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Water-Soluble Copolymers. 14. Potentiometric and Turbidimetric Studies of Water-Soluble Copolymers of Acrylamide: Comparison of Carboxylated and Sulfonated Copolymers

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ABSTRACT: Comparisons of copolymers of acrylamide (AM) with sodium acrylate (NaA), sodium 3-acrylamide-3-methylbutanoate (NaAMB), and sodium 2-acrylamido-2-methylpropanesulfonate (NaAMPS) were made with respect to their phase separation behavior in aqueous solutions and their potentiometric properties. Analogous copolymer series containing *N,N*-dimethylacrylamide (DMAM) with NaA, NaAMB, and NaAMPS were synthesized and compared to the acrylamide series. Phase separation in the presence of calcium ions is found to be a function of the length of the side chain, the acidity of the ionic group, and the local microstructure of the copolymers. Copolymers of NaAMPS and NaAMB with AM and DMAM are found to remain soluble in aqueous calcium chloride solutions up to 100 °C. Correlations between copolymer sequence distributions and pK_a values suggest that hydrogen bonding of the charged units with acrylamide units in the copolymer lowers the pK_a value by stabilizing the charged groups. This hydrogen bonding and the length of the side chain of the NaAMB and NaAMPS monomers appear to explain the observed phase behavior and pK_a values.

Introduction

In previous studies in our laboratories, copolymers of acrylamide (AM) with sodium acrylate (NaA), sodium 3-acrylamido-3-methylbutanoate (NaAMB), and sodium 2-acrylamido-2-methylpropanesulfonate (NaAMPS) have been found to be useful as viscosity-modifying agents in enhanced oil recovery.[1] Further experimentation involving phase separation behavior studies and potentiometric titrations has been performed in an effort to relate local ionic effects, copolymer sequence distribution, and other molecular interactions (such as hydrogen bonding) to the macromolecular properties such as viscosity and salt sensitivity previously observed.

The purpose of this research is to compare the phase behavior of the three AM copolymer series and the three DMAM series in terms of the nature of the anion-containing side group, the hydrogen bonding of the anion with AM units in the copolymer, and the local microstructure of the copolymers. The observed phase behavior is correlated to the acidities of the AM and DMAM series as determined from the potentiometric studies.

Experimental Section

Materials. Poly(acrylamide-*co*-sodium acrylates) were prepared by alkaline hydrolysis of polyacrylamide (MW = 5 000 000) (HPAM series) and free radical polymerization of the two monomers (NaA series). The synthetic copolymers had molecular weights (M_n) ranging from 300 000 to 800 000.[1a] Copolymer composition was determined by elemental analysis[1a] and C-13 NMR.

Poly(acrylamide-*co*-sodium 3-acrylamido-3-methylbutanoates) (NaAMB series) were prepared by free radical polymerization and characterized as reported previously.[2,3] Their molecular weights (M_n) ranged from 500 000 to 1 500 000.

Poly(acrylamido-*co*-sodium 2-acrylamido-2-methylpropanesulfonates) (NaAMPS series) were prepared by free radical polymerization and characterized as reported elsewhere.[1a] Their M_n values were found to be from 600 000 to 1 000 000.[1a] The compositional data for these copolymers are shown in Table I.

N,N-Dimethylacrylamide (DMAM) monomer was obtained from Aldrich Chemical Co. and distilled at 35 °C (10 mmHg). Acrylic acid monomer from Aldrich Chemical Co. was also distilled at 35 °C (10 mmHg). Poly(sodium vinylsulfonate) (NaPVS) was obtained from Polysciences and used without purification. NaAMB and NaAMPS monomers were recrystallized and neutralized as previously reported.[1a,2]

