

Synthesis and solubility of the poly(sulfobetaine)s and the corresponding cationic polymers: 1. Synthesis and characterization of sulfobetaines and the corresponding cationic monomers by nuclear magnetic resonance spectra

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Sulfobetaines of two types and the corresponding cationic monomers were synthesized; the preparation of their polymers is described. The solubilities and moisture regain properties of the poly(sulfobetaine)s and cationic polymers were investigated in relation to their molecular structures. It was very difficult to distinguish in ^1H nuclear magnetic resonance (n.m.r.) and ^{13}C n.m.r. spectra the chemical shift of the methylene moiety ($-\text{CH}_2-$) in the neighbourhood of the quaternary ammonium group. By comparison of the chemical shifts of the corresponding cationic monomers and sulfobetaines in both ^1H and ^{13}C n.m.r. spectra, the respective methylene groups were clearly distinguished from their chemical shifts in the ^1H and ^{13}C n.m.r. spectra; the conformations of sulfobetaines and the form of cationic monomers in aqueous solution were identified.

(Keywords: sulfobetaine; cationic polymer; n.m.r. spectroscopy)

INTRODUCTION

Sulfobetaines or carboxybetaines and related cationic monomers derived from dimethylaminoalkyl acrylates and dimethylaminoalkyl acrylamides are extensively utilized in industries concerned with textiles, dispersion agents, antistatic agents, surfactants, protective colloids, adhesives, coatings, flocculants, hair conditioners, etc.¹⁻⁹. The properties of poly(betaine)s in aqueous solution, such as carboxybetaine and sulfobetaine, have been extensively investigated¹⁰⁻²⁶. For instance, Asonova *et al.* reported that the reduced viscosity of a poly(carboxybetaine) varied with pH¹³. The synthesis and solution properties of poly(sulfobetaine)s were examined by Salamone and coworkers, especially the vinylimidazole series^{12,22}; they also studied the properties of cationic and anionic copolymers²³. N.m.r. spectra of poly(sulfopropylbetaine)s of vinylpyridinium and methacrylate were measured by Galin and Monroy Soto, who also studied the aqueous and bulk properties of such poly(sulfopropylbetaine)s^{16,17}. The syntheses of sulfobetaine and cationic electrolytes derived from acrylate, acrylamide, pyridinium acrylate and pyridinium acrylamide were reported by Laschewsky and Zerbe¹⁸, who studied the bulk and surface-activity properties of such polymers. The ampholytic polymers copolymerized through cationic and anionic monomers were also investigated²³⁻²⁵.

It is difficult to identify individually the signals of the aliphatic group that lie adjacent to lines of the quaternary ammonium group for such sulfobetaines in n.m.r. spectra; hence the chemical shifts of those aliphatic signals were roughly considered collectively¹⁶⁻¹⁸. We prepared several cationic monomers related to respective sulfobetaines, and clearly identified the ^1H n.m.r. signals of the aliphatic group near the lines due to the quaternary ammonium group of sulfobetaine monomers with the assistance of the respective cationic monomers. Our objective was to prove that the ampholytic monomer formed the inner ionic network and the counterion of the cationic monomer ionized in aqueous solution by comparing the hydrogen signals in the relevant positions.

EXPERIMENTAL

Materials

After the solvents for synthetic monomers were purified, these solvents were directly distilled and dried over either 3 Å molecular sieve for acetonitrile or anhydrous calcium chloride for acetone and butanone. Diethyl ether and propan-2-ol were analytical-grade. Deionized water (18 MΩ) was used to polymerize monomers.

The materials used for synthetic monomer were purchased from Tokyo Kasei Industries Ltd. Propane sultone and iodomethane were used directly, but other materials were distilled under reduced pressure before

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use, as follows:

dimethylaminoethyl methacrylate	160°C/16 kPa
diethylaminoethyl methacrylate	170°C/14 kPa
<i>N</i> -(3-dimethylaminopropyl)acrylamide	174°C/16 kPa
<i>N</i> -(3-dimethylaminopropyl)methacrylamide	163°C/14 kPa

Synthesis of monomers

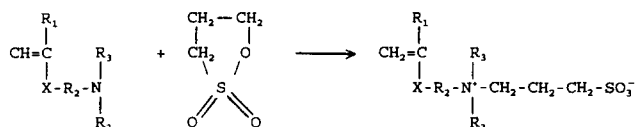
3-Dimethyl(methacryloyloxyethyl)ammonium propanesulfonate (DMAPS) (sample I). The monomer was prepared as described previously²⁷⁻²⁹. The structure of DMAPS is shown in Scheme 1 (sample I). Yield, 92%; m.p., 95°C.

3-Diethyl(methacryloyloxyethyl)ammonium propanesulfonate (DEAPS) (sample II). Into a 100 ml flask equipped with a stirrer, a condenser and a thermometer, *N,N*-diethylaminoethyl methacrylate (5.55 g, 0.03 mol), acetonitrile (10 g) and hydroquinone (0.06 g) were added; the contents were stirred at 70°C. A mixture of 1,3-propane sultone (3.66 g, 0.03 mol) and acetonitrile (3 g) was added dropwise for 1 h. After completion of the addition, the mixture was stirred at the same temperature for 7 h and then allowed to stand at 5°C for two days. The precipitated white crystals were collected by filtration, washed with diethyl ether several times, and dried under reduced pressure for 24 h to obtain DEAPS. Yield, 60%; m.p., 123°C. Elemental analysis (C₁₃H₂₅NO₅S): calculated, C 50.54%, H 8.14%, N 4.58%, S 10.70%; found, C 50.81%, H 8.14%, N 4.56%, S 10.42%.

