decreases as the intrinsic viscosity increases. This decrease in the Huggins constant may be associated with an increase of polymer-solvent interaction.



**Figure 15** Relationships of pH versus  $\log\left(\frac{1-\alpha}{\alpha}\right)$ . (□) 0.1 g of poly(SPM) in 0.1M  $NaCl_{(aq)}$ , ( $\bullet$ ) 0.1 g of poly(SPM) in 0.3M  $NaCl_{(aq)}$ , ( $\Delta$ ) 0.1 g of poly(SPM) in 0.75M  $NaCl_{(aq)}$ .

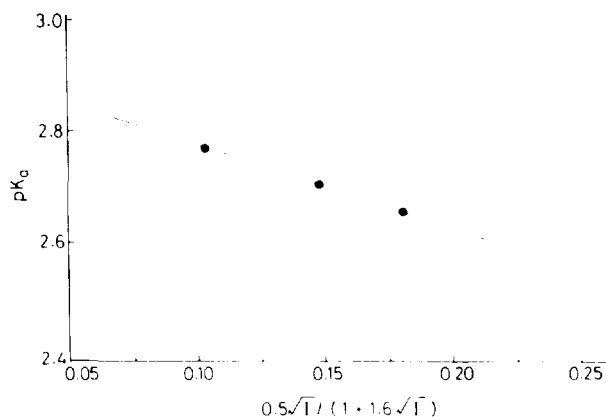
**Table V** Effect of the  $\text{NaCl}_{(\text{aq})}$  Concentration on the  $K_a$  of SPM and Poly(SPM) Titrated with  $\text{HCl}_{(\text{aq})}$ 

Sample	$K_a \times 10^{-3}$ in:		
	$\text{H}_2\text{O}$	$0.3M \text{ NaCl}_{(\text{aq})}$	$1.0M \text{ NaCl}_{(\text{aq})}$
SPM	0.65	1.57	2.23
Poly(SPM)	—	1.97	3.31

The influence of different electrolytes with a common anion,  $\text{Cl}^-$ , on the intrinsic viscosity of poly(SPM) is shown in Figure 5. The data show an increase in the intrinsic viscosity of poly(SPM) in  $0.1M$  aqueous solution in the order  $\text{LiCl} > \text{NaCl} > \text{KCl}$ . This is because the negative charge on the polymeric side chains could be effectively neutralized by the larger cation, thus reducing the intrinsic viscosity of poly(SPM) in  $0.1M$  aqueous salt solution. Furthermore, Table II shows the Huggins constant in a common anion solution to be in the order  $\text{LiCl} < \text{NaCl} < \text{KCl}$ . This tendency is the same as that for the common cations.

The intrinsic viscosity and Huggins constant of poly(SPM) influenced by divalent cations are shown in Figure 6 and Table III. The data show an increase in the intrinsic viscosity of poly(SPM) in  $0.1M$  aqueous salt solution in the order  $\text{MgCl}_2 > \text{CaCl}_2 > \text{SrCl}_2$ . This trend is similar to that of monovalent common anions (Table I); that is, as the radius of the cation decreases, the intrinsic viscosity begins to increase and the Huggins constant starts to decrease.

The intrinsic viscosities and Huggins constant of solutions of  $\text{NaCl}$  of different concentrations containing fixed poly(SPM) 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 the Huggins constant started to increase. These phenomena might be due to the addition of salt, which can loosen the compact structure caused by the intermolecular and intramolecular ionic interactions; thus, the polymer can


**Figure 16** The  $pK_a$  as a function of ionic strength ( $I$ ).

behave more freely in the salt solution.<sup>19</sup> In other words, the higher the salt concentration is, the lower the electrostatic repulsive force is, and thus, the lower the intrinsic viscosity. This result was also observed by Lee and Tsai,<sup>8</sup> and Wielema and Engberts,<sup>27</sup> and Eisenberg.<sup>28</sup> The intrinsic viscosities  $[\eta]$ , obtained by extrapolating the curves of Figure 7 at constant simple electrolyte concentration  $[\text{NaCl}]$  to zero concentration of the polymer, are plotted in Figure 8 as a function of the ionic strength of the medium. The results of the various salts for poly(SPM) are the same as those obtained for cationic polyelectrolyte<sup>19</sup> but are reversed from those for polyampholyte.<sup>20</sup>

