Aqueous Solution Properties of Poly[3-Dimethyl (Methacryloyloxyethyl) Ammonium Propane Sulfonate]

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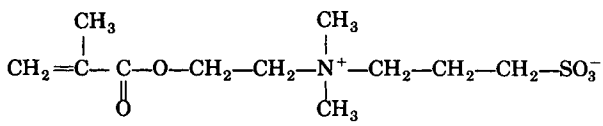
Synopsis

The aqueous solution properties of an ampholytic poly[3-dimethyl (methacryloyloxyethyl) ammonium propane sulfonate] [poly(DMAPS)] are studied by measurements of cloud point determination, intrinsic viscosity, degree of binding, and ionic strength. The minimum salt concentration and intrinsic viscosity of this polyampholyte are related to the type and concentration of added salt. Both the polymeric and monomeric betaines in the presence of NaCl have the lower degree of binding, indicating that the proton ion (H^+) is relatively difficult to bind the SO_3^- at the end of sulfobetaine. An increase in ionic strength causes the pK_a to decrease at the half-neutralization point.

INTRODUCTION

Zwitterionic monomers of the sulfobetaine type such as methacryloyl ammonium propanesulfonate,



are widely considered as one of the functional monomers used as minor components for copolymers in various fields, such as textile, medical, charged dispersing agents, and protective colloids.[1-10] For example, Szita et al. and Spriestersbach et al. reported that such a monomer is polymerizable with acrylonitrile and able to be applied to the dyeing processing of textiles.[4-8] Ishikura and his co-workers also used this polymerizable monomer to improve the physical properties of emulsions.[9,10]

The aqueous solution properties of betaines such as carboxybetaine and sulfobetaine are studied by several scholars.[11-19] Topchiev et al. investigated the kinetic features of the radical polymerization of an unsaturated carboxybetaine in the various pH ranges.[11] Asonova et al. also reported that such polycarboxybetaine had a varied reduced viscosity as a function of pH.[13] The solution properties of sulfobetaine homopolymers were also studied in detail by Salamone and his co-workers, especially in the vinylimidazole series.[17-19] Furthermore, Salamone stated that the anionic sulfonate group is more

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difficult to protonate than the anionic carboxylate group and would maintain an inner salt structure over a wider pH range.[18] However, they have published only a few experimental results for similar systems involving methacryloyl sulfobetaine.

In the previous paper,[20] we investigated the thermal degradation of such a polysulfobetaine. The aim of the present paper is to examine the aqueous solution properties, especially in the cloud point determination, intrinsic viscosity in the presence of various salts, and degree of binding in various pH ranges.

EXPERIMENTAL

Preparation of Monomer

The monomer 3-dimethyl (methacryloyloxyethyl) ammonium propane sulfonate, (DMAPS), was prepared as described previously.[20] The monomer was characterized by elemental analysis techniques, IR, and NMR as described before, and was quite hygroscopic [mp 280°C (decomposition)].[20]

Preparation of Polymer

Into a 50 mL polymerization tube was introduced 1.0 g (3.58×10^{-3} mol) of DMAPS monomer and 0.02 g (2 mol %) of 4, 4′-azobis-4-cyanovaleric acid (ACVA). To this, 20 mL of distilled water was added yielding a 0.18 M aqueous solution. The contents of the tube were then flushed with nitrogen and sealed *in vacuo* after utilization of the freeze–thaw technique.

The tube was then placed in a constant temperature bath at 60°C for 24 h. The heterogeneous mixture was then precipitated with acetone, washed with water to eliminate the unchanged monomer, dried for 24 h at 100°C under vacuum, and weighed. The dried, brittle, and white polymer was obtained in 92% yield.

Cloud Point Determinations

Cloud point titrations to determine the point at which the 1% wt/vol polymer solution becomes insoluble in the aqueous salt solution were performed by dissolving the material in an aqueous salt solution of sufficient salt content and titrating the stirred solution with distilled water to the first indication of turbidity.

Viscometric Measurements

Viscometric measurements were carried out with an Ubbelohde viscometer (The viscometer has the flow time 108.15 s for the pure water) at 30.00 ± 0.01°C. The polymer samples were dissolved in the salt concentration to yield stock solution of approximately 1 g/100 mL solvent.

Viscosity data were calculated by the Mark–Huggins equation

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

pH Measurements

The Seibold-Messtechnik pH G103 instrument was used with 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 monomer or polymer 0.1021 g in 50 mL salt solution at starting NaCl molarities of 0.0, 0.005, 0.1, and 0.5.

