

Description

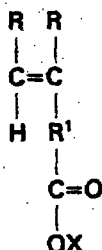
Polyampholytes are polymers containing both a cationic and an anionic mer unit, nonionic mer units optionally being present. Polyampholytes have found particular use as retention aids in the paper industry (see for example, U.S. Patents US—A—3,639,208 and US—A—4,171,417). There has also been some use of polyampholytes in the oil-drilling industry (see for example, published British Patent Application GB—A—2,044,321, which discloses a copolymer additive prepared from (1) a meth(acrylamido alkyl sulfonic acid) or alkali metal salt thereof and (2) a (meth)acrylamide or N-alkyl (meth)acrylamide, which copolymer may be crosslinked with a quaternary ammonium salt, and US Patent US—A—4,330,450).

Scale deposits are incrustation coatings which may be formed from a wide variety of simple and complex inorganic salts that accumulate on the metallic surfaces of a water-carrying system through a number of different causes. Various industrial and commercial water-carrying systems are subject to scale-formation problems. Scale is of particular concern in heat-exchange systems using water, for example, boiler systems and once-through an open recirculating water-cooling systems.

The use of polyampholytes as scale and corrosion inhibitors appears unknown.

The present invention provides a method of inhibiting corrosion and scale by inhibiting the precipitation and deposition of inorganic salts in an aqueous system, comprising adding to the aqueous system at least 0.1 ppm of a carboxylic functional polyampholyte or a salt of such a polyampholyte, prepared from:

(i) 5 to 90 percent, by weight, of at least one carboxylic functional monomer of the formula:



in which each R, which may be the same as or different from the other, is hydrogen, phenyl, C_{1-3} alkyl or $-\text{COOX}$, R' is a straight or branched chain of from 0 to 12 carbon atoms, and X is hydrogen or an alkali or alkaline-earth metal;

(ii) 0.5 to 20 percent by weight of at least one cationic-group-containing monomer; and
(iii) optionally, at least one non-ionic monomer.

In the formula, R is preferably hydrogen, methyl or ethyl, R' is preferably a straight or branched chain of from 0 to 3 carbon atoms, and X is preferably hydrogen, sodium, potassium or caesium.

The invention also provides a carboxylic polyampholyte polymer, having an intrinsic viscosity of 0.05 to 4.5 in 1.0 M NaCl and prepared from:

- (a) 32.5 to 90 weight % of acrylic acid and/or methacrylic acid;
- (b) 1.5 to 65 weight % of acrylamide; and
- (c) 0.5 to 20 weight % of dimethyldiallyl ammonium chloride and/or diethyldiallyl ammonium chloride.

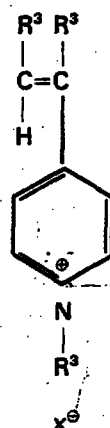
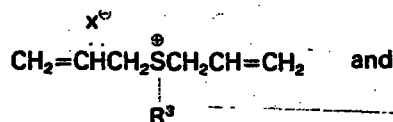
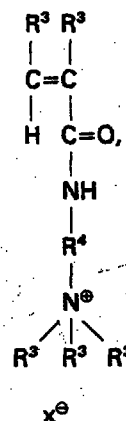
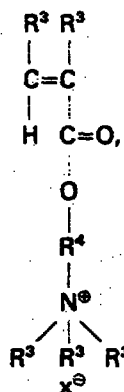
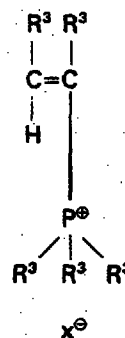
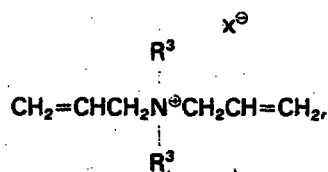
While the method of the present invention has been found particularly useful in providing inhibition of calcium phosphate scales and silica polymerization, inhibition of magnesium hydroxide, calcium fluoride, calcium carbonate, calcium sulfate and other scales may also be obtained.

Examples of the carboxylic functional monomer used as the anionic component include acrylic acid, crotonic acid, methacrylic acid, vinyl acetic acid, allylacetic acid, 4-methyl-4-pentenoic acid, and dicarboxylic acids such as maleic acid and itaconic acid, and their salts. The preferred carboxylic functional monomers are acrylic acid and methacrylic acid. Mixtures of carboxylic functional monomers may be used in preparing the polyampholyte.