#### Determination of Degree of Binding

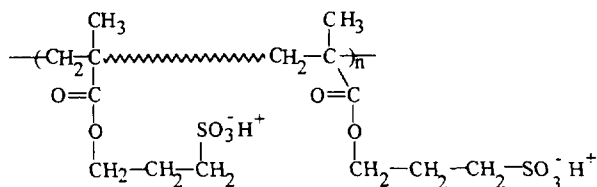
The potentiometric titration of the anionic poly(SPM) and SPM with hydrochloric acid in aqueous solution was carried out in the presence and absence of salt. The result is shown in Figure 9 for the SPM. From Figure 9, it is seen that SPM monomer in the presence of  $\text{NaCl}$  has a lower pH value at the same amount of added  $\text{HCl}$  solution. Similar behavior was also observed for the monomer SPM in various salt solutions, e.g.,  $\text{LiCl}_{(\text{aq})}$  and  $\text{KCl}_{(\text{aq})}$ . Similar behavior is shown in Figure 10 for the poly(SPM) in the  $\text{NaCl}$  aqueous solution. This

**Table VI** Effect of the Various Salt Solutions with Common Anion ( $\text{Cl}^-$ ) on the  $K_a$  of SPM and Poly(SPM) Titrated with  $\text{HCl}_{(\text{aq})}$ 

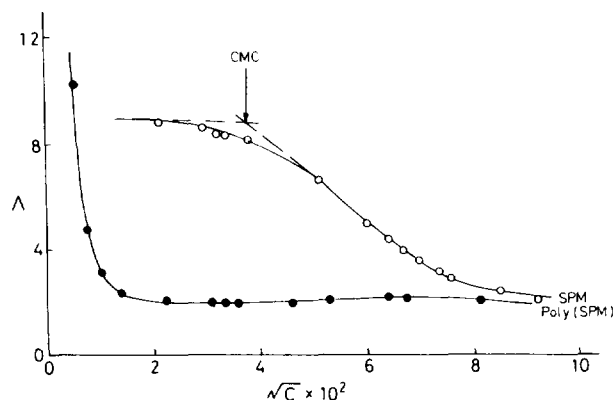
Sample	$K_a \times 10^{-3}$ in:		
	$0.1M \text{ LiCl}_{(\text{aq})}$	$0.1M \text{ NaCl}_{(\text{aq})}$	$0.1M \text{ KCl}_{(\text{aq})}$
SPM	2.17	1.50	0.69
Poly(SPM)	2.45	1.55	0.76

means that poly(SPM) and/or SPM monomer has a certain degree of site binding with salt, e.g.,  $\text{LiCl}_{(\text{aq})}$ ,  $\text{NaCl}_{(\text{aq})}$ , and  $\text{KCl}_{(\text{aq})}$ . The salt hinders the binding ability of the anionic poly(SPM) and/or SPM monomer with HCl solution. Consequently, the concentration of free HCl solution increases, resulting in the lower pH value in the presence of salt. Figure 11 shows that anionic poly(SPM) with a common anion ( $\text{Cl}^-$ ) in the various salt aqueous solutions has decreasing pH values in the order  $\text{KCl}_{(\text{aq})} > \text{NaCl}_{(\text{aq})} > \text{LiCl}_{(\text{aq})}$ . Similar behavior was also observed for the anionic monomer SPM (Fig. 12). These phenomena occur because the lithium ion ( $\text{Li}^+$ ) has a smaller radius than the sodium ion ( $\text{Na}^+$ ) and the potassium ion ( $\text{K}^+$ ). Hence, the lithium ion is more easily bound to the the sulfonate group ( $\text{SO}_3^-$ ) at the poly(SPM) and/or SPM monomer end. Consequently, the proton ion ( $\text{H}^+$ ) is relatively difficult to bind to it. Increasing ion radius results in the higher pH values and a greater degree of binding.