RESULTS AND DISCUSSION

Cloud Point Determinations

In order to study the solution behavior of the poly[3-dimethyl(methacryloyloxyethyl) ammonium propane sulfonate] [poly(DMAPS)], and how readily they dissolved in certain aqueous salt solutions of sufficient salt content, it was necessary to measure the minimum salt concentration needed for solubilization of the polymer. Utilizing salt solutions containing a common cation but different anions, we got the data that show a definite increase in the solubility of
poly(DMAPS) in aqueous salt solution in the order $F^- < Cl^- < NO_3^- < Br^- < I^- < ClO_4^-$ for KF, KCl, KNO_3, KBr, KI, and $KClO_4$, respectively, as shown in Table I. These data are consistent with those for the sulfobetaine derived from poly(4-vinylpyridine)[16] and polyvinylimidazole[19] and seem to relate to the site binding ability of the anion.[19,21-23]

Table II shows the cloud points of polymer solutions containing salts with a common anion but different cations. For the chloride salts, the data indicate an increase in the solubility of the polymer in the order $Li^+ < NH_4^+ < Na^+$

TABLE I
Minimum Salt Concentration of Poly(DMAPS) in Salt Solutions with a Common Cation

Electrolyte	Minimum salt concentration
KF	Insoluble
KCl	0.070*M*
KNO_3	0.024*M*
KBr	0.019*M*
KI	0.006*M*
$KClO_4$	0.004*M*

TABLE II
Minimum Salt Concentration of Poly(DMAPS) in Salt Solutions with a Common Anion

Electrolyte	Minimum salt concentration
LiCl	0.084*M*
NaCl	0.071*M*
KCl	0.070*M*
NH_4Cl	0.078*M*
$NaClO_4$	0.005*M*
$KClO_4$	0.004*M*
NH_4ClO_4	0.004*M*

TABLE III
Minimum Salt Concentrations of Poly(DMAPS) in Salt Solutions Containing Divalent Cations

Electrolyte	Minimum salt concentration
$Mg(ClO_4)_2$	0.004*M*
BaI_2	0.007*M*
$MgCl_2$	0.048*M*
$BaCl_2$	0.050*M*
$SrCl_2$	0.068*M*
$CaCl_2$	0.071*M*

$< K^+$ for LiCl, NH_4Cl, NaCl, and KCl, respectively. For the perchlorate salts no order is observed. A similar tendency has been observed for the binding of these cations to polyelectrolytes containing pendant sulfonate group with the potassium ion being bound the strongest and lithium ion being bound the weakest.[24-26] Salamone reported that the anions and cations of the low molecular weight electrolyte could be considered to enter the ionically cross-linked network of the polymer through osmotic forces, and it could be these forces which caused the polymer to swell when placed in water.[19] The reason that the polymer does not dissolve in water could therefore be that the osmotic force which tends to draw solvent into the polymer is not of sufficient strength to rupture the ionic crosslinks. From Tables I and II, it seems apparent that either the common anions or cations with a small charge/radius ratio are easy to dissolve into polymer.

For the divalent cations, the data show an increase in the solubility of poly (DMAPS) in aqueous salt solution in the order $Mg^{++} < Ba^{++} < Sr^{++} < Ca^{++}$ for $MgCl_2$, $BaCl_2$, $SrCl_2$, and $CaCl_2$, respectively, as shown in Table III. The solubility of poly(DMAPS) shows an increase in the order $MgCl_2 < Mg(ClO_4)_2$ and $BaCl_2 < BaI_2$. This tendency is similar to the monovalent common cations (Table I).

Viscosity Measurements

It is well known that the intrinsic viscosity is a good measure of the hydrodynamic volume of the polymer containing the same molecular weight. Therefore, determination of the intrinsic viscosity of poly(DMAPS) in the presence of different electrolytes should reflect the influence of these salts on the hydrodynamic volume of the polymer chain. The influence of different electrolytes having a common cation, $\cdot K^+$, on the intrinsic viscosities of poly(DMAPS) is shown in Figure 1. The data show an increase in the intrinsic viscosity of poly(DMAPS) in 0.5*M* aqueous salt solution in the order $Cl^- < Br^- < I^-$ for KCl, KBr, and KI, respectively. This phenomenon is similar to the result of cloud point determination as illustrated in Table I. It would appear to suggest that the zwitterionic polymer is able to effectively site bind the less hydrated anion (I^-) to the positively charged quaternary ammonium ion. In fact, the hydration numbers of I^- and Cl^- are 0.7 and 2, respectively.[27]

An analogous viscosity experiment was conducted employing a common anion Cl^-. The results obtained are shown in Figure 2. The results of viscosity experiments of common anion coincided with that of cloud point determina-