Table I
Compositional Data and Observed Phase Behavior of Acrylamide Copolymers

sample	mol % ionizable comonomer	critical temp, °C		
		0.25% $CaCl_2$	1% $CaCl_2$	3% $CaCl_2$
NaA-10	6	*a*	*a*	*a*
NaA-20	14	*a*	*a*	*a*
NaA-35	25	*a*	94.3	98.0
NaA-50	30	65.5	48.6	62.9
NaA-65	48	25.1	<rt	<rt
HPAM-823	15	74.9	45.6	59.7
HPAM-309	36	60.4	41.0	58.1
HPAM-301	48	26.2	<rt	<rt
HPAM-305	65	<rt	<rt	<rt
NaAMB-10	8	*a*	*a*	*a*
NaAMB-25	20	*a*	*a*	*a*
NaAMB-40	31	*a*	*a*	*a*
NaAMB-60	48	*a*	*a*	*a*
NaAMB-75	63	*a*	*a*	*a*
NaAMB-hom	100	82.3	74.9	70.8
NaAMPS-15	14	*a*	*a*	*a*
NaAMPS-20	17	*a*	*a*	*a*
NaAMPS-35	29	*a*	*a*	*a*
NaAMPS-hom	100	*a*	*a*	*a*
DMNA-25	12	*a*	*a*	*a*
DMNA-40	24	45.1	41.9	42.7
DMAMB-10	9	*a*	*a*	*a*
DMAMB-20	18	*a*	*a*	*a*
DMAMB-40	34	*a*	*a*	*a*
DMAMB-60	46	*a*	*a*	*a*
DMAMP-5	5	*a*	*a*	*a*
DMAMP-15	11	*a*	*a*	*a*
DMAMP-30	23	*a*	*a*	*a*
DMAMP-50	43	*a*	*a*	*a*
NaPVS	100	83.4	64.0	67.5

[a] No phase separation observed up to 100 °C.

Synthesis. Copolymers of *N,N*-dimethylacrylamide with NaA, NaAMB, and NaAMPS were prepared by free radical polymerization at 30 °C with potassium persulfate initiator. Copolymer composition was determined by C-13 NMR quantitative analysis by using the method of Hutchinson.[3] The copolymers were precipitated twice in methyl ethyl ketone and then freeze-dried. Polymerization times ranged from 1 to 3 h. The results are summarized in Table II. Aliquots were taken at low conversions, analyzed, and compared to compositions at the higher conversions shown. No compositional drift was found to occur. The reactivity

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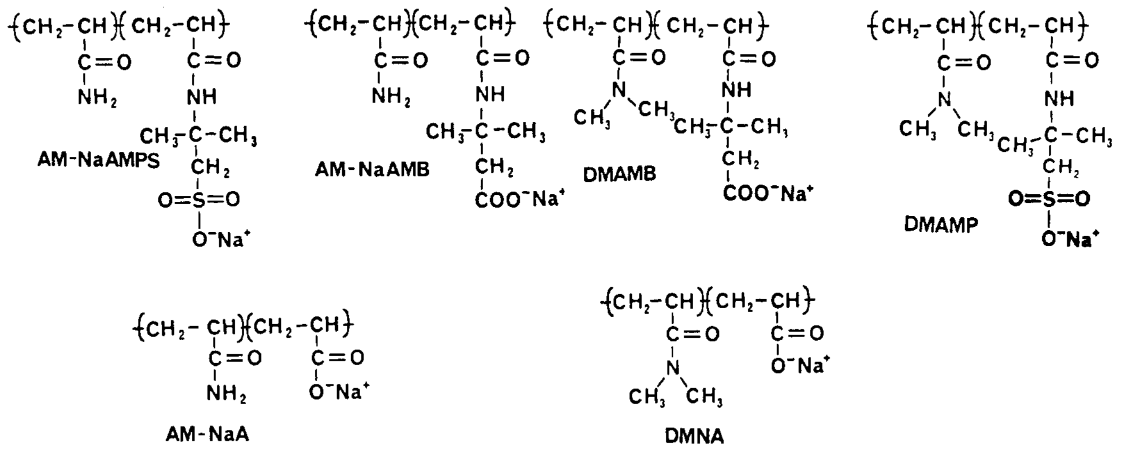

Figure 1. Structures of the copolymers of AM and DMAM with NaA, NaAMB, and NaAMPS.

Table II
Synthesis of Copolymers of *N*,*N*-Dimethylacrylamide (DMAM)

sample	feed ratio	copolym % M_1	copolym % M_2	copolym conversn, %	init ratio $K_2S_2O_8$
		M_2 = NaAMB			
DMAMB-10	90:10	90.72	9.28	35	1:1000
DMAMB-20	80:20	81.78	18.22	36	1:1000
DMAMB-40	60:40	65.91	34.09	40	1:1000
DMAMB-60	40:60	54.23	45.77	35	1:1000
		M_2 = NaAMPS			
DMAMP-5	95:5	95.23	4.77	29	1:500
DMAMP-15	85:15	89.12	10.88	30	1:1000
DMAMP-30	70:30	76.65	23.35	33	1:1000
DMAMP-50	50:50	56.52	43.48	34	1:1000
		M_2 = NaA			
DMNA-25	75:25	89.53	10.47	26	1:1000
DMNA-40	60:40	75.73	24.27	32	1:1000

Table III
Reactivity Ratios of DMAMB and DMAMP Series

	r_{DMAM}	r_{NaAMB} or r_{NaAMPS}
	DMAMB Series	
Fineman–Ross	1.02	0.91
Kelen–Tüdös	1.18	0.99
	DMAMP Series	
Fineman–Ross	1.26	0.68
Kelen–Tüdös	1.18	0.92

ratios were calculated with the methods of Kelen and Tüdös[9] and Fineman and Ross.[10] The reactivity ratios are shown in Table III.