***N,N*-Dimethyl(acrylamidopropyl)ammonium propanesulfonate (DMAAPS) (sample III).** DMAAPS was prepared similarly to DEAPS except that the temperature was altered to 30°C; the precipitated white crystals were collected by filtration, washed with acetone several times, and dried under reduced pressure for 24 h. Finally, the reaction produced *N,N*-dimethyl(acrylamidopropyl)ammonium propanesulfonate (DMAAPS). Yield, 92%; m.p., 105°C. Elemental analysis (C₁₁H₂₂N₂O₄S): calculated, C 48.02%, H 7.91%, N 10.11%, S 11.40%; found, C 47.48%, H 7.91%, N 10.07%, S 11.51%.

***N,N*-Dimethyl(methacrylamidopropyl)ammonium propanesulfonate (DMMAAPS) (sample IV).** The synthetic method of DMMAAPS was the same as for DMAAPS to obtain white crystals. Yield, 88%; m.p., 112°C. Elemental analysis (C₁₂H₂₄N₂O₄S): calculated, C 46.91%, H 8.21%, N 9.07%, S 10.30%; found, C 49.31%, H 8.22%, N 9.58%, S 10.75%.

Comparing the synthetic methods for DMAPS, DEAPS, DMAAPS and DMMAAPS, the synthetic reaction of DEAPS was distinct, because the replaced groups of the tertiary ammonium of diethylaminoethyl methacrylate were large and steric hindrance of the structure impeded the reaction. An elevated temperature was required to accelerate the reaction of quaternary ammonium. The general formulae of these reactions follow the equation:



in which R₁ is H or CH₃, R₂ is -(CH₂)_{*n*}- (*n*=2,3), R₃ is -CH₃ or -C₂H₅ and X is -CONH- or -COO-.

Trimethylmethacryloyloxyethylammonium iodide (TMMAI) (sample A), diethylmethacryloyloxyethylammonium iodide (DEMMAI) (sample B), trimethylacrylamidopropylammonium iodide (TMAAI) (sample C) and trimethylmethacrylamidopropylammonium iodide (TMMAAI) (sample D). The general procedure was that, to a spherical flask (0.3 litre) sheathed in aluminium foil and equipped with a stirrer, a condenser and a thermometer, the starting material, either dimethylaminoethyl methacrylate (15.7 g, 0.1 mol), or diethylaminoethyl methacrylate (18.5 g, 0.1 mol), or *N*-(3-dimethylaminopropyl)acrylamide (15.7 g, 0.1 mol), or *N*-(3-dimethylaminopropyl)methacrylamide (17.0 g, 0.1 mol), and butanone (20 g) were added. The contents were stirred at 3°C. A mixture of methyl iodide (14.2 g, 0.1 mol) and butanone (20 g) was added dropwise for 1 h. After completion of the addition, the mixture was stirred at the same temperature for 7 h and then allowed to stand at 5°C for two days. The yellow solution was removed by filtration and the white crystals were washed several times with dry butanone, and dried under darkness and under reduced pressure for 24 h. The desired monomers were recovered and their purities were checked by melting point and elemental analyses.

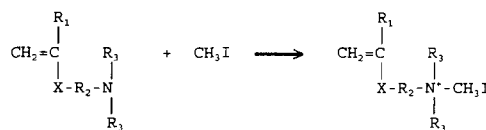
Trimethylmethacryloyloxyethylammonium iodide (TMMAI) (sample A): yield, 97%; m.p., 178°C. Elemental analysis (C₉H₁₈NO₂I): calculated, C 36.13%, H 5.82%, N 4.71%; found, C 36.12%, H 6.02%, N 4.68%.

Diethylmethacryloyloxyethylammonium iodide (DEMMAI) (sample B): yield, 87%; m.p., 85°C. Elemental analysis (C₁₁H₂₂NO₂I): calculated, C 40.28%, H 6.45%, N 4.23%; found, C 40.36%, H 6.75%, N 4.28%.

Trimethylacrylamidopropylammonium iodide (TMAAI) (sample C): yield, 96%; m.p., 148°C. Elemental analysis (C₉H₁₉N₂OI): calculated, C 36.45%, H 6.18%, N 9.40%; found, C 36.24%, H 6.37%, N 9.40%.

Trimethylmethacrylamidopropylammonium iodide (TMMAAI) (sample D): yield, 94%; m.p., 112°C. Elemental analysis (C₁₀H₂₁N₂OI): calculated, C 38.21%, H 6.51%, N 8.72%; found, C 38.46%, H 6.73%, N 8.97%.