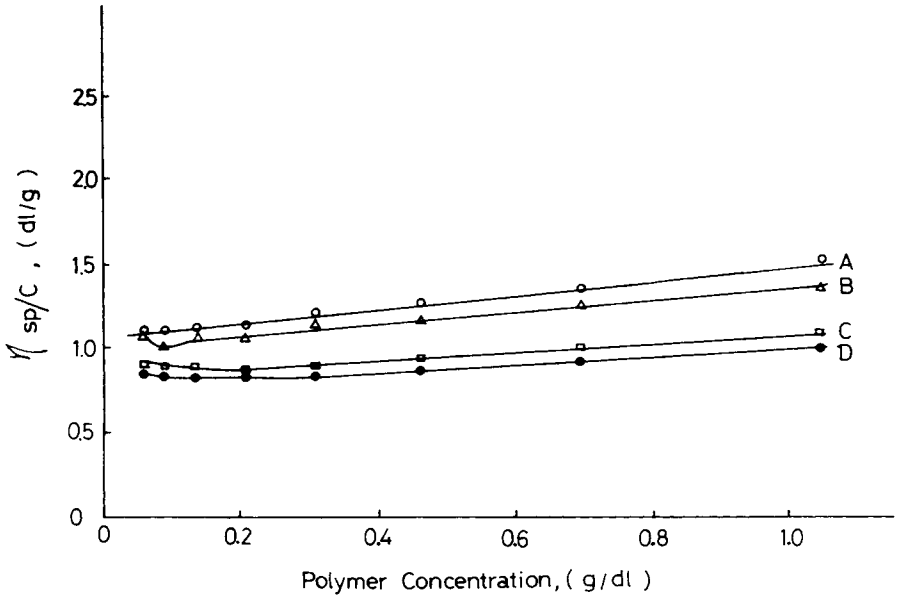


Fig. 1. Reduced viscosities of poly(DMAPS) as a function of concentration for salts containing a common cation: (A) 0.20*M* $KClO_4$; (B) 0.50*M* KI; (C) 0.50*M* KBr; (D) 0.50*M* KCl.

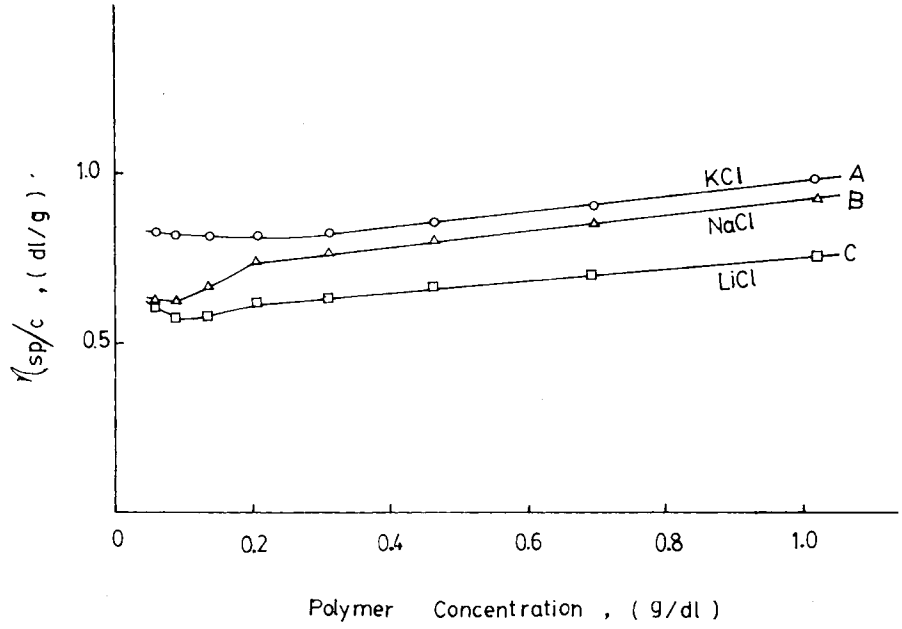


Fig. 2. Reduced viscosities of poly(DMAPS) as a function of concentration for salts containing a common anion: (A) 0.50*M* KCl; (B) 0.50*M* NaCl; (C) 0.50*M* LiCl.

TABLE IV
Effect of Anion and Cation on the Viscosity Behavior of Poly(DMAPS) at 30°C

Salt solution (0.5*M*)	Slope	Intercept [η]	k'
LiCl	0.183	0.57	0.56
NaCl	0.233	0.68	0.50
KCl	0.217	0.74	0.41
KBr	0.250	0.80	0.39
KI	0.367	0.98	0.38
$KClO_4$	0.417	1.06	0.37
$CaCl_2$	0.217	0.77	0.37

tion experiments (Table II). From Figures 1 and 2 and eq. (1), the slope, intercept, and Huggins constant k' could be calculated. The results are shown in Table IV. From Table IV, the value for the Huggins constant decreases as the intrinsic viscosity increases. This decrease in the Huggins constant may be associated with an increased polymer–solvent interaction, which is reaffirmed by the cloud point determinations (Tables I and II).[19]

From Tables I and II, it seems apparent that the effect of the anion (common cation) on the solution properties of this polymer is much greater than the effect of the cation (common anion). This concept was examined more closely in an experiment in which the intrinsic viscosities of solutions of KCl of several different concentrations containing fixed poly(DMAPS) were determined. The results are shown in Table V and Figure 3.