Turbidimetry Measurements.[4] Calcium chloride solutions were prepared gravimetrically and the concentrations verified by refractive index measurements. Polymer solutions with concentrations of 1.5 g/L were prepared by dissolving the appropriate amount of polymer in deionized water. Salt concentrations were prepared by addition of the appropriate amounts of solid salt (for higher salt concentrations) of appropriate amounts of salt solution (for lower salt concentrations). The weight of the solution was determined both before and after each measurement, and water lost by evaporation was replaced.

A phototurbidimeter was used for the phase behavior measurements. The sample of polymer solution (30–36 mL) was stirred by a magnetic stirrer and heated slowly (<1 °C/min) by an air-heating system. A thermometer was used to record the temperature (minimum reading of 0.1 °C). The decrease in photoelectric current caused by a decrease in transmittance was used to determine the onset of precipitation. The cloud point (critical temperature) was taken as the temperature at which precipitation was first observed. The process is reversible with temperature; however, two slightly different critical temperatures were observed depending upon whether the solution was cooled or heated. The average of the two observed temperatures was taken as the cloud point temperature, T_c. The temperatures were found to be repeatable, giving T_c readings which were within ±0.5 °C.

Potentiometry Measurements. All measurements of pH were made with a Corning 130 pH–mV meter with an Orion pH electrode and an Orion double-junction reference electrode. The meter was standardized with a two-point calibration method. All measurements were conducted at 25 ± 0.05 °C.

Copolymer concentrations ranged from 0.5 to 1.5 g/L. Two titrations were performed on each sample: one with adjustment of ionic strength of 0.36 M using potassium chloride and one with no ionic strength adjustment. Acid solutions, of less than 0.1 M were prepared and standardized with sodium carbonate. The titrations were conducted under nitrogen atmosphere.

The degree of ionization α, defined as the fraction of acid groups dissociated, was determined for each addition of titrant. For observed pH values between 4.5 and 8.5, no correction was needed, and α was calculated as C_{A^-}/C_{HA}, where C_{A^-} is the concentration of the dissociated acid groups and C_{HA} is the total concentration of acid groups in the sample.[5] For pH values below 4.5 or above 8.5, correction for free acid groups was found to be negligible. Values of the dissociation constant (pK_a) were calculated with the Henderson–Hasselbalch equation[6]

$$pK_a = \mathrm{pH} - \log\,[\alpha/(1 - \alpha)]$$

Because no corrections for free energy, etc., were made, all pK_a values reported are apparent pK_a values. Values of ΔpK_a were obtained by measuring the change in pK_a as changes from 0 to 1 ($\delta pK_a/\delta\alpha$). These values were made to compare the changes in microenvironment of the charged groups as a function of α. Plots of pH vs. log $[\alpha/(1 - \alpha)]$ were made as well to determine pK' and n values for each sample titration using the modified Henderson–Hasselbalch equation[7,8]

$$\mathrm{pH} = pK' + n \log\,[\alpha/(1 - \alpha)]$$

These results are shown in Table VI.

Results and Discussion

It is believed that local hydrogen bonding between anionic groups along a polymer chain and neighboring acrylamide units may account for the observed ionic properties. Therefore, three analogous copolymer series containing *N*,*N*-dimethylacrylamide (DMAM) with NaA, NaAMB, and NaAMPS were synthesized to compare with acrylamide-based copolymers. The AM copolymers contain amide hydrogens available for hydrogen bonding while the DMAM copolymers contain no amide hydrogens. The structures of the three series of copolymers of AM and the three series of DMAM are shown in Figure 1.

The NaAMPS copolymers were originally prepared as models for viscosity modification in enhanced oil recovery. The NaAMB series was subsequently made as a carboxylated analogue to the NaAMPS and to the NaA series in order to compare their respective viscosities, salt sensi-

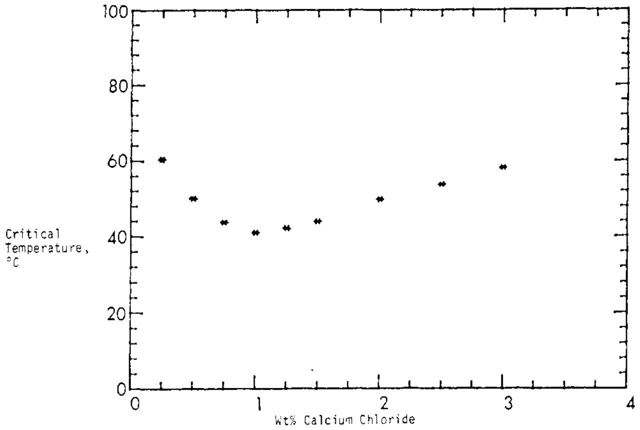

Figure 2. Phase separation of HPAM-309 (polymer concentration of 1.5 g/L).