From Figure 10, it is seen that the pH value curve of the poly(SPM) in water (non-salt aqueous solution) is not similar to the others. When the  $\text{HCl}_{(\text{aq})}$  added did not exceed a certain limit ( $<0.2$  mL), the pH also remained constant ( $\text{pH} = 5.83$ ). The behavior is due to the hydrogen-bonding effect between  $\sim \text{SO}_3^- \text{H}^+$  and the ketone group ( $\begin{matrix} \text{O} \\ \parallel \\ \text{C} \end{matrix}$ ) of the polymer chain. High concentrations of poly(SPM) in aqueous solution would mean that the polymer chains have a more closely knit and "entangled" situation than do those in low concentrations of poly(SPM). When it is titrated with  $\text{HCl}_{(\text{aq})}$ , the proton ion ( $\text{H}^+$ ) not only binds to the sulfonate group ( $\text{SO}_3^-$ ), but it can also form hydrogen bonding with the neighboring ( $\begin{matrix} \text{O} \\ \parallel \\ \text{C} \end{matrix}$ ) in the polymer chain, making it difficult for  $\text{H}^+$  to be released as free proton ions in solution. Thus, although in principle, adding  $\text{HCl}_{(\text{aq})}$  would mean an increase in the free proton ion in solution, in reality, this does not occur in the initial region.



The  $\text{pK}_a$  (dissociation constant) can be calculated from the modified Henderson-Hasselbach equation:

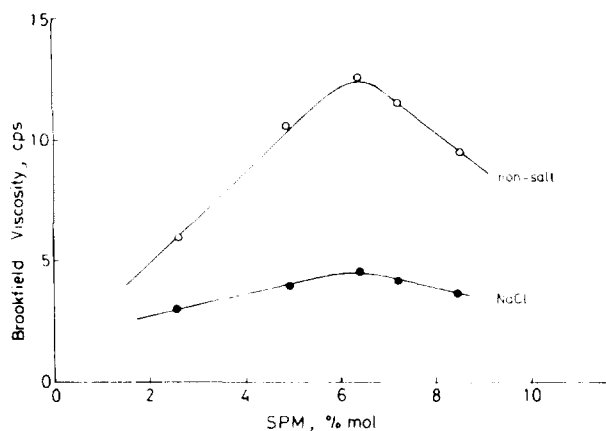


**Figure 17** The CMC of monomer SPM or poly(SPM); (●) poly(SPM) solution, (○) SPM solution.

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

where  $\alpha$  is the degree of binding for the anionic polyelectrolyte poly(SPM) and/or SPM monomer with HCl solution and  $K_a$  is the constant of binding. From Figure 9 and eq. (2), the relationship between pH and  $\alpha$  can be calculated. The results are shown in Figure 13. It is clear that the polyelectrolyte in the presence of NaCl has a lower degree of binding ( $\alpha$ ) at the same pH value. A similar tendency was also observed for the monomeric electrolyte (SPM). These phenomena could be explained by the difficulty of the proton ion ( $\text{H}^+$ ) in binding to the sulfonate group ( $\text{SO}_3^-$ ) at the polymer end, thus resulting in the lower degree of binding in the presence of NaCl. From the plot of pH versus  $\log \left[ \frac{(1 - \alpha)}{\alpha} \right]$ , the  $\text{pK}_a$  could be calculated. The  $\text{pK}_a$  is equal to the pH as  $\alpha$  is equal to 0.5. The results are shown in Figures 14 and 15 for the monomer and polymer in NaCl aqueous solution, respectively. From Table V, both the monomer and polymer electrolyte in the  $K_a$  value increase with the addition of NaCl. These phenomena were the same as those mentioned above; that is, more free proton ions resulted in an increase of the  $K_a$  value in the presence of NaCl. The same results have also been observed in previous reports.<sup>19,20</sup> Similarly, the  $\text{pK}_a$  value of the other salt aqueous solutions can also be obtained; the results are shown in Table VI. Smaller ions in the common anionic system are easily bound to the sulfonate group ( $\text{SO}_3^-$ ) on the poly(SPM) and/or SPM monomer, thus increasing free proton ions ( $\text{H}^+$ ) present in the aqueous solution. The following trend can thus be drawn:  $\text{KCl} > \text{NaCl} > \text{LiCl}$ . Therefore, the