The presumed concept of chain expansion of the polysulfobetaine (a partial neutralization of one of the charges results in an excess of the opposite charge) is corrected, then the phenomenon of an increase in reduced viscosity in increased salt concentration can perhaps be rationalized.[19] The effect is illustrated in Figure 3 for the polysulfobetaine in varying KCl concentrations. It is apparent that there is a significant increase in reduced viscosity as the KCl concentration is increased. This effect could be related to the formation of a partial negative charge on the polysulfobetaine due, possibly, to a greater degree of counterion binding efficiency of Cl^- to the quaternary ammonium group in comparison of that of K^+ to the sulfonate group. Such an overall negative charge density would then be greater in increased KCl concentration. The intrinsic viscosities versus the KCl concentration are plotted in Figure 4. It is possible to consider Figure 4 to be composed of two straight lines. This

TABLE V
Effect of Salt Concentration on the Intrinsic Viscosity and Huggins Constant of Poly(DMAPS)

KCl concentration	[η] (dL/g)	k'
0.25 M	0.49	0.70
0.30 M	0.55	0.55
0.40 M	0.62	0.41
0.50 M	0.74	0.40
0.80 M	0.80	0.34
1.50 M	0.93	0.29

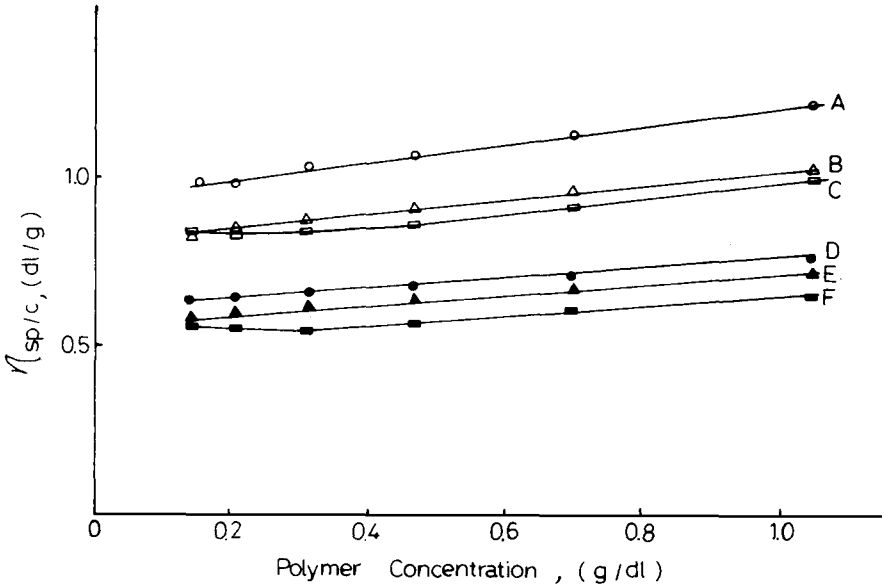


Fig. 3. Reduced viscosities of poly(DMAPS) as a function of concentration for KCl: (A) 1.5*M*; (B) 0.80*M*; (C) 0.50*M*; (D) 0.40*M*; (E) 0.30*M*; (F) 0.25*M*.