Any cationic monomer may be used, preferably one containing a quaternary ammonium, phosphonium or sulfonium ion. The preferred cationic monomers are:

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where R^3 is hydrogen, phenyl, or C_{1-3} alkyl, preferably hydrogen or methyl; R^4 is a straight or branched chain or from 1 to 12 and preferably 1 to 3 carbon atoms; and X is an anion, preferably a halide or alkyl sulfate. Other examples of X include sulfate, sulfonate, phosphate, hydroxide, borate, cyanide, carbonate, thiocyanate, thiosulfate, isocyanate, sulfite, bisulfite, nitrate, nitrite, oxalate, silicate, sulfide, cyanate and acetate; other common inorganic and organic anions are also suitable.

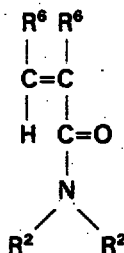
Specific examples of the particularly preferred cationic group containing monomers include diethyldiallyl ammonium chloride, dimethyldiallyl ammonium chloride, methacryloyloxy ethyl trimethyl ammonium methylsulfate and methacrylamido propyl trimethyl ammonium chloride. Mixtures of cationic-containing monomers may be used in preparing the polyampholyte.

The polyampholyte may also be prepared by polymerizing a monomer containing a tertiary amine as the pendant group with subsequent quaternization of the nitrogen in the polymer to form the cationic mer units. Likewise, sulfur-containing and phosphorus-containing monomers may be exhaustively methylated to form cations.

One or more non-ionic monomers may optionally be used. They are preferably of the formula:

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where each R^6 , which may be the same as or different from the other, is hydrogen, phenyl or C_{1-3} alkyl, preferably hydrogen, methyl, or ethyl, and each R^2 , which may be the same as or different from the other, is hydrogen or C_{1-3} alkyl. Examples of suitable non-ionic monomers include: acrylamide and its derivatives, such as methacrylamide and *N,N*-dimethyl acrylamide; acrylonitrile; vinyl acetate; vinyl pyridine; hydroxyalkyl acrylates; methacrylate and its derivatives; butadiene; styrene and its derivatives, including substituted styrenes; esters of olefinic carboxylic acids; alkylene oxides; divinyl ketones; vinyl ketones; divinyl ethers and alkyl vinyl ethers. The preferred non-ionic monomer is acrylamide. Mixtures of non-ionic monomers may be used in preparing the polyampholyte.

A non-ionic monomer may be used and subsequently hydrolysed to obtain the desired amount of anionic component. Likewise, a copolymer may be prepared from non-ionic monomer and cationic monomer with subsequent hydrolysis of the non-ionic monomer to form the anionic portion, e.g. acrylamide can be hydrolysed to form acrylic acid.

The term "aqueous", as used herein, is intended to include water in any physical state and to include water in which is dissolved or dispersed any substance, for example, inorganic salts in brine or seawater.

The polyampholyte polymers may be prepared by mixing the monomers preferably in the presence of a free radical initiator. Any free radical initiator may be used. Examples include peroxides, azo initiators and redox systems. The preferred catalysts are sodium persulfate or a mixture of ammonium persulfate and any azo type initiator, such as 2,2'-azobis-(2,4-dimethyl-4-methoxyvaleronitrile). The polymerization may also be initiated photochemically.

The polyampholyte may be made by any of a variety of procedures, for example, in solution, suspension, bulk and emulsions.

The temperature is not critical. The reaction will generally occur between 10 and 100°C., preferably 40 to 60°C. It is generally impractical to run the reaction below room temperature because the reaction is too slow. Above a temperature of 60°C., the molecular weight of the polymer tends to decrease. The reaction, depending on the temperature, generally takes from 1 to 12 hours. Measuring for residual monomer will verify when the reaction is complete.

The pH of the reaction mixture is not critical. The pH is generally in the range of 4.5 to 9.0.

The molecular weight of ampholytic polymers is difficult to accurately measure. The polymers are instead, usually identified by intrinsic viscosity. The intrinsic viscosity of the polyampholyte is not critical in the invention. It is preferred that it be at least .05 dl/g. in 1.0 *M* sodium chloride (measured on a 75 Cannon Ubbelohde capillary viscometer).

The polymer may be produced from any ratio of the monomers. It is preferred for scale and corrosion inhibition that the polymer be prepared from 5 to 90%, most preferably 22.5 to 70%, by weight, carboxylic functional monomer; 0.5 to 85%, most preferably 2.5 to 25%, by weight, cationic monomer; and 0 to 85%, more preferably 1.5 to 85%, and most preferably 5 to 67.5%, by weight, non-ionic monomer.

The treatment concentration of the polyampholyte employed in the present invention to inhibit corrosion and scale deposit and formation is generally at least 0.1 ppm, preferably 0.1 to 500 ppm by weight of the total solution of the water-carrying system being treated. Preferably, the concentration level range will be from about 1.0 to 200 ppm.