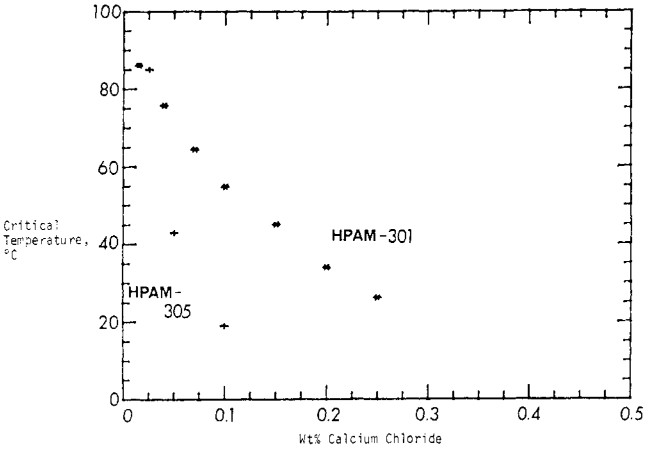

Figure 3. Phase separation of HPAM-301 and 305 (polymer concentration of 1.5 g/L).

tivities, and phase behavior. The NaAMB series was found to exhibit unusual phase behavior in the presence of divalent salts, and to investigate this further a study of these systems using potentiometric titrations was undertaken to correlate structure, functional group properties, and ionic effects to the observed phase behavior.

Turbidimetry. Temperature and Salt Concentration. All copolymers were tested for phase separation in aqueous calcium chloride solutions as a function of temperature and calcium chloride concentration. Table I gives representative data for each copolymer series. The NaA series exhibited phase separation when the copolymer contained more than 25% sodium acrylate units, while the HPAM series exhibited phase separation when the copolymer contained more than 15% sodium acrylate units. The difference in critical NaA content is due to the HPAM series having a much higher molecular weight. Examples of these phase diagrams showing all the data are given in Figures 2 and 3. Previous reports have verified these results.[11-13]

It might be expected that the NaAMB copolymers would show phase separation behavior in the presence of calcium chloride as a function of temperature. However, they were found to be fully soluble up to 100 °C and in all salt concentrations studied. Even the copolymer containing 63 mol % NaAMB did not precipitate. The homopolymer of NaAMB did show phase separation but at much higher temperatures than copolymers of the NaA and HPAM series (Table I).

Previous work in these laboratories[4] has shown no precipitation in the presence of calcium chloride for the NaAMPS copolymers and the NaAMPS homopolymer. Other sulfonated polymers and copolymers such as poly(sodium vinylsulfonate), which is comparable to the NaA polymers, do exhibit phase separation in the presence of divalent salts.[14,15] Polymers such as poly(sodium styrenesulfonate) exhibit phase separation under certain conditions,[16] but under the conditions used here no phase separation is observed.

The copolymers containing *N*,*N*-dimethylacrylamide also showed no phase separation, with the exception of DMNA-40, which contained about 24% NaA groups. The copolymers of DMAM with NaAMB and NaAMPS remained soluble up to 100 °C (Table I).

A mechanism of precipitation of anionic polymers in the presence of divalent cations has been proposed.[13,15] Divalent salts such as calcium are strong chelating ions that readily penetrate the hydration shell about the polymer chain to bind with ionic groups. The temperature increase appears to "activate" both the polymer and the ion by increasing the mobility of each. When a divalent ion binds two carboxylate groups or sulfonate groups, an insoluble salt forms. These salt bonds may be intrachain or interchain (i.e., an ionic cross-link). When the number of insoluble bonds reaches a critical concentration, the polymer becomes insoluble and precipitation occurs. The polymer–solvent interaction, which is affected by the molecular weight, will also be a factor in the polymer's phase behavior (e.g., the observed difference between the NaA and the HPAM series (Table I)). Thus, different polymer and copolymer systems will show different phase behavior based on these properties.