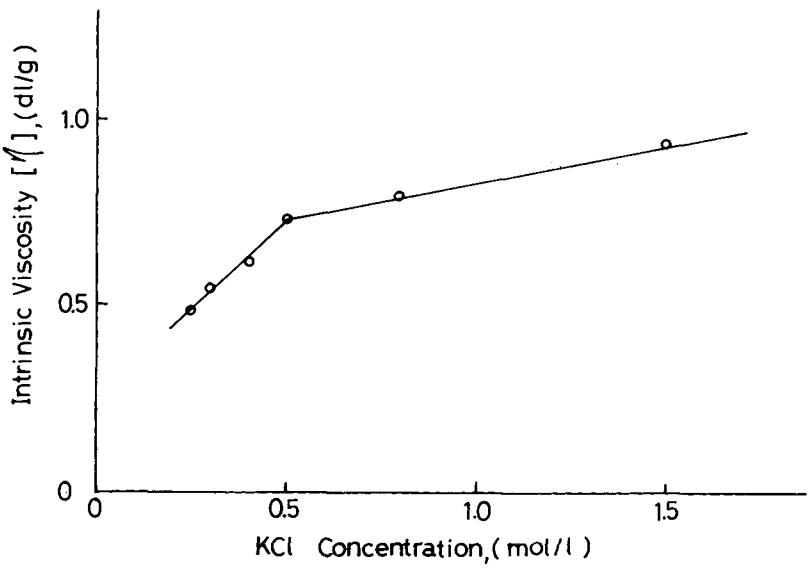


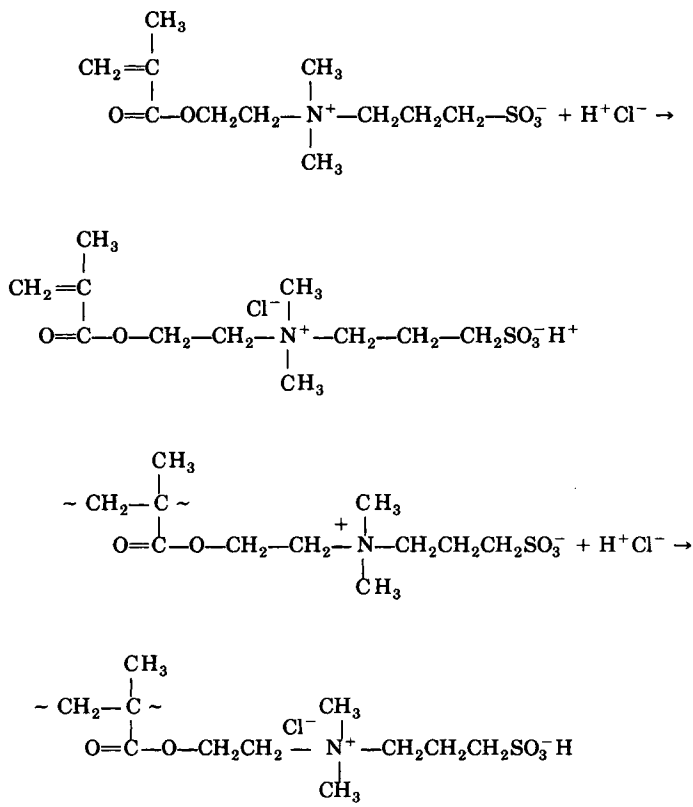
Fig. 4. Intrinsic viscosity of poly(DMAPS) as a function of KCl concentration.

phenomenon is similar to Salamone's result.[19] The first line, which had the higher slope, may be due to site binding of the chloride ion by the quaternary ammonium group. This line is characterized by a relatively rapid change in the intrinsic viscosity as the chloride ion concentration is increased, perhaps due to atmospheric binding of the Cl^- by the polyampholyte. At the lower concentrations shown site binding of the Cl^- is predominant. As the concentration of the salt is increased, more and more of the potential binding

sites are occupied, resulting in a decreased tendency for further site building. This explanation seems to agree with the fact that k' decreases as the salt concentration is increased. The Huggins constant k' is generally considered to be related to the polymer–solvent interaction.

Determination of Degree of Binding

The potentiometric titration of the polymeric and monomeric sulfobetaine with hydrochloric acid in aqueous solution was carried out in the presence and absence of NaCl salt. The result is shown in Figure 5. The nature of the potentiometric titration curve resembles that of the titration of a salt of a weak acid and a strong base with a strong acid (HCl). This permits the assumption that in neutral solutions we are dealing with a betaine existing 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 sulfobetaine:



(2)

(3)

From Figure 5, it is seen that either monomer or polymer in the presence of salt, has a lower pH value at the same amount of added HCl solution. This means that poly (DMAPS) and/or DMAPS monomer has a certain degree of site-binding with NaCl. The salt NaCl hinders the binding ability for the sulfobetaine and HCl solution. Consequently, the concentration of free HCl solution increases results in the lower pH value in the presence of NaCl salt.

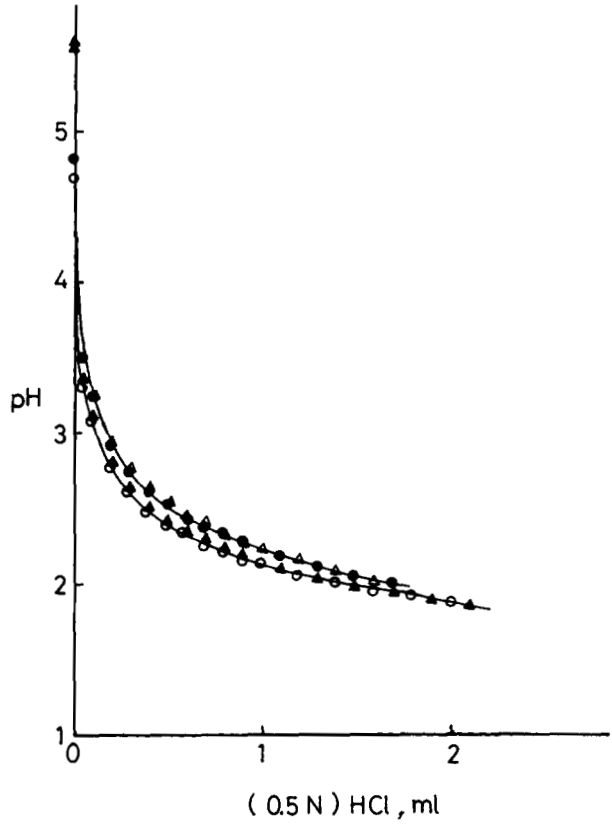


Fig. 5. Relationships of pH vs. 0.50*N* HCl: (●) poly(DMAPS) 0.1021 g in 50 mL H_2O; (○) poly(DMAPS) 0.1021 g in 50 mL 0.1*M* NaCl; (△) DMAPS 0.1021 g in 50 mL H_2O; (▲) DMAPS 0.1021 g in 50 mL 0.1*M* NaCl.