The aqueous system may be any aqueous system, for example, a cooling water, boiler water, desalination or gas scrubber system. If the system is a desalination system, the polyampholyte should have an intrinsic viscosity below 2.8 dl/g in 1.0 *M* sodium chloride.

Examples

Preparation of the polymers Polymers 1 to 58

The polymers of the examples were produced by mixing the cationic, anionic and optional non-ionic monomers indicated in Table I, using the amounts, solids concentration, initial temperatures and pH indicated. The monomer mix was purged with nitrogen for one hour. The solvent was deionized water. The initiator was added and the components allowed to react for about 3 hours.

Polymers 31 to 37 of Table I were prepared by mixing the cationic, anionic and nonionic monomers in the ratios indicated in Table I. The solutions were then neutralized to a pH of 7.0 with 50% w/v aqueous sodium hydroxide. Chain transfer agent and catalyst were added in the amounts indicated in Table I. The solutions were placed under fluorescent lights for sixty minutes. The resulting gels were diluted to 600 mg/L active polymer.



TABLE I

Polymer	Monomer cationic/anionic/ non-ionic	Weight percent	Initiator (moles initiator/ moles monomer)	Chain transfer agent	Percent solids	pH	Tempera- ture (°C)	$[\eta]^a$
1	DMDAAC/AA ² /AM ³	1.5/48.2/50.3	.003 SPS/ 1.6×10^{-4} SMBS ⁵	—	30	4.5	50	1.8
2	DMDAAC/AA/AM	2.5/32.5/65	.003 SPS/ 1.6×10^{-4} SMBS	—	30	4.5	50	1.3
3	DMDAAC/AA/AM	2.5/47.5/50	.003 SPS/ 1.6×10^{-4} SMBS	—	30	4.5	50	1.8
4	DMDAAC/AA/AM	25/55/20	.003 SPS/ 1.6×10^{-4} SMBS	—	30	4.5	50	2.2
5	DMDAAC/AA/AM	2.5/62.5/35	.003 SPS/ 1.6×10^{-4} SMBS	—	30	4.5	50	1.9
6	DMDAAC/AA/AM	5/85/10	.003 SPS/ 1.6×10^{-4} SMBS	—	30	4.5	50	0.82
7	DMDAAC/AA/AM	8/44/48	.003 SPS/ 1.6×10^{-4} SMBS	—	30	4.5	50	0.91
8	DMDAAC/AA/AM	8/50/42	.003 SPS/ 1.6×10^{-4} SMBS	—	30	4.5	50	0.93
9	DMDAAC/AA/AM	10/35/55	.003 SPS/ 1.6×10^{-4} SMBS	—	30	4.5	50	1.50
10	DMDAAC/AA/AM	10/40/50	.003 SPS/ 1.6×10^{-4} SMBS	—	30	4.5	50	1.60
11	DMDAAC/AA/AM	10/47/43	.003 SPS/ 1.6×10^{-4} SMBS	—	30	4.5	75	0.55
12	DMDAAC/AA/AM	10/55/35	.003 SPS/ 1.6×10^{-4} SMBS	—	30	4.5	50	2.2
13	DMDAAC/AA/AM	10/70/20	.003 SPS/ 1.6×10^{-4} SMBS	—	30	4.5	50	2.8
14	DMDAAC/AA/AM	12/44/44	.003 SPS/ 1.6×10^{-4} SMBS	—	30	4.5	50	1.54
15	DMDAAC/AA/AM	12/50/38	.003 SPS/ 1.6×10^{-4} SMBS	—	30	4.5	50	1.70
16	DMDAAC/AA/AM	17.5/32.5/50	.003 SPS/ 1.6×10^{-4} SMBS	—	30	4.5	50	1.0
17	DMDAAC/AA/AM	17.5/47.5/35	.003 SPS/ 1.6×10^{-4} SMBS	—	30	4.5	50	1.6
18	DMDAAC/AA/AM	17.5/62.5/20	.003 SPS/ 1.6×10^{-4} SMBS	—	30	4.5	50	3.3
19	DMDAAC/AA/AM	25/70/5	.003 SPS/ 1.6×10^{-4} SMBS	—	30	4.5	50	4.3
20	DMDAAC/AA/DMAM ⁶	20/70/10	.003 APS/ 1.0005 ADM ⁶	—	10	7.0	60	4.3

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TABLE I (contd.)