In addition, the microstructure of the polymers and copolymers may be an important factor. The copolymer sequence distributions and the tacticity (of the homopolymers) as well as the configurational differences in the copolymers affect the properties of the ionic groups and thereby alter the ability to bind divalent ions.[12,13]

Effect of Side-Chain Length. It appears that, in the case of the NaA copolymers that precipitate in the presence of divalent ions and the NaAMB copolymers that do not precipitate, the length of the NaAMB side chain causes decreased salt sensitivity and decreased divalent ion binding. We can rationalize that two adjacent sodium acrylate units might easily bind a divalent ion due to their close proximity. Two adjacent NaAMB units, on the other hand, have a much greater number of conformational states possible and thus are less likely to form insoluble ionic bonds. Copolymers containing acrylamide units separating the NaAMB units would increase the distance between charges, thus making them even less likely to bind calcium ions and form ionic bonds. This explanation is aided by the fact that model compounds of the repeat units of NaA and NaAMB show little difference in their pK_a values. Propionic acid, a model compound of an acrylate repeat unit, has a pK_a value of 4.87, while 3-propionamido-3-methylbutanoic acid, a model compound of a NaAMB unit, has a pK_a value of 4.65. Thus there is little difference in the binding strengths of the individual NaA and NaAMB carboxyl groups, and this small difference in ion binding affinity does not explain the observed differences in phase behavior for polymers and copolymers of these two monomers.

The above theory of the mechanism of precipitation does not specify that the ionic bonds formed be intrachain or interchain. Furthermore, it can be assumed that either intrachain bonds between adjacent groups, or intrachain bonds involving two separate units of the same chain (two nonadjacent groups), or two groups on different chains are equally able to form insoluble ionic bonds, which can ac-

Table IV
Dissociation Constants of Acrylamide and *N*,*N*-Dimethylacrylamide Copolymers in 0.36 M KCl

sample	pK_a ± 0.06	ΔpK_a
	AM–NaAMB	
NaAMB–10	4.79 ± 0.06	0.10
NaAMB-25	4.74 ± 0.05	0.10
NaAMB-40	4.90 ± 0.04	0.05
NaAMB-60	5.01 ± 0.04	0.12
NaAMB-75	5.10 ± 0.05	0.12
NaAMB-hom	5.49 ± 0.05	0.20
	AM–NaA	
NaA-10	4.60 ± 0.04	0.12
NaA-20	4.53 ± 0.04	0.14
NaA-35	4.48 ± 0.05	0.12
NaA-50	4.63 ± 0.04	0.14
NaA-65	4.74 ± 0.04	0.14
	AM–NaAMPS	
NaAMPS-15	3.64 ± 0.06	0.28
NaAMPS-20	3.57 ± 0.06	0.32
NaAMPS-35	3.30 ± 0.05	0.33
NaAMPS-hom	2.79 ± 0.06	0.27
	DMAM–NaAMB	
DMAMB-10	5.15 ± 0.06	0.08
DMAMB-20	5.07 ± 0.06	0.14
DMAMB-40	5.09 ± 0.05	0.17
DMAMB-60	5.23 ± 0.06	0.10
	DMAM–NaA	
DMNA-25	5.93 ± 0.05	0.14
DMNA-40	5.82 ± 0.04	0.14
	DMAM–NaAMPS	
DMAMP-5	4.22 ± 0.06	0.16
DMAMP-15	3.48 ± 0.06	0.19
DMAMP-30	3.22 ± 0.06	0.25
DMAMP-50	3.10 ± 0.06	0.14

count for the phase behavior of these polymers.

In the similar comparison between poly(sodium vinylsulfonate) and the NaAMPS series, the same argument can be used when explaining the precipitation of the former and the lack of phase separation of the NaAMPS series. However, both of these systems contain sulfonate groups, which are known to bind divalent ions more weakly, as potentiometric results indicate. Poly(sodium styrenesulfonate) was found not to exhibit phase separation in our studies using calcium chloride. This further illustrates the conclusion that moving the anionic site away from the polymer backbone suppresses or prevents precipitation by divalent cations. Under other conditions, poly(sodium styrenesulfonate) has been found to undergo phase separation in the presence of barium ions.[15,16] It should be noted that the amide bond in the NaAMPS and NaAMB repeat units may be important in the stability of these copolymers and homopolymers in the presence of divalent ions. The strong water solubility and large degree of hydration of the primary and secondary amide units in the copolymers may account for their increased stability in aqueous calcium solutions.

Potentiometry. The apparent pK_a values are shown in Table IV for the three copolymer series containing acrylamide and the three series containing *N*,*N*-dimethylacrylamide. The pK_a values at constant ionic strength show several trends. The measured pK_a values of the NaA and NaAMB copolymers are found to be very similar, with the NaAMB series having slightly higher values in the AM copolymers. This may be due to the distance from the backbone of the acid group and the destabilization due to the hydrophobic geminal dimethyl groups on the side chain of the NaAMB units. In the DMAM copolymers, the NaA copolymers have higher pK_a values than the NaAMB polymers, possibly due to the proximity of the NaA charged groups to the hydrophobic methyl groups of the DMAM units. But the differences in pK_a values do not account for the observed differences in their phase behavior.