During the syntheses of TMMAI, DEMMAI, TMAAI and TMMAAI, the products became yellow from the irradiation of light and the existence of impurities in the solution. When the yellow product was washed with butanone to recover white crystals, the yield of synthetic monomer was diminished. The synthetic methods followed the general equation:

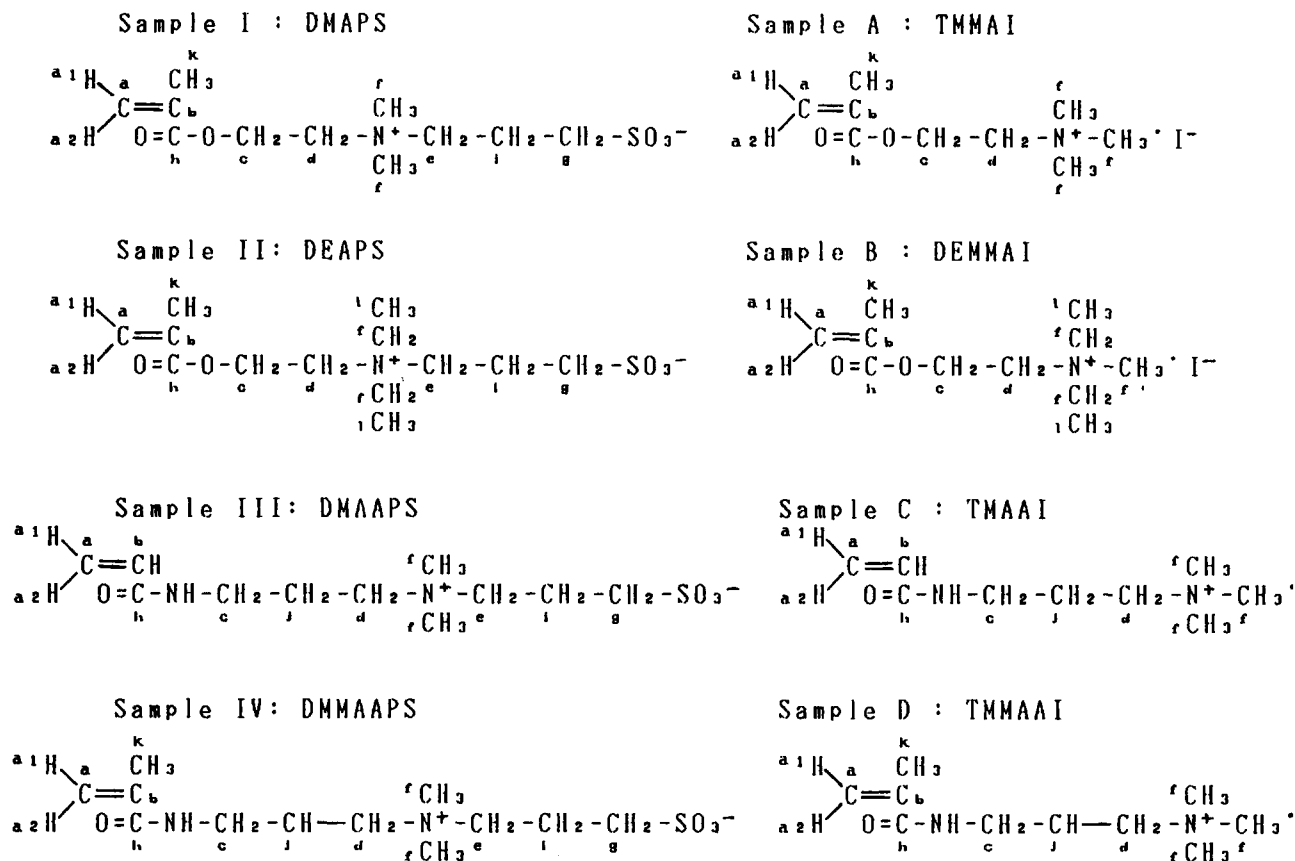


in which R₁ is H or CH₃, R₂ is -(CH₂)_{*n*}- (*n*=2,3), R₃ is -CH₃ or -C₂H₅ and X is -CONH- or -COO-.

The structures of these synthetic monomers are shown in Scheme 1.

Preparation of polymers

Polymerization of sulfobetaine monomers (DMAPS, DEAPS, DMAAPS and DMMAAPS). The respective monomer (DMAPS, DEAPS, DMAAPS and DMMAAPS) aqueous solution (0.5 M, 30 ml) and K₂S₂O₈ (0.04 g)



Scheme 1 The structures of the various monomers

were charged into an ampoule (100 ml), which was evacuated several times on a high-vacuum system (0.03 Pa) and sealed off; the ampoule was placed in a thermostated bath at 70°C for 4 h. The polymer product was precipitated with acetone, washed with water to eliminate the unchanged monomer, and dried for about 24 h at 100°C under vacuum to obtain a white solid that was weighed. The yield of the polymers was respectively: poly(DMAPS), 86%; poly(DEAPS), 79%; poly(DMAAPS), 95%; poly(DMMAAPS), 94%.

Polymerization of cationic monomers (TMAAI, DEMMAI, TMAAI and TMMAAI). The respective monomer (TMAAI, DEMMAI, TMAAI and TMMAAI) aqueous solution (0.8 M, 30 ml) and 4,4'-azobis(4-cyanovaleic acid) (ACVA) were charged into an ampoule (100 ml) that was covered with aluminium foil. The cationic monomers were polymerized similarly to the sulfobetaine monomers. The polymer product was precipitated with a mixture of propan-2-ol and diethyl ether (3:2), and dried for 24 h at 70°C under vacuum in darkness. The yield of the polymers was respectively: poly(TMAAI), 92%; poly(DEMAAI), 97%; poly(TMAAI), 95%; poly(TMMAAI), 93%.

Measurement of moisture regain

The polymer powders (0.2 g) of samples I-IV and samples A-D were simultaneously put in closed desiccators in which the humidity was controlled at 80, 92 and 96% ± 4% at 30°C. The moisture regain of the polymer powder was determined after the samples reached constant weight (about four days).