Polymer	Monomer cationic/anionic/ non-ionic	Weight percent	Initiator (moles initiator/ moles monomer)	Chain transfer agent	Percent solids	pH	Tempera- ture (°C)	$[\eta]^{19}$
21	DMDAAC/AA/MA ⁹	20/70/10	.003 APS/.0005 ADM	—	10	7.0	60	4.3
22	DMDAAC/AA	30/70	.003 SPS/ 6.4×10^{-5} SMBS	—	15	7.0	60	—
23	DMDAAC/AA/Vinyl Acetate	20/70/10	.003 SPS/ 6.4×10^{-5} SMBS	—	10	7.0	50	—
24	DMDAAC/AA/Styrene ¹⁰	10/70/20	.003 SPS/ 6.4×10^{-5} SMBS	—	20	4.5	50	—
25	DMDAAC/MAA ¹¹ /AM	10/70/20	.003 APS/.0005 ADM	—	10	7.0	60	4.3
26	MAPTAC ¹² /AA/AM	20/70/10	.003 APS/.0005 ADM	—	10	7.0	60	4.3
27	MAPTAC/AA/AM	40/40/20	.003 APS/.0005 ADM	—	10	7.0	50	2.25
28	METAMS ¹³ /AA/AM	10/70/10	.002 APS	—	10	7.0	40	4.3
29	VTPB ¹⁴ /AA/AM	10/70/20	.003 APS/.0005 ADM	—	10	7.0	60	1.1
30	DMDAAC/DEDAAC/AA/AM	27.5/2.5/30/40	.05 TBP ²⁰	—	30	4.5	50	11.4
31	MAPTAC/AMPS ¹⁵ /AM	10/70/20	5.3×10^{-5} Riboflavin	1% IPA ¹⁶	30	4.5	50	5.5
32	METAMS/AA/AM	5/47/48	5.3×10^{-5} Riboflavin	1% IPA	30	4.5	50	14.0
33	DMDAAC/AA/AM	8/60/32	1.06×10^{-4} Riboflavin/.053 SPS	1% IPA	30	4.5	50	3.3
34	METAMS/AA/AM	8/60/32	7.35×10^{-5} Riboflavin	20% TEA ¹⁷	30	4.5	50	11.2
35	DMDAAC/AA/AM	8/60/32	1.06×10^{-4} Riboflavin	20% TEA	30	4.5	50	5.1
36	METAMS/AA/AM	8/60/32	7.35×10^{-5} Riboflavin	2.1% TEA	30	4.5	50	11.0



TABLE I (contd.)

Polymer	Monomer cationic/anionic/ non-ionic	Weight percent	Initiator (moles initiator/ moles monomer)	Chain transfer agent	Percent solids	pH	Tempera- ture (°C)	$[\eta]^{19}$
37	METAMS/AA/AM	8/60/32	4.2×10^{-5} Riboflavin	1% IPA	30	4.5	50	11.2
38	DMDAAC/AA/HPA ¹⁸	10/67.5/22.5	.003 SPS/ 6.4×10^{-5} SMBS	10% IPA	30	4.5	50	0.5
39	DMDAAC/AA/HPA	10/22.5/67.5	.003 SPS/ 6.4×10^{-5} SMBS	10% IPA	30	4.5	50	0.5
40	DMDAAC/AA/HPA	10/67.5/22.5	.003 SPS/ 6.4×10^{-5} SMBS	10% IPA	30	4.5	50	0.5
41	DMDAAC/AA/HPA	10/22.5/67.5	.003 SPS/ 6.4×10^{-5} SMBS	10% IPA	30	4.5	50	0.5
42	MAPTAC/AA/AM	10/35/55	.003 SPS/ 6.4×10^{-5} SMBS	12.5% IPA	30	4.5	50	0.5
43	VTPPB/AA/AM	20/30/50	.003 SPS/ 6.4×10^{-4} SMBS	10% IPA	30	4.5	50	0.4
44	METAMS/AA/AM	10/30/60	.003 SPS/ 6.4×10^{-4} SMBS	10% IPA	30	4.5	50	0.84
45	DMDAAC/AMPS/AM	11/39/50	.003 SPS/ 6.4×10^{-4} SMBS	10% IPA	30	4.5	50	0.57
46	DMDAAC/AA/AM	10/47/43	.003 SPS/ 6.4×10^{-4} SMBS	1.5% IPA	30	4.5	50	1.1
47	DMDAAC/AA/AM	10/47/43	.003 SPS/ 6.4×10^{-4} SMBS	2.0% IPA	30	4.5	50	0.9
48	DMDAAC/AA/AM	10/47/43	.003 SPS/ 6.4×10^{-4} SMBS	2.5% IPA	30	4.5	50	0.9
49	DMDAAC/AA/AM	10/47/43	.003 SPS/ 6.4×10^{-4} SMBS	3.0% IPA	30	4.5	50	0.9
50	DMDAAC/AA/AM	10/47/43	.003 SPS/ 6.4×10^{-4} SMBS	3.5% IPA	30	4.5	50	0.8
51	DMDAAC/AA/AM	10/47/43	.003 SPS/ 6.4×10^{-4} SMBS	5.0% IPA	30	4.5	50	1.4

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TABLE I (contd.)