Effect of Copolymer Composition. It is observed that within each series the pK_a values change depending on the number of charged groups in the copolymer. The NaA and NaAMB series show trends of increasing pK_a values for their acid groups with increasing NaA or NaAMB content in the copolymer. However, the NaA series also show trends of decreasing pK_a values up to about 25 mol % NaA in the copolymer, followed by a slow increase in pK_a values above this point. The NaAMPS series shows the opposite trend, with decreasing pK_a values observed with increasing NaAMPS content. The pK_a is expected to increase as the charge density increases due to increased charge–charge interactions, which will destabilize the anionic groups. This destabilization due to increased charge density results in counterion condensation along the chain as predicted by the Manning theory.[17] This effect is observed above 33% charges according to Manning's theory. Below this value, the pK_a value is affected by the frequency of charges in the copolymer chain.

Another explanation for this trend may be due to the changing acrylamide availability. In copolymers containing fewer acid groups and thus more acrylamide units on the chain, the probability of hydrogen bonding of the anion with a neighboring acrylamide hydrogen increases. The resulting stability of the conjugate base is illustrated in Table V, where statistical copolymer sequence distributions[18] are compared to pK_a values in water and in 0.36 M KCl solutions. This method as outlined by Harwood and Ritchey is a statistical procedure for measuring sequence distributions in copolymers and is based on the copolymer composition and the reactivity ratios. It is assumed to be valid for copolymer systems that follow the

Table V
Correlation between pK_a and Copolymer Sequence Distribution

	H_2O		0.36 M KCl				
sample	pK_a	ΔpK_a	pK_a	ΔpK_a	P_{ABA}	P_{BBB}	P_{ABB}
NaAMB-10	5.23 ± 0.05	0.08	4.79 ± 0.06	0.10	0.946	0.001	0.053
NaAMB-25	5.31 ± 0.06	0.22	4.74 ± 0.05	0.10	0.754	0.018	0.228
NaAMB-40	5.75 ± 0.08	0.28	4.90 ± 0.04	0.05	0.615	0.047	0.338
NaAMB-60	5.88 ± 0.05	0.55	5.01 ± 0.04	0.12	0.339	0.175	0.486
NaAMB-75	6.19 ± 0.06	0.46	5.10 ± 0.05	0.12	0.205	0.299	0.495
NaAMB-hom	6.86 ± 0.07	0.41	5.49 ± 0.05	0.20			
NaA-10	5.28 ± 0.04	0.09	4.60 ± 0.04	0.12	0.901	0.003	0.095
NaA-20	5.05 ± 0.05	0.21	4.53 ± 0.04	0.14	0.597	0.052	0.351
NaA-35	5.39 ± 0.06	0.23	4.48 ± 0.05	0.12	0.483	0.093	0.424
NaA-50	5.61 ± 0.06	0.31	4.63 ± 0.04	0.14	0.530	0.074	0.396
NaA-65	5.83 ± 0.06	0.38	4.74 ± 0.04	0.14	0.277	0.224	0.499
NaA-hom	6.39 ± 0.06	0.40					

Table VI
Analysis of Electrostatic Interactions Using the Modified Henderson–Hasselbalch Equation

	0.36 M KCl				H_2O			
sample	pK_a	n	pK'	CC	pK_a	n	pK'	CC
NaK-10	4.60	0.9	4.62	0.97	5.28	0.9	5.28	0.99
NaA-20	4.53	1.0	4.49	0.99	5.05	1.3	5.05	0.99
NaA-35	4.48	1.0	4.48	0.98	5.39	1.3	5.43	0.99
NaA-50	4.63	1.2	4.55	0.99	5.61	1.5	5.60	0.99
NaA-65	4.74	1.2	4.74	0.99	5.83	1.6	5.83	0.99
NaAMB-10	4.79	1.1	4.71	0.99	5.23	1.1	5.23	0.99
NaAMB-25	4.74	1.1	4.69	0.99	5.31	1.4	5.29	0.99
NaAMB-40	4.90	1.1	4.82	0.99	5.75	1.5	5.74	0.99
NaAMB-60	5.01	1.1	5.03	0.99	5.88	1.8	5.96	0.99
NaAMB-75	5.10	1.0	5.18	0.98	6.19	1.7	6.19	0.99
NaAMPS-15	3.64	0.8	3.63	0.97	3.45	0.6	3.49	0.99
NaAMPS-35	3.30	0.7	3.34	0.97	3.31	0.5	3.31	0.96
NaAMPS-hom	2.79	0.6	2.85	0.96	2.86	0.7	2.91	0.97
DMNA-25	5.93	0.9	5.95	0.98	6.61	0.9	6.61	0.97
DMNA-40	5.82	0.9	5.82	0.99	6.58	1.0	6.56	0.99
DMAMB-10	5.15	1.1	5.21	0.99	5.70	1.2	5.71	0.99
DMAMB-20	5.07	1.2	5.07	0.99	5.72	1.5	5.70	0.99
DMAMB-40	5.09	1.3	5.13	0.99	5.99	1.7	5.96	0.99
DMAMB-60	5.23	1.0	5.24	0.99	6.02	1.7	5.93	0.99
DMAMP-30	3.22	0.9	3.29	0.90	3.14	0.6	3.14	0.96
DMAMP-50	3.10	0.8	3.14	0.95	3.04	0.5	3.04	0.97