The moisture regain was calculated according to the relation:

$$\text{moisture regain (\%)} = \frac{m_w - m_d}{m_d} \times 100$$

where m_w is mass of wet polymer and m_d is mass of dry polymer.

RESULTS AND DISCUSSION

Solubility of monomers and polymers

The sulfobetaine monomers were hygroscopic. The ampholytic monomers dissolved only in water, not in organic solvents. Their polymers were insoluble in water and became transparent gels in aqueous solution (Table 1), because the collective positive charges on the polyampholyte attracted the collective negative charges to form an ionically crosslinked network that made these polymers gel in aqueous solution. Salts were added to these polymeric aqueous solutions to make these polymers dissolve. The cationic monomers were soluble in water and in strongly polar organic solvents, but their cationic polymers dissolved in only water and methanol (Table 2). Because the cationic monomers and polymers were ionized in aqueous solution, the cationic polymers and monomers were more soluble than the zwitterionic monomers and polymers. The mutual repulsion of the charges on the polymeric chain caused expansion and rotation of the polymeric chain and formed a long screw chain. These properties are common characteristics of polyelectrolytes.

Table 1 Solubility^a of sulfobetaine monomers and poly(sulfobetaine)s in various solvents

	DMAPS	Poly-(DMAPS)	DEAPS	Poly-(DEAPS)	DMAAPS	Poly-(DMAAPS)	DMMAAPS	Poly-(DMMAAPS)
H ₂ O	v	o	v	o	v	o	v	o
CH ₃ OH	v	o	v	o	v	o	v	o
C ₂ H ₅ OH	o	x	o	o	o	o	o	o
C ₃ H ₇ OH	x	x	o	x	o	x	o	x
n-Butanol	x	x	o	x	x	x	x	x
Acetone	x	x	x	x	x	x	x	x
MEK	x	x	x	x	x	x	x	x
Ether	x	x	x	x	x	x	x	x
CH ₃ CN	o	x	o	x	o	x	o	x
MIBK	x	x	x	x	x	x	x	x
CH ₃ Cl	x	x	o	x	x	x	x	x
CCl ₄	x	x	x	x	x	x	x	x
DMF	x	x	x	x	x	x	x	x
THF	x	x	x	x	x	x	x	x
Dioxane	x	x	x	x	x	x	x	x
DMAc	o	x	x	x	x	x	x	x

^a v = soluble, o = slightly soluble, x = insoluble**Table 2** Solubility^a of cationic electrolytes and their polymers in various solvents

	TMAAI	Poly-(TMAAI)	DEMMAI	Poly-(DEMMAI)	TMAAI	Poly-(TMAAI)	TMMAAI	Poly-(TMMAAI)
H ₂ O	v	v	v	v	v	v	v	v
CH ₃ OH	v	o	v	o	v	o	v	o
C ₂ H ₅ OH	o	x	o	x	o	x	o	x
C ₃ H ₇ OH	o	x	o	x	o	x	o	x
n-Butanol	x	x	x	x	x	x	x	x
Acetone	o	x	v	o	o	o	v	o
MEK	o	x	o	x	o	x	o	x
Ether	x	x	o	x	x	x	x	x
CH ₃ CN	v	x	v	o	v	x	v	x
MIBK	x	x	x	x	x	x	x	x
CH ₃ Cl	o	x	v	x	o	x	o	x
CCl ₄	x	x	x	x	x	x	x	x
DMF	v	x	v	x	v	x	v	x
THF	x	x	x	x	x	x	x	x
Dioxane	o	x	o	x	o	x	o	x
DMAc	v	x	v	x	v	x	v	x

^a v = soluble, o = slightly soluble, x = insoluble**Analysis and characterization of n.m.r. spectra of sulfobetaines and corresponding cationic monomers**

N.m.r. spectra were measured with a spectrometer (JEOL 100) operating at 400 MHz for ¹H and at 100 MHz for ¹³C at 30°C. Sulfobetaines and cationic monomers were dissolved in D₂O with sodium 2,2-dimethyl-2-silapentane-5-sulfonate (DSS) as internal standard to measure ¹H and ¹³C n.m.r. spectra; the signals of the respective groups were identified from the spectra of sulfobetaines and the corresponding cationic monomers.

Characterization of ¹H n.m.r. Because the density of the electronic cloud about the proton becomes diminished under the influence of the medium or various chemical structures, the chemical shift of ¹H n.m.r. spectra becomes

increased. The shielding or deshielding effect was used to decide the position of signals in the ¹H n.m.r. spectra. The chemical shift of amine was 14.0 ppm. The well known range of chemical shift, 5.5–6.5 ppm, of H_{a1}, H_{a2} and H_b shown in *Figures 1* or *2* is due to protons of the vinyl group in the monomers. The chemical shifts of H_{a1}, H_{a2} and H_b were deduced from the abilities of the functional groups to attract electrons^{13–20,29,30}.

According to these figures, the signals of H_c, H_d, H_e, H_f and H_g were identified in the ¹H n.m.r. spectra from the density of the electronic cloud due to various effects. The abilities to attract electrons varied for various functional groups. The values of chemical shifts followed the order H_c > H_d > (H_e) > H_f > H_g for DMAPS, DEAPS, TMAAI and DEMMAI shown in *Figure 1*^{13–20,29,30}.