Polymer	Monomer cationic/anionic/ non-ionic	Weight percent	Initiator (moles initiator/ moles monomer)	Chain transfer agent	Percent solids	pH	Tempera- ture (°C)	[η] ¹⁹
52	DMDAAC/AA/AM	10/47/43	.003 SPS/6.4x10 ⁻⁴ SMBS	10.0% IPA	30	4.5	50	1.0
53	DMDAAC/AA/AM	10/47/43	.003 SPS/6.4x10 ⁻⁴ SMBS	15% IPA	30	4.5	50	0.6
54	DMDAAC/AA/AM	10/47/43	.003 SPS/6.4x10 ⁻⁴ SMBS	10% TGA ²¹	30	4.5	50	0.38
55	DMDAAC/AA/AM	10/47/43	.003 SPS/6.4x10 ⁻⁴ SMBS	12% TGA	30	4.5	50	0.36
56	DMDAAC/AA/AM	10/70/20	.003 SPS/6.4x10 ⁻⁴ SMBS	8% TGA	30	4.5	70	0.30
57	DMDAAC/AA/AM	10/70/20	.003 SPS/6.4x10 ⁻⁴ SMBS	12% TGA	30	4.5	70	0.23
58	DMDAAC/AA/AM	10/47/43	.003 SPS/6.4x10 ⁻⁴ SMBS	—	30	4.5	50	2.0

¹DMDAAC=dimethyldiallyl ammonium chloride²AA=acrylic acid³AM=acrylamide⁴=SPS=sodium persulfate⁵SMBS=sodium metabisulfite⁶DMAM=N,N-dimethyl acrylamide⁷APS=ammonium persulfate⁸ADM=2,2'-azobis-(2,4-dimethyl-4-methoxyvaleronitrile)⁹MA=methacrylamide¹⁰A 50/50 dimethylformamide/water solvent was used¹¹MAA=methacrylic acid¹²MAPTAC=methacrylamido propyl trimethyl ammonium chloride¹³METAMS=methacryloyloxyethyl trimethyl ammonium methylsulfate¹⁴VTPPB=vinyl-triphenyl phosphonium bromide¹⁵AMPS=acrylamido methylpropane sulfonic acid¹⁶IPA=isopropyl alcohol¹⁷TEA=triethanol amine¹⁸HPA=hydroxypropyl acrylate¹⁹dl/g in 1.0 M sodium chloride, measured on a 75 Cannon Ubbelohde Capillary Viscometer²⁰TBP=t-butyl peroxy pivalate²¹TGA=thio glycolic acid

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Polymer 59:

A 90/10 acrylamide/dimethyldiallyl ammonium chloride copolymer was prepared in the same manner as Polymers 1 to 30 and 38 to 58. The copolymer was then hydrolysed by adding a stoichiometric amount of sodium hydroxide to achieve a 70/20/10 terpolymer of acrylic acid/acrylamide/dimethyldiallyl ammonium chloride.

Examples 1—31 (cooling water)

Calcium phosphate inhibition was tested using 250 ppm Ca^{++} and 6.0 mg/l PO_4^{--} with 10 ppm of inhibitor, at a pH of 8.5 and at 60°C for 24 hours. The percent inhibition, as reported in Table II, was determined by measuring the PO_4^{--} concentration in solution before and after the 24 hour period.

TABLE II

	Example	Polymer	Percent inhibition
15	1	19	10
	2	13	40
20	3	18	80
	4	5	60
	5	4	5
25	6	12	90
	7	15	90
30	8	8	90
	9	17	95
35	10	3	90
	11	14	90
	12	7	95
40	13	10	90
	14	16	90
45	15	2	95
	16	38	92
	17	39	78
50	18	40	85
	19	41	92
55	20	42	100
	21	43	94
	22	44	100
60	23	45	0

The percent inhibition of calcium phosphate was measured using 2.5 ppm and 5 ppm inhibitor, by the method outlined in Examples 1—23. The results are reported in Table III.