conventional copolymerization kinetics.[19] The pK_a values are observed to be inversely proportional to the frequency of ABA triads present in the copolymer. In addition, the copolymer sequence data suggest a general trend of increasing pK_a values with increasing BBB triads. This is expected since a charged NaA or NaAMB unit between two acrylamide units can be stabilized by the amide hydrogens on its nearest neighbors, while a charged group between two other charged groups will be destabilized by the lack of nearest-neighbor hydrogen bonding and the repulsion of the neighboring charges. The hydrogen bonding between the charged monomers and acrylamide is a stabilizing factor on the anionic groups, making them weaker bases and consequently resulting in lower pK_a values. Acrylamide units, being uncharged, also act as "spacer units" between anionic groups and thereby decrease the charge density along the polymer chain.

Effect of Ionic Strength. Comparisons of the observed pK_a values in water and in 0.36 M KCl shown in Table V show that the pK_a values are lower in salt water than in water. This is due to several factors: (a) the slight acidity of the KCl solutions; (b) the stabilization of the anions through shielding of the charge–charge interactions by the potassium counterions; (c) the increase in neighboring-group effects due to the random coil nature of the polymer chains in salt water.

The pK_a values are also lower in the KCl solutions than in water. This is likely due to the lack of conformational change occuring as a function of the degree of ionization α. In other words, the charge–charge interactions are greatly diminished in salt solutions as compared to pure water. The polymers in pure water are much more extended (almost rodlike) due to charge–charge repulsion and are much more sensitive to pH changes. Greater conformational changes apparently are responsible for the wider pK_a range (greater ΔpK_a values) observed.

The NaAMPS copolymers, which contain sulfonate groups, are expected to show much lower pK_a values. As mentioned above, the pK_a values decrease with increasing acid content (Table IV). This suggests that the main factor affecting the acidity of these copolymers is the number of NaAMPS groups per chain. The sulfonate anion is not destabilized by the charge–charge interactions to the extent observed in the carboxylated series because of the strong stabilization of the NaAMPS sulfonate anion in solution. This is further evidenced by the pK_a values when compared in salt water and in pure water. Little or no change in the pK_a values is observed, suggesting that the sulfonate's stability makes it very insensitive to its local environment. The acid groups of the NaAMPS units remain dissociated at almost any pH range, resulting in only minor changes in the degree of ionization. The large dissociation constants account for the observed potentiometric properties of the NaAMPS groups.

It can be concluded after studying the potentiometric properties of these thre model systems that the phase behavior characteristics of each cannot be fully explained by the acidity of the ionic group, the extent of hydrogen bonding, or the ion-binding strengths of the ionic groups. Instead, the length of the side chain appears to be the dominant factor and must be studied in conjunction with ionic effects to fully understand the differences in phase behavior. In addition, the favorable hydration of the secondary amide on the NaAMB and the NaAMPS side chain may be important to the stability of these copolymers and must be considered when attempting to explain the observed phase behavior.

Effect of Charge–Charge Interactions. Further understanding of the role of charge–charge interactions can be obtained by using the modified Henderson–Hasselbalch equation.[11,20] A measure of the electrostatic interactions can be determined from the slope, n, by plotting the pH of the solution vs. log $[\alpha/(1 - \alpha)]$ as shown in eq 2; the intercept will yield the apparent pK_a value. Typically a value of $n = 1$ is given to a nonpolymeric monoacid.[8,20] In polymers, however, electrostatic repulsion between charged groups along the chain gives values of $n > 1$. For NaA and NaAMB copolymers, n increases with an increasing number of charges per chain in pure water (Table VI). In 0.36 M KCl, values of $n = 1$ are observed due to the decreased interaction between charges in electrolyte solutions, causing each charge to act similar to a monoacid ($n = 1$). The NaAMPS copolymers give values of $n < 1$, indicating little or no interaction between groups and suggesting that the sulfonate groups are not affected by added salt. Little physical meaning can be given to the n values that are less than 1 because of the high degree of dissociation of the sulfonate groups.