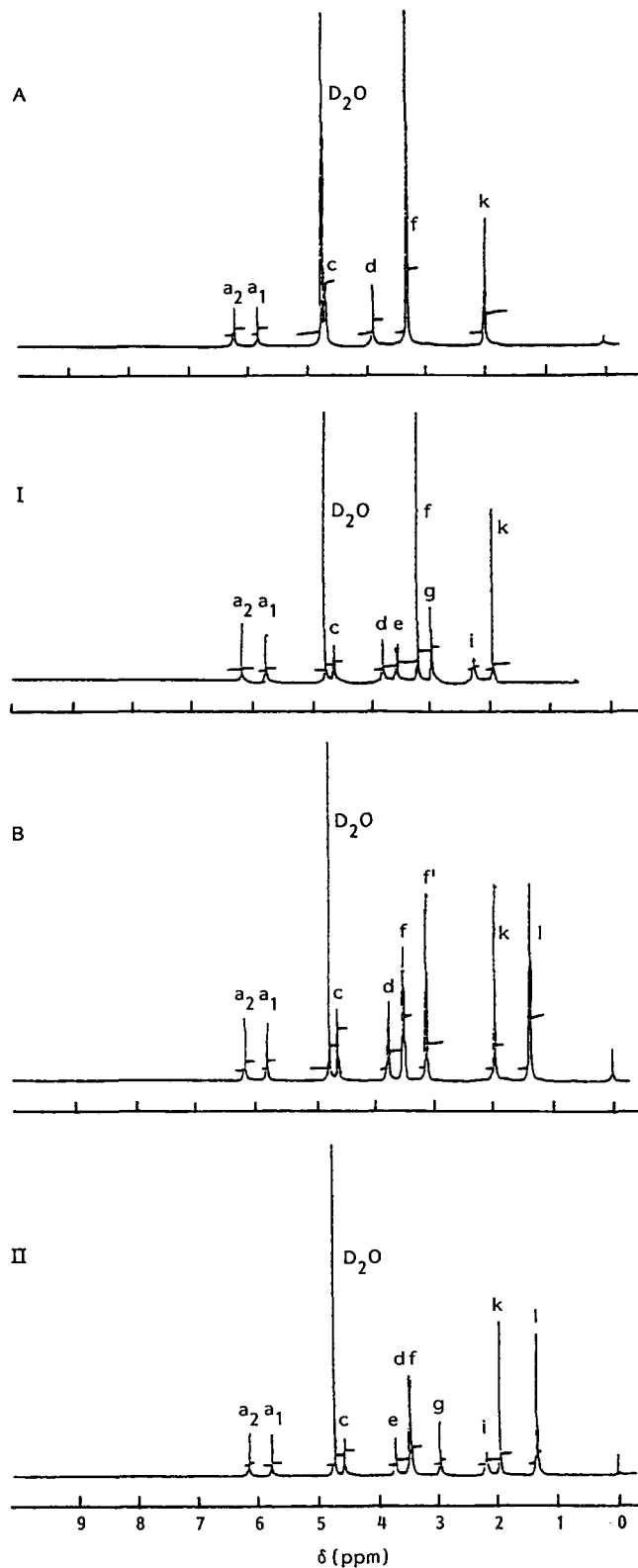


Figure 1 ^1H n.m.r. spectra of sulfobetaine monomers in D_2O (chemical shift calibrated with the water signal at $\delta=4.8$ ppm): (I) DMAAPS, (A) TMAAI, (II) DEAPS, (B) DEMMAI

By comparison of the chemical shifts of H_c and H_d for DMAAPS, DMMAAPS, TMAAI and TMMAAI, the ability of the nitrogen atom (NH) to attract the electron of H_c was increased by the β -substituted group ($\text{C}=\text{O}$); hence the signal of H_c was shifted to larger δ . As the α -substituted group (R_4N^+) of H_d had a positive charge that increased the ability to attract electrons, the signal of H_d was also shifted to larger δ in the ^1H n.m.r. spectra.

Because the two effects were similar, the two chemical shifts were similar.

Because the total area of hydrogen atoms on the quaternary ammonium (H_f) (Figures 1 and 2) was greatest (4H, 6H, or 9H) for all monomers, the signal due to H_f was readily recognized. The chemical shifts of H_f were the same in the spectra of TMAAI, TMAAI and TMMAAI (Figures 1 and 2). Hence, they were of ionic type in aqueous solution.

The signals in the ^1H n.m.r. spectra of these cationic monomers (TMAAI, DEMMAI, TMAAI, TMMAAI)