TABLE III

	Example	Polymer	Percent inhibition	
			2.5 ppm	5 ppm
5	24	46	25	100
	25	47	—	30
10	26	48	25	100
	27	49	20	100
15	28	50	0	100
	29	51	70	100
	30	52	25	100
20	31	53	30	100

¹DMDAAC=dimethyldiallylammonium chloride²IPA=isopropyl alcohol

25 Examples 32—40 (Desalination)

Steam was passed through a metal U tube to maintain the temperature at 240°F (115°C). The U tube was immersed in a cylindrical cell. Seawater, with a concentration factor of 1.6 times normal seawater, (pH 8.2) was passed through the cell at a rate of 600 ml/hr. After 24 hours, the scale deposited on the U tube was removed, weighed and analyzed. The effectiveness is reported as % inhibition, defined by the equation:

$$\% \text{ inhibition} = \frac{\text{blank scale rate} - \text{inhibition scale rate}}{\text{blank scale rate}} \times 100$$

35 The scaling rates were determined by the equation:

$$\text{scale rate} = \frac{\text{weight of scale on tube (mg)}}{\text{test volume throughput (l)}}$$

40 The % inhibition of various scale inhibitor mixtures is indicated in Table IV.

TABLE IV

	Example	Polymer	Active	Percent inhibition
45	32	54	5	85
	33	55	5	95
50	34	56	5	76
	35	57	5	70
55	36	55	2.5	79
	37	55	7.5	78
	38	58	5	62
60	39	13	5	0 (90% Increase)
65	40	19	5	0 (70% Increase)



Examples 41—56 (boiler water)

Polymer 11 was added in the amount indicated in Table V to samples of synthetic boiler water containing varying amounts of PO_4^{3-} , OH^- , SiO_2 , Mg^{++} and chelant (sodium nitrilotriacetic acid). Each Example was tested under three conditions; without any terpolymer, with 1 mg/l and with 10 mg/l of terpolymer. The mixtures were heated to 90°C and held at that temperature throughout the tests. The pH was maintained between 10 to 12. Each sample was observed after 1 hour, 4 or 5 hours, and 21 or 22 hours. The observations are described in Table V. The test is used to predict the effectiveness of the inhibitors in boiler water systems. Under the observation rankings, A is the most preferred result, whereas F is the least preferred result.



TABLE V

Observations														
Dosage(mg/l)						No inhibitor			Terpolymer (1 mg/l)			Terpolymer (10 m g/l)		
Example	Na ₃ NTA	PO ₄	OH ⁻	SiO ₂	Mg ⁺⁺	1 hr.	4 hrs.	21 hrs.	1 hr.	5 hrs.	22 hrs.	1 hr.	5 hrs.	22 hrs.
41	56	50	500	100	10	F	F	F	F	F	F	A	D	D
42	56	5	500	100	10	F	F	F	F	F	F	D	E	E
43	56	50	50	100	10	F	F	F	E	E	F	A	A	A
44	56	5	50	100	10	F	F	F	E	F	F	A	A	A
45	56	50	500	10	10	B	B/C	B/C	C	C	C	A	A	A
46	56	5	500	10	10	B	B/C	B/C	C	C	C	A	A	A
47	56	50	50	10	10	B/C	C	C	C	C	C	A	A	A
48	56	5	50	10	10	C	C	F	E	E	E	A	A	A
49	5.6	50	500	100	1	D	D	D	A	A	A	A	A	A
50	5.6	5	500	100	1	C	C	F	A	A	A	A	A	A
51	5.6	50	50	100	1	A	A	A	A	A	A	A	A	A
52	5.6	5	50	100	1	A	A	C	A	A	A	A	A	A
53	5.6	50	500	10	1	A	B	B	A	A	A	A	A	A
54	5.6	5	500	10	1	A	B	B	A	A	A	A	A	A
55	5.6	50	50	10	1	A	A	A	A	A	A	A	A	A
56	5.6	5	50	10	1	A	A	A	A	A	A	A	A	A

A clear

B small particulates dispersed throughout the mixture

C small particulates settled on the bottom

D particulates agglomerated on the bottom to the size of a small cotton ball

E particulates agglomerated on the bottom to the size of a medium cotton ball

F particulates agglomerated on the bottom to the size of a large cotton ball



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Examples 57—72 (gas scrubbers)

Zeta potential is a measure of particle surface charge at the particle/water shear surface. An effective inhibitor will increase the charge, thus increasing the repulsive forces between particles. This will increase the dispersibility of the particles and decrease the coagulation, precipitation and subsequent scaling.

The zeta potentials of magnetite (iron oxide) particles and of calcium carbonate and magnetite in a 70/30 weight blend were determined for 1,000 ppm suspensions in deionized water at varying pHs. 0.5 ppm and 5 ppm of various polymers were added to the suspensions and the zeta potential was remeasured. The change in the zeta potential after inhibitor addition, or zeta potential increase, is noted in Table VI. When the zeta potential increased, more stable suspensions were created. Mixed deposits of magnetite and calcium carbonate are particularly typical of deposits found in many gas scrubbing systems.