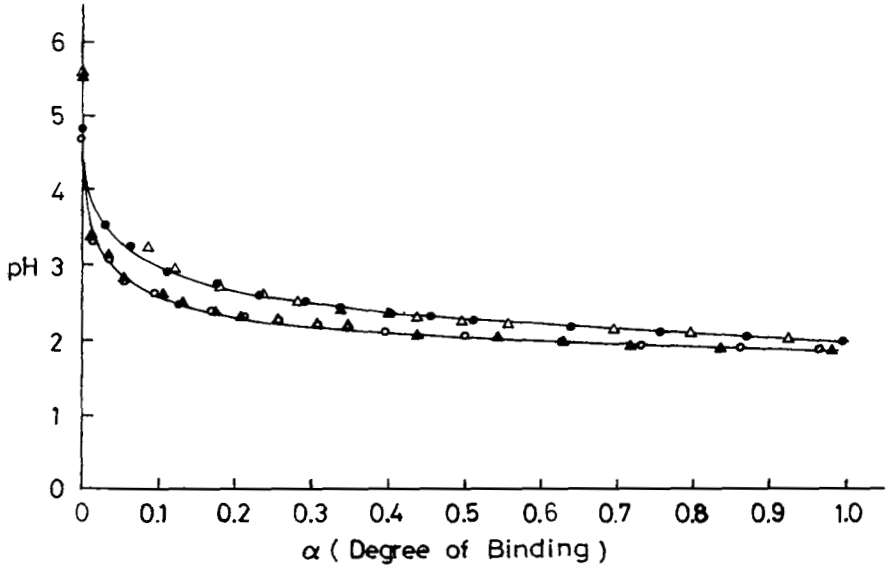


Fig. 6. Relationships of pH vs. α: (●) poly(DMAPS) 0.1021 g in 50 mL H_2O; (○) poly(DMAPS) 0.1021 g in 50 mL 0.1*M* NaCl; (△) DMAPS 0.1021 g in 50 mL H_2O; (▲) DMAPS 0.1021 g in 50 mL 0.1*M* NaCl.

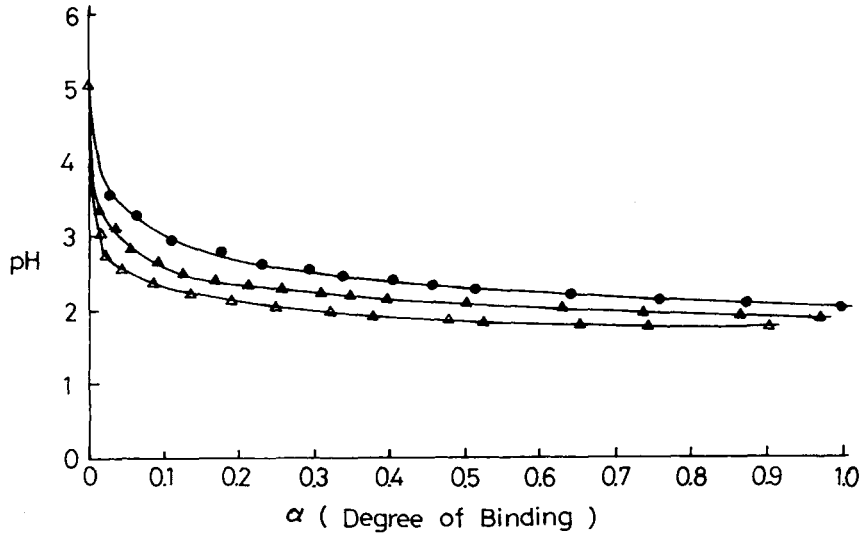


Fig. 7. Relationships of pH vs. α in various concentration of NaCl: (•) poly(DMAPS) in no salt exist; (▲) poly(DMAPS) in 0.1M NaCl; (△) poly(DMAPS) in 0.5M NaCl.