**Figure 18** Brookfield viscosity versus mol % SPM for AAm-SPM copolymer solution in water and 500 ppm NaCl<sub>(aq)</sub>; (○) AAm-SPM copolymers in water, (●) AAm-SPM copolymers in brine solution.

concentration of free proton ion ( $H^+$ ) increases and the pKa value decreases. The plots of pKa against the ionic strength for the poly(SPM) (Figure 16) make it clear that an increase in ionic strength from 0.1 to 0.75M causes the pKa to decrease from 2.77 to 2.66 at the half-neutralization point. The good linear relationship obtained means that pKa values drop as the ionic strength increases.

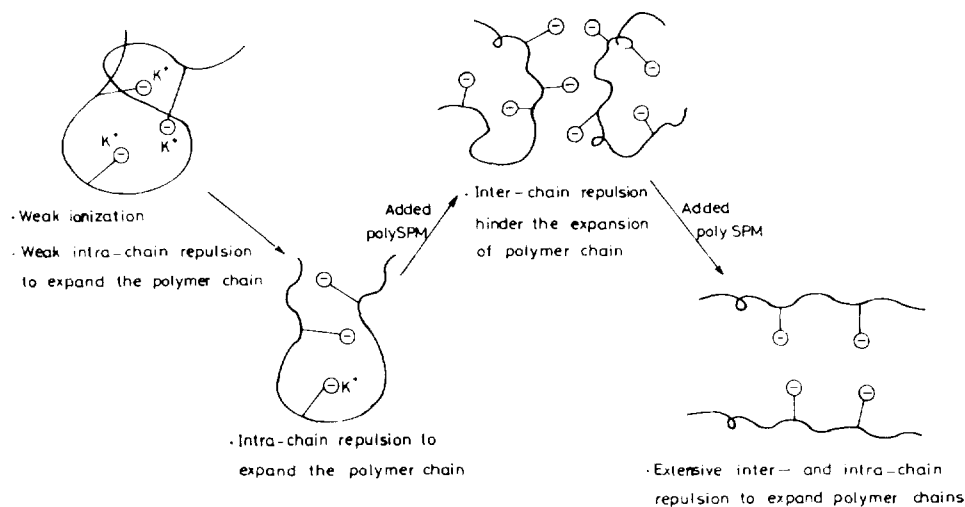
## CMC

In Figure 17 is shown a plot of equivalent conductance versus concentration for a solution of monomer and polymer. The monomer solutions exhibit a

plot typical of those observed for detergents, with a break in the curve occurring at the CMC.<sup>29-32</sup> The CMC determined for the monomer was taken at the intersection of the extrapolation lines in the regions above and below the CMC. From the shape of the curve in this region, it would appear that the formation of micelles occurs over a range of concentrations, with the experimentally determined value of CMC = 0.008M being the average value for this region. For the polymer solutions, no break in the equivalent conductance curve was found for the concentrations studied. It would appear that the long side chain poly(SPM) could display a zero CMC, such as has been reported for other polyelectrolytes by Salamone et al.<sup>29</sup>

## Application of Viscosity-Controlling Agents

Brookfield viscosity is plotted as functions of the mol % SPM of AAm-SPM copolymer in Figure 18, which demonstrates that aqueous solutions with a polymer concentration of 1,000 ppm give Brookfield viscosities. The copolymer AAm-SPM system showed Brookfield viscosity characteristics similar to those reported for other polymers.<sup>33,34</sup> Figure 18 shows the relative resistance of the present copolymers to viscosity loss in the presence of sodium chloride. The results indicate that copolymer AAm-SPM is effective in water or in brine solutions and that the copolymers in brine solutions are more effective than in water. The addition of salt would result in a rapid disruption of the conformation of copolymer AAm-SPM. This is because  $Na^+$  neutralizes the negative charges of poly(SPM), decreas-



**Figure 19** The proposed model for the effect of polymer concentration on poly(SPM) solution viscometrics.

ing the interrepulsive and intrarepulsive forces, which are what holds the expanded conformation of the polymers. The expanded conformation of the polymer gives high hydrodynamic volume and viscosity to the aqueous solution of the polyelectrolyte. When the conformation disintegrates, hydrodynamic volume and viscosity decrease. At this point, one can say that any type of salt that can neutralize the sulfonate group ( $\text{SO}_3^-$ ) can also disrupt chain repulsion and eventually decrease the Brookfield viscosity of the copolymer AAm-SPM.