Effect of Hydrogen Bonding. The *N*,*N*-dimethylacrylamide copolymers show many of the same trends as the acrylamide copolymers. The absence of any available amide hydrogens causes the pK_a values to be higher; the anionic groups cannot be stabilized by hydrogen bonding.[21] The NaAMPS copolymers again are not affected by the number of acid groups per chain. This suggests that the neighboring-group effects such as acrylamide hydrogen bonding are not factors in the stability of the NaAMPS anionic groups. The n values from the modified Henderson–Hasselbalch equation show the same trends as in the acrylamide copolymers. Therefore, increased electrostatic repulsion causes higher pK_a values.

The similar phase behavior of the AM and the DMAM copolymers again suggests that the length of the side chain must be considered as well as the binding ability of the ionic group. The absence of hydrogen bonding in the DMAM copolymers affects the pK_a values of the ionic groups but does not affect the phase behavior of the system. The DMAM units in the chain act as spacer units; the longer side chains of the NaAMB and NaAMPS units again prevent the formation of insoluble bonds that cause phase separation.

Conclusions

The phase separation behavior of a polymer is dependent on several factors, ranging from molecular weight and solubility on a macromolecular scale to local ionic effects and microstructure on a much more localized scale. In the systems discussed here, phase separation is most affected by the geometry of the anion. The NaAMB and NaAMPS repeat units, whose side chains are longer, contain charged groups that are several bonds removed from the backbone, giving the charged group more mobility and conformational freedom and reducing the charge density along the chain. These longer side chains render NaAMB and NaAMPS copolymers more stable from precipitation in the presence of divalent ions and more resistant to phase separation in electrolyte solutions.

Another example of the effect of the side-chain length is apparent when studying the homopolymers of NaAMPS and sodium vinylsulfonate. The latter undergoes phase separation due to the close proximity of the ionic groups to the backbone. The observed difference in phase behavior is similar to that observed in the carboxylated analogues.

The phase separation behavior is also affected by the basicity of the anion. Copolymers such as those of the NaA and NaAMB series will be stronger bases and are expected to bind with divalent salts more readily than the NaAMPS copolymers, whose charged groups are much more stable in the anionic form (weaker bases). The NaAMPS homopolymer does not precipitate in calcium chloride solutions, while the NaAMB homopolymer does. This behavior is readily explained by the difference in acidity of the two polymers, with the NaAMPS homopolymer being much more stable in the anioic form and therefore much less likely to bind the divalent salt.

Acrylamide units in the copolymer chain appear to be excellent sites for hydrogen bonding by anionic groups in the chain. Thus local microstructure will directly affect the pK_a of a copolymer. A charged group placed between two acrylamide units will be more stable than one placed between a charged group and an acrylamide unit or between two charged groups because of the availability of the neighboring acrylamide units for forming stabilizing hydrogen bonds. Thus copolymer composition, copolymer sequence distributions, and linear charge density in the chain will affect pK_a values.

The effect of hydrogen bonding can be shown by comparing copolymers of acrylamide and of *N*,*N*-dimethylacrylamide. The DMAM copolymers, which have no amide hydrogens available for hydrogen bonding, show larger pK_a values, meaning the anionic groups are less stabilized through hydrogen bonding than in the AM copolymers.

Model compound studies have been utilized in an effort to clearly correlate structural and geometric information to the observed phenomena. Further understanding of phase behavior, however, is needed on these carefully tailored models. Ongoing work includes potentiometric titrations using calcium-sensitive electrodes and microstructural studies to compare the ion-binding ability in different microstructural environments. In addition, the nature of the secondary amide group in the NaAMB and NaAMPS repeat units will be studied to determine its importance to the observed behavior.

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Registry No. DMAM, 2680-03-7; NaAMB, 45005-74-1; NaAMPS, 5165-97-9; (NaAMB)·(acrylamide) (copolymer), 100047-18-5; (NaAMPS)·(acrylamide) (copolymer), 38193-60-1; (NaA)·(acrylamide) (copolymer), 25085-02-3; (NaA)·(DMAM) (copolymer), 92078-73-4; (NaAMB)·(DMAM) (copolymer), 100047-19-6; (NaAMPS)·(DMAM) (copolymer), 92815-96-8; calcium chloride, 10043-52-4.

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