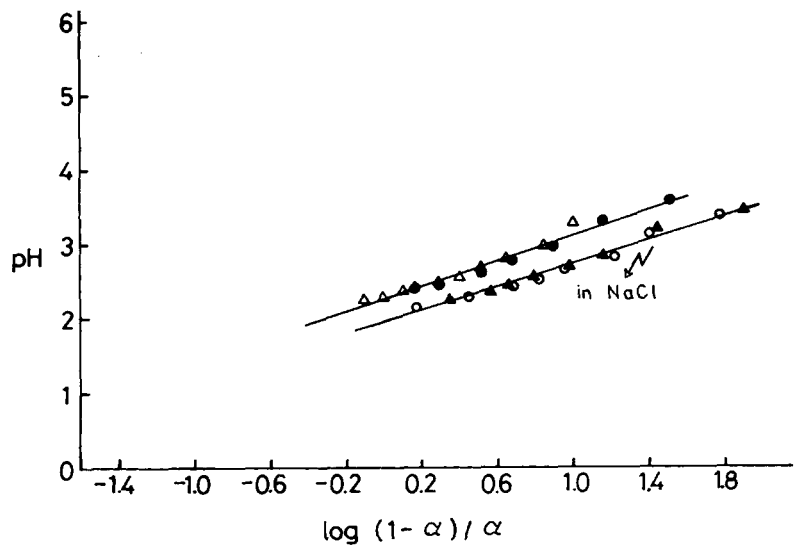


Fig. 8. The dependence of pH on degree of binding (α): (•) poly(DMAPS) in 50 mL H_2O; (○) poly(DMAPS) in 50 mL 0.1M NaCl; (△) DMAPS in 50 mL H_2O; (▲) DMAPS in 50 mL 0.1M NaCl.

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

$$pH = pK_a + n \log \frac{1 - \alpha}{\alpha} \tag{4}$$

where α is the degree of binding for the zwitterionic betaine and hydrochloric acid solution and K_a is the constant of binding. From Figure 5 and eq. (4), the relationship of pH and α can be calculated. The result is shown in Figure 6. It is clear that both the polymeric and monomeric betaines in the presence of NaCl have a lower degree of binding at the same pH value in comparison with the absence of NaCl. This phenomenon could be explained by the argument that the proton ion (H^+) is relatively difficult to bind the SO_3^- at the polymer end resulted in the lower degree of binding in the presence of NaCl.

Figure 7 shows the relationship between pH and degree of binding (α) in various concentration of NaCl. The higher concentration of NaCl has the lower pH value. This result is consistent with Figure 6. From the plot of pH versus $\log[(1 - \alpha)/\alpha]$, the pK_a could be calculated. That is, pK_a is equal to pH as α is equal to 0.5. The results are shown in Figure 8. From the figure both the monomer and polymer sulfobetaine have the pK_a value 2.24 and 1.94 in the presence and absence of NaCl, respectively. This phenomenon was the same as above-mentioned, that is, the more free proton ions exist in the presence of NaCl which is resulted in the lower pH value, the lower pK_a value was obtained.

Figure 9 shows the dependence of pH on $\log[(1 - \alpha)/\alpha]$ in the various concentration of NaCl. From Figure 9, pK_a decreases with the NaCl concentration increases. This tendency is due to the fact that the binding ability

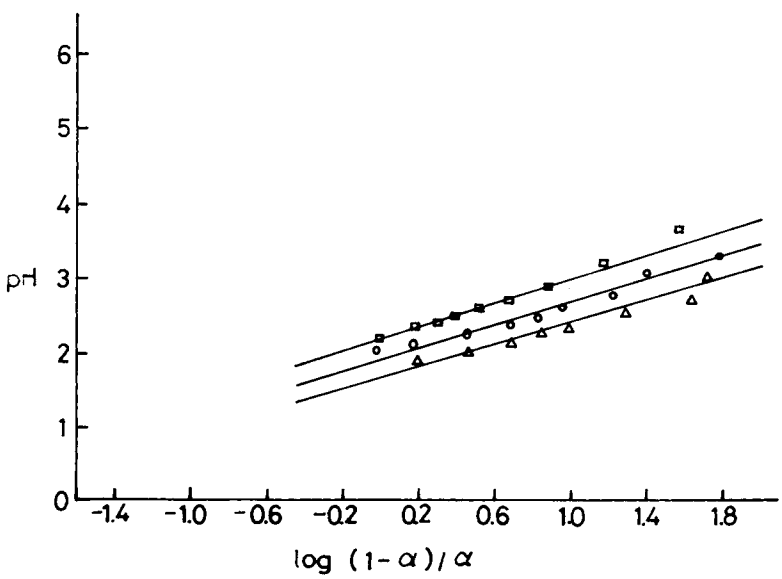


Fig. 9. The dependence of pH on $\log[(1 - \alpha)/\alpha]$ in various concentration of NaCl poly(DMAPS): (□) in 0.005*M* NaCl; (○) in 0.1*M* NaCl; (△) in 0.5*M* NaCl.