TABLE VI

Example	Polymer	Concentration (ppm)	pH	Zeta potential increase (mV)	
				Magnetite	70/30 Carbonate/magnetite
57	17	5.0	8	-0.2	21.5
58	17	5.0	10	3.5	15.0
59	17	0.5	8	1.4	24.5
60	17	0.5	10	-1.6	11.9
61	19	5.0	8	11.1	21.4
62	19	5.0	10	11.4	27.4
63	19	0.5	8	2.1	27.2
64	19	0.5	10	1.6	26.8
65	13	5.0	8	10.2	31.9
66	13	5.0	10	8.6	41.4
67	13	0.5	8	3.4	27.2
68	13	0.5	10	7.4	38.1
69	6	5.0	8	9.1	36.9
70	6	5.0	10	13.4	39.0
71	6	0.5	8	5.9	39.1
72	6	0.5	10	6.6	32.5

Examples 73 to 75 (silica inhibition)

20.0 cc of 1.0 M sodium chloride, 8 cc of 0.1 M sodium silicate solution, and a predetermined amount of inhibitor, if any, were mixed and diluted with distilled water to give 100 mls final volume. The temperature of the mixture was held at about 40°C. throughout the experiment and the pH was adjusted to 8.0 by the addition of hydrochloric acid. The silica monomer concentration was determined after 5.0 minutes by the molybdate method [Alexander, G.B.; J.A.C.S. 75, 5055 (1953)] and at subsequent time intervals. The data were analysed by use of a second order kinetic plot and the polymerization rate was determined. Table VII records the effects of inhibitor on the silica polymerization process. A reduction in this polymerization rate is indicative of an expected reduction in the rate of silica deposition onto heat transfer and water transport surfaces in aqueous systems.



TABLE VII

Example	Polymer	Dosage (ppm)	SiO ₂ Polymerization rate (M ⁻¹ minute ⁻¹)
73	None	—	1.7
74	16	100	0.6
75	30	50	0.12

Example 76 (corrosion)

The coupon immersion test consisted of a cylindrical battery jar with a capacity of 8 liters. A Haake constant temperature immersion circulator (Model E-52) was used to control the solution temperature and agitate the controlled bath. The unit contained a 1000 watt fully adjustable stainless steel heater which permitted temperature control to $\pm 0.01^\circ\text{C}$, and a 10 liter per minute pump with a built-in pressure nozzle agitator that ensured high temperature uniformity in the bath. A measured contact thermoregulator was used as the temperature sensing element.

The pH of the solution was controlled with a Kruger and Eckels Model 440 pH Controller. This unit was capable of turning power on and off to a Dias minipump whenever the pH of the corrosive liquid environment fell below the set point. The peristaltic Dias pump, with a pumping capacity of 20 ml per hour, maintained the solution pH with the addition of sulfuric acid. Standard glass and saturated calomel electrodes were used as the sensing elements. The bath was continuously aerated at the rate of 60 cc per minute through a medium porosity plastic gas dispersion tube to ensure air saturation.

Two SAE 1010 steel coupons, each having a surface area of 4.2 square inches (24.1 cm²), were suspended by a glass hook. The solution volume to test metal surface area ratio for the test was approximately 1000:1.

The composition of the synthetic water used in the test was as follows; indicating content per liter of distilled water:

Ion:	Ca ⁺⁺	Mg ⁺⁺	HCO ₃ ⁻	Cl ⁻	SO ₄ ⁻
ppm:	88	24	40	70	328

The total hardness as CaCO₃ was 318 ppm and the pH was 7.5. The temperature was 50°C.

The test was conducted on the basis of a 2—3 day cycle: the system was treated with the corrosion inhibitor compositions indicated in Table I. After every second or third day, the test solution was discharged and a fresh solution was prepared. At the end of a 14 day cycle, the coupons were removed and analyzed and the test was terminated. The corrosion rate of the coupons was measured by their weight loss during the 14 day cycle, and the result was calculated as mils per year (mpy). The test results are summarized in Table VIII.