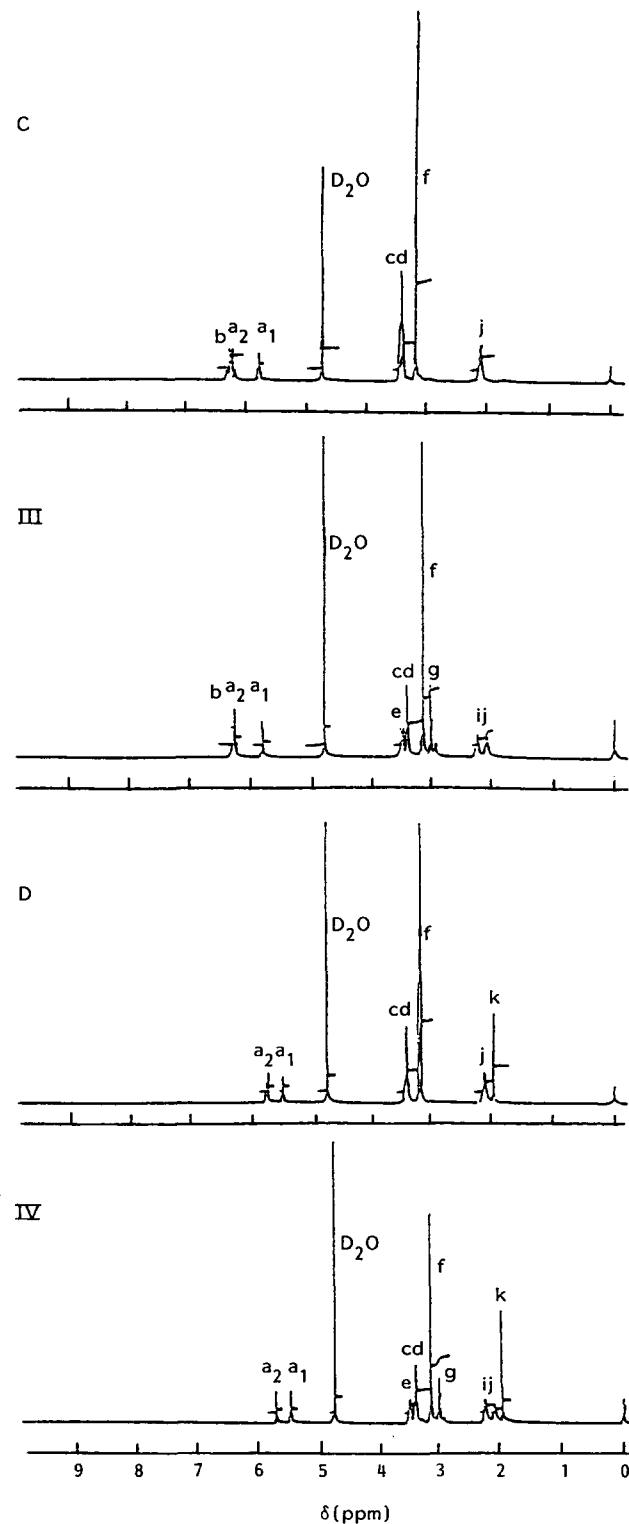
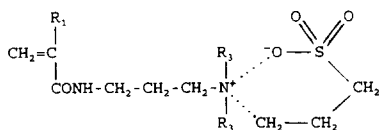


Figure 2 ^1H n.m.r. spectra of cationic monomers in D_2O (chemical shift calibrated with the water signal at $\delta=4.8$ ppm): (III) DMAAPS, (C) TMAAI, (IV) DMMAAPS, (D) TMMAAI

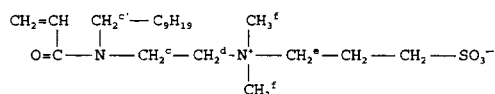
were affirmed accordingly. Contrasting the ^1H n.m.r. spectra of DMAAPS with that of TMAAI, the lines in the DMAAPS spectra numbered three more than that of TMAAI; the three peaks recognized from the point of view of electronic cloud density were H_e , H_i and H_g . According to the same methods, these signals of DEAPS, DMAPS and DMMAAPS were affirmed by reference to DEMMAI, TMAAI and TMMAAI. In a comparison of the chemical shifts of H_i and H_j in ^1H n.m.r. spectra of DMAAPS (or DMMAAPS), the β -substituted groups of H_j belonged to the amide group ($-\text{CONH}-$) and quaternary ammonium group (R_4N^+), and the β -substituted groups of H_i belonged to the quaternary ammonium group (R_4N^+) and sulfonate group (SO_3^-). Owing to the effects of electronic cloud density, the chemical shift of H_j was generally increased 0.3–0.6 ppm more than that of H_i (the ability of the sulfonate group to attract electrons was less than that for the amide group, and the negative charge on the sulfonate group would decrease the ability of the sulfonate group to attract the electrons on the methylene group); on the contrary, the shift of H_i was 0.2 ppm more than that of H_j . This phenomenon was neglected in the literature^{16–18}. DMAPS, DEAPS, DMAAPS and DMMAAPS are ampholytic monomers, and the sulfonate groups (SO_3^-) site-binding to the quaternary ammonium group (R_4N^+) formed an ionically crosslinked network, which was regarded as a ring, as in the following schematic model:



According to the ring current effect, that is, when π electrons exist in the ring, if a hydrogen atom were outside the ring, the chemical shift of that hydrogen would be increased 2–5 ppm (such as for benzene, cyclo-octene, etc.); whereas if hydrogen were inside the ring, its chemical shift would be decreased 2–6 ppm^{30,31}. When the ring involves only σ bonding, the chemical shift of hydrogen would be increased or decreased 0.2–0.8 ppm (such as for cyclohexane, cellulose, etc.) for hydrogen outside or inside the ring, respectively^{30,31}. For the spectra of DMAAPS and DMMAAPS shown in Figure 2, as the chemical shift of the peak of H_i was greater than that of H_j , it was confirmed that the proton of H_i existed outside the ring (diminished steric hindrance and increased stability of the ring). Similarly, the chemical shift of H_e exceeded that of H_d and the proton of H_e also existed outside the ring.