The copolymer AAm-SPM should be compatible with salts such as sodium chloride and provide viscosity control in the presence as well as in the absence of such salts, since natural waters are often used instead of pure water for water flooding. The copolymer AAm-SPM is extremely well adapted for use as a "family" of viscosity-controlling agents in secondary oil recovery operations by water flooding.<sup>34</sup>

#### Proposed Model for the Poly(SPM) Solution Viscometrics

A proposed model is used to rationalize the effect of polymer concentration on the viscosity behavior of poly(SPM) (Fig. 19).

Initially, the ionization of poly(SPM) is weak; the corresponding negative charges in the polymer chain also have weak intrachain repulsion. In other words, weak ionization would mean that the  $\text{K}^+$  can neutralize the negative charge of poly(SPM) and decrease repulsion between the sulfonate ion groups, thus preventing the expansion of the polymer chains.

After some time, the degree of ionization of poly(SPM) increases. This will cause intrachain repulsion to increase the expansion of the polymer chain. Thus, the hydrodynamic volume of the chain is increased.

With a slight increase in the concentration of the poly(SPM), interchain repulsion could hinder the expansion of poly(SPM) by intrachain repulsion. However, as more poly(SPM) is added, the interaction of its molecules is affected, and with full ionization, interchain and intrachain repulsion is increased among and within the polymer chains. Eventually, the chain expands to a greater extent. This explains the sharp increase in viscosity, as seen in Figure 3. However, at high concentrations of the polymer, crowding among the polymer chains slows down the increase in viscosity.

#### CONCLUSIONS

The behavior of aqueous solution properties of an anionic polyelectrolyte, poly(SPM), would be evi-

dently transferred as salts were added in polymeric aqueous solution. Because the radius of the salt ion was large, the degree of attracting poly(SPM) to salt was increased and the intrinsic viscosity was decreased. As the salt concentration was increased, the intrinsic viscosity was decreased and Huggins constant  $k'$  was increased (Huggins constant  $k'$  was affected from polymer-solvent and polymer-polymer interactions). The polymerization of SPM in 0.5M NaCl aqueous solution proceeded more easily than that of SPM in pure water. The polymerization rate of SPM is found to pass through an extreme value as a function of pH. The polyelectrolyte in a high concentration of NaCl has a low degree of binding, indicating that the proton ion ( $\text{H}^+$ ) is relatively difficult to bind to the sulfonate group ( $\text{SO}_3^-$ ) at the polymer end. Smaller cations such as  $\text{Li}^+$  with a common anion,  $\text{Cl}^-$ , are found to be easily bound to the sulfonate group ( $\text{SO}_3^-$ ), resulting in the higher concentration of the free proton ion ( $\text{H}^+$ ) and the lower pH value. Smaller anions such as  $\text{F}^-$  with a common cation ( $\text{K}^+$ ) are found to be the most difficult to bind to the sulfonate group ( $\text{SO}_3^-$ ), indicating that the proton ion ( $\text{H}^+$ ) is relatively easy to bind to the sulfonate group ( $\text{SO}_3^-$ ) at the polymer end of polysulfonate, resulting in a high pH value. An increase in ionic strength causes the pKa to decrease at the half-neutralization point. The monomer solutions exhibit a plot typical to those observed for detergents, with a break in the curve occurring at the CMC. For the polymer solutions, no break in the equivalent conductance curve was found for the concentrations studied. The polymer is adapted for use as a viscosity-controlling agent in secondary oil recovery operations by water flooding. We have the proposed models to account for the poly(SPM) solution viscometrics.

We thank the National Science Council of the Republic of China for their financial support.

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Received January 5, 1996

Accepted July 25, 1996