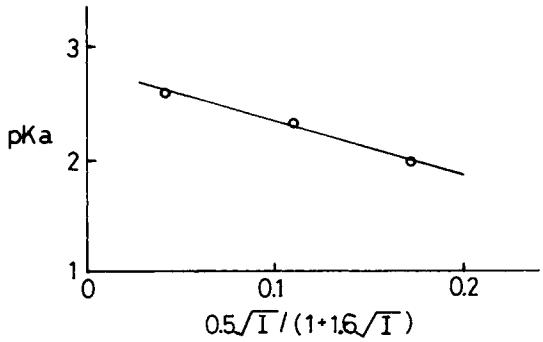


Fig. 10. The pK_a as a function of ionic strength (I).

of sodium ion (Na^+) to the SO_3^- group of polysulfobetaine increases with the increase of concentration of NaCl. These results lead to the decrease of degree of binding for the proton ion (H^+). Therefore, the concentration of free proton ion (H^+) increases and then the pK_a value decreases. The plots of pK_a against the ionic strength for the polysulfobetaine (Fig. 10) make it clear that an increase in ionic strength from 0.005 to 0.5M causes the pK_a to decrease from 2.20 to 1.65 at the half-neutralization point. The good linear relationship obtained means that the pK_a values drop as the ionic strength increases, i.e., at the higher concentration of NaCl.

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References

1. Rohm and Hass Co., Neth. Pat. Appl. 6,411,736 (1965).
2. Rohm and Hass Co., Br. Pat. 1,077,772 (1967).
3. U. Bahr, H. Wieden, H. A. Rinkler, and G. E. Nischk, *Makromol. Chem.*, **161**, 1 (1972).
4. J. Szita, U. Bahr, H. Wieden, H. Marzolph, and G. E. Nischk, Belg. Pat. 659,316 (1965).
5. J. Szita, U. Bahr, H. Wieden, and G. E. Nichk, Ger. Pat. 1,211,156 (1966).
6. J. Szita, U. Bahr, H. Wieden, H. Marzolph, and G. E. Nischk, Br. Amended Pat. 1,024,029 (1966).
7. J. Szita, U. Bahr, H. Widen, H. Marzolph, and G. E. Nischk, U.S. Pat. 3,478,001 (1969).
8. D. R. Spriestersbach, R. A. Clarke, M. Couper, and H. T. Patterson, U.S. Pat. 3,473,998 (1969).
9. S. Ishikura, R. Mizuguchi, and A. Takahashi, Jpn. Kokai 80,386 and 80,387 (1977).
10. R. Mizuguchi, S. Ishikura, A. Takahashi, and A. Uenaka, U.S. Pat. 4,215,028 (1980).
11. D. A. Topchiev, L. A. Mkrtchyan, R. A. Simonyan, M. B. Lachinov, and R. A. Kabanov, *Vysokomol. Soyed.*, **A19**, 506 (1977).
12. T. A. Asonova, Ye. F. Razvodovkii, A. B. Zezin, and V. A. Kargin, *Dokl. Akad. Nauk SSSR*, **118**, 583 (1969).
13. T. A. Asonova, Ye. F. Razvodovkii, and A. B. Zezin, *Vysokomol. Soyed.*, **A16**, 777 (1974).
14. V. M. Monroy Soto and J. C. Galin, *Polymer*, **25**, 121 (1984).
15. V. M. Monroy Stot and J. C. Galin, *Polymer*, **25**, 254 (1984).
16. R. Hart and D. Timmerman, *J. Polym. Sci.*, **28**, 638 (1958).
17. J. C. Salamone, W. Volkson, S. C. Israel, D. C. Raia, A. Broggi, and T. D. Hsu, *Polym. Prepr.*, **14**, 731 (1973).

18. J. C. Salamone, W. Volkson, S. C. Israel, A. P. Olson, and D. C. Raia, *Polymer*, **18**, 1058 (1977).
19. J. C. Salamone, W. Volkson, A. P. Olson, and S. C. Israel, *Polymer*, **19**, 1157 (1978).
20. D. J. Liaw and W. F. Lee, *J. Appl. Polym. Sci.*, **30**, 4697 (1985).
21. D. Casson and A. Rembaum, *Macromolecules*, **5**, 75 (1972).
22. G. Scatchard and W. Yap, *J. Am. Chem. Soc.*, **96**, 3434 (1964).
23. U. P. Gergor, J. Belle, and R. A. Marcus, *J. Am. Chem. Soc.*, **77**, 2713 (1955).
24. U. P. Strauss and Y. P. Leung, *J. Am. Chem. Soc.*, **87**, 1476 (1965).
25. J. Hen and U. P. Strauss, *J. Phys. Chem.*, **78**, 1013 (1954).
26. U. P. Strauss, C. Helfgott, and H. Pink, *J. Phys. Chem.*, **71**, 2555 (1967).
27. J. O'M. Bockris, *Quart. Rev., London*, **3**, 173 (1949).

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