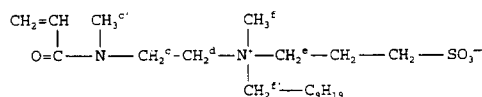
Sulfobetaine surfactants were synthesized by Laschewsky and Zerbe¹⁸. The chemical shifts of those compounds in ^1H n.m.r. spectra, similar to the peaks H_e , H_d and H_e of the present compounds, DMAAPS and DMMAAPS, were not definitely characterized. The identification of ^1H n.m.r. spectra of 3-[*N,N*-dimethyl-*N*-3'-(*N'*-acryloyl)azatridecyl]ammonium propanesulfonate (sample 1) and 3-[*N*-decyl-*N*-methyl-*N*-(2-(*N*-methyl)acrylamidoethyl)]-ammonium propanesulfonate (sample 2) was doubtful. According to their report, the monomers had chemical shifts as follows:

Sample 1:



δ (ppm): H_e , 3.56; H_d , H_e , 3.7–3.9; H_c , 3.44; H_f , 3.24.

Sample 2:



δ (ppm): H_f , 3.15; H_c , H_f , 3.2–3.3; H_e , H_e , 3.5–3.8; H_d , 3.87.

The chemical shifts of H_c (H_d , H_e or H_f) of samples 1 and 2 were similar to these for the corresponding positions of samples 1 and 2. According to our discussion of ^1H n.m.r. spectra of DMAAPS and DMMAAPS, the chemical shifts of the signals are expected to follow the order $\text{H}_e > \text{H}_d \geq \text{H}_c > (\text{H}_f) > \text{H}_f$.

For the spectra of DMAPS and DEAPS (Figure 1), the electron-attracting effect of the carboxyl group ($-\text{COO}-$) at the β -position on H_d was stronger than the ring current effect for H_e , and hence the chemical shifts were in the order $\text{H}_d > \text{H}_e$.

Characterization of ^{13}C n.m.r. The characterization of these spectra was similar to the methods of identification of ^1H n.m.r. spectra in which the major method used involved judgement of electronic cloud density. The chemical shift of C_b (Figures 3 and 4) increased from 170 to 175 ppm for acrylamido and acryloyloxy, and the chemical shifts of ^{13}C n.m.r. were in the order $\text{C}_b > \text{C}_a$ and $\text{C}_j > \text{C}_i$ (C_k) $> \text{C}_l$ for these monomers. The signal of C_f was stronger (two superimposed ^{13}C signals). The signals of C_d and C_e were confirmed from the ratio of intensity with corresponding C_f in the ratio C_d (or C_e): $\text{C}_f \approx 1:2$ for sulfobetaines and DEMMAI and the ratio C_d : $\text{C}_f \approx 1:3$ for cationic monomers. The slightly altered structure sensitively shifted the signal of C_e for various monomers. Because the ^{13}C n.m.r. spectra were less affected by the ring current effect, the sequences of chemical shift of ^1H n.m.r. and ^{13}C n.m.r. were distinct ($\text{C}_d \approx \text{C}_e > \text{C}_f$ but $\text{H}_e > \text{H}_d > \text{H}_f$) for DMAAPS and DMMAAPS.

Moisture regain

Polyelectrolytes have the following properties: solubility in water, water affinity and strong deliquescence. After polyelectrolytes are left in air for 30 min, poly(sulfobetaine)s absorbed water from the air to form a gel and the cationic polymer powder became agglomerated. The moisture regain of poly(sulfobetaine)s was two or three times that of the cationic polymers in air, because poly(sulfobetaine)s had a strongly water-absorptive group ($-\text{SO}_3^-$). In various functional groups for poly(sulfobetaine)s, the order of tendency for moisture regain was $-\text{COO}- > -\text{CONH}-$, except DEAPS (the mass ratio of water absorption for DEAPS was less than that of other poly(sulfobetaine)s); the tendency for moisture regain of cationic polymers was in the contrary order of $-\text{CONH}- > -\text{COO}-$ (the ratio between TMMAAI (or TMAAI) and TMAAI (or DEMMAI) was about 2:1). The moisture regains of various polyelectrolytes are listed in Table 3 at various humidities.

CONCLUSION

Because of steric hindrance from the large substituted group of tertiary ammonium, the synthesis of DEAPS was performed at elevated temperature. Cationic monomers

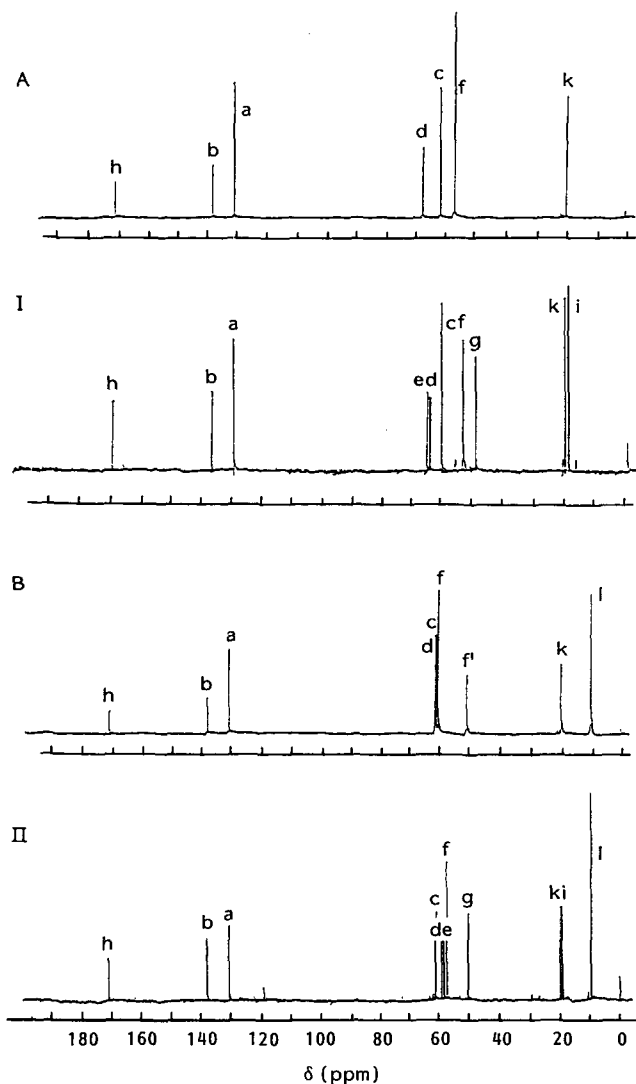


Figure 3 ^{13}C n.m.r. spectra of sulfobetaine monomers in D_2O : (I) DMAPS, (A) TMMAL, (II) DEAPS, (B) DEMMAI

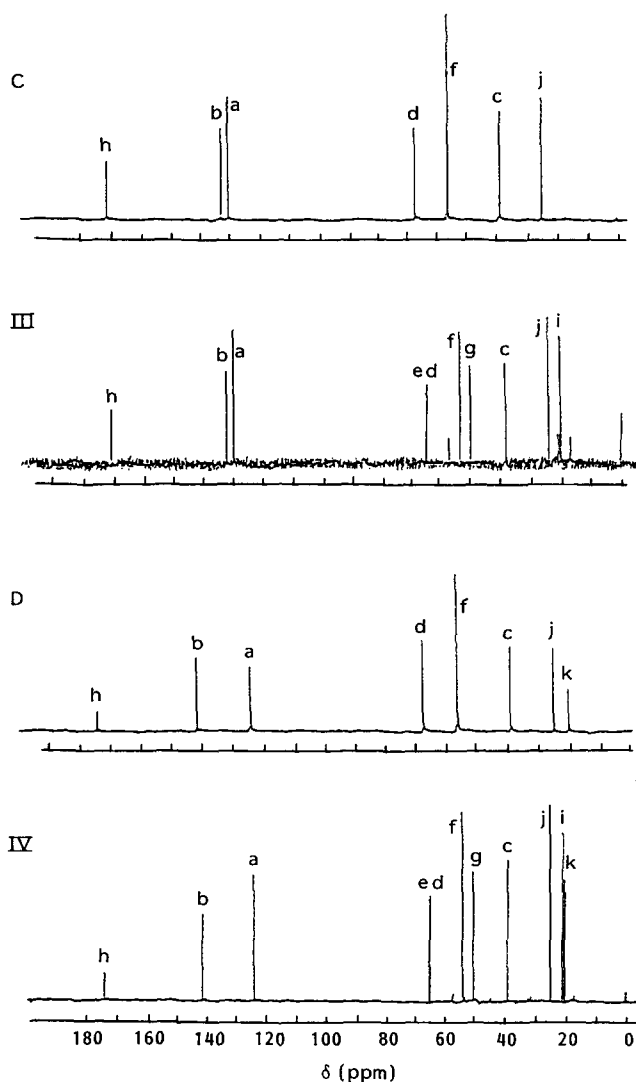


Figure 4 ^{13}C n.m.r. spectra of cationic monomers in D_2O : (III) DMAAPS, (C) TMAAI, (IV) DMMAAPS, (D) TMMAAI

Table 3 Moisture regain for various polymers in different humidities at 30°C

Polymer	Degree of water absorption (wt%)			Degree of water absorption for repeat unit (HO mole/unit mole)		
	<i>RH</i> = 80%	92%	96%	<i>RH</i> = 80%	92%	96%
Poly(DMAPS)	35.62	57.38	86.17	5.52	8.83	13.36
Poly(DEAPS)	26.26	48.02	68.53	4.47	8.19	11.69
Poly(DMAAPS)	29.44	47.52	75.86	4.54	7.34	11.72
Poly(DMMAAPS)	29.23	44.72	73.66	4.74	6.52	11.95
Poly(TMMAL)	8.30	13.37	20.08	1.38	2.22	3.36
Poly(DEMMAI)	8.26	13.30	19.97	1.49	2.42	3.66
Poly(TMAAI)	17.20	27.72	40.63	2.83	4.59	6.94
Poly(TMMAAI)	15.75	25.37	37.95	2.64	4.40	6.65

(polymers) were of the ionic type in aqueous solution and ampholytic monomers (polymers) had a ring structure confirmed by the ring current effect in ^1H n.m.r. spectra. The effect of the β -substituted group ($\text{C}=\text{O}$) on the ability of the nitrogen atom (NH) to attract an electron (H_c) was similar to the effect of positive charge of quaternary ammonium at the α -positions of the DMAAPS,

DMMAAPS, TMAAI and TMMAAI series. When only a σ electron existed in the ring structure, the ring current effect caused only a small shift of the signals in the ^1H n.m.r. spectra (shifts 0.2–0.8 ppm); this effect was generally neglected. The effect was revealed and the ^1H n.m.r. signals were characterized by comparison between sulfobetaines and the corresponding cationic monomers.

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