TABLE VIII

Polymer	Dosage (ppm)	Corrosion rate (mpy)			Turbidity (NTU) steel
		Steel	Copper	Admiralty	
—	0	78.7	0.58	0.79	145
9	10	60.0	0.56	0.39	41

Claims

1. A method of inhibiting the precipitation and deposition of inorganic salts in an aqueous system comprising adding to the aqueous system at least 0.1 ppm of a carboxylic functional polyampholyte or a salt of such a polyampholyte, prepared from:

(i) 5 to 90 percent, by weight, of at least one carboxylic functional monomer of the formula:



TABLE VII

	Example	Polymer	Dosage (ppm)	SiO ₂ Polymerization rate (M ⁻¹ minute ⁻¹)
5	73	None	—	1.7
	74	16	100	0.6
10	75	30	50	0.12

Example 76 (corrosion)

The coupon immersion test consisted of a cylindrical battery jar with a capacity of 8 liters. A Haake constant temperature immersion circulator (Model E-52) was used to control the solution temperature and agitate the controlled bath. The unit contained a 1000 watt fully adjustable stainless steel heater which permitted temperature control to $\pm 0.01^\circ\text{C}$, and a 10 liter per minute pump with a built-in pressure nozzle agitator that ensured high temperature uniformity in the bath. A measured contact thermoregulator was used as the temperature sensing element.

The pH of the solution was controlled with a Kruger and Eckels Model 440 pH Controller. This unit was capable of turning power on and off to a Dias minipump whenever the pH of the corrosive liquid environment fell below the set point. The peristaltic Dias pump, with a pumping capacity of 20 ml per hour, maintained the solution pH with the addition of sulfuric acid. Standard glass and saturated calomel electrodes were used as the sensing elements. The bath was continuously aerated at the rate of 60 cc per minute through a medium porosity plastic gas dispersion tube to ensure air saturation.

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The composition of the synthetic water used in the test was as follows; indicating content per liter of distilled water:

Ion:	Ca ⁺⁺	Mg ⁺⁺	HCO ₃ ⁻	Cl ⁻	SO ₄ ⁻
ppm:	88	24	40	70	328

The total hardness as CaCO₃ was 318 ppm and the pH was 7.5. The temperature was 50°C.

The test was conducted on the basis of a 2—3 day cycle: the system was treated with the corrosion inhibitor compositions indicated in Table I. After every second or third day, the test solution was discharged and a fresh solution was prepared. At the end of a 14 day cycle, the coupons were removed and analyzed and the test was terminated. The corrosion rate of the coupons was measured by their weight loss during the 14 day cycle, and the result was calculated as mils per year (mpy). The test results are summarized in Table VIII.

TABLE VIII

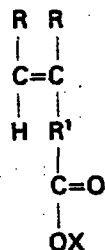
	Polymer	Dosage (ppm)	Corrosion rate (mpy)			Turbidity (NTU) steel
			Steel	Copper	Admiralty	
45	—	0	78.7	0.58	0.79	145
50	9	10	60.0	0.56	0.39	41

Claims

1. A method of inhibiting the precipitation and deposition of inorganic salts in an aqueous system comprising adding to the aqueous system at least 0.1 ppm of a carboxylic functional polyampholyte or a salt of such a polyampholyte, prepared from:

(i) 5 to 90 percent, by weight, of at least one carboxylic functional monomer of the formula:



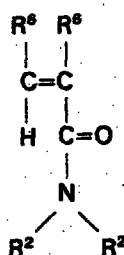


in which each R, which may be the same as or different from the other, is hydrogen, phenyl, C₁₋₃ alkyl or —COOX, R¹ is a straight or branched chain of from 0 to 12 carbon atoms, and X is hydrogen or an alkali or alkaline-earth metal;

- (ii) 0.5 to 20 percent by weight of at least one cationic-group containing monomer; and
 (iii) optionally, at least one non-ionic monomer.

2. A method as claimed in Claim 1, in which the carboxylic functional polyampholyte is a terpolymer prepared from:

- (i) a carboxylic functional monomer of the formula set forth in Claim 1, except that R is not —COOX;
 (ii) at least one non-ionic monomer of the formula:



where each R², which may be the same as or different from the other, is hydrogen, phenyl or C₁₋₃ alkyl, and each R², which may be the same as or different from the other, is hydrogen or C₁₋₃ alkyl, and

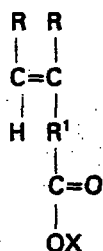
- (iii) a cationic-containing monomer containing a quaternary ammonium, phosphonium or sulfonium ion.

3. A polyampholyte polymer having an intrinsic viscosity of 0.05 to 4.5 in 1.0 M NaCl and prepared from
 (a) 32.5 to 90 weight % of acrylic acid and/or methacrylic acid;
 (b) 1.5 to 65 weight % of acrylamide; and
 (c) 0.5 to 20 weight % of dimethyldiallyl ammonium chloride and/or diethyldiallyl ammonium chloride.

Patentansprüche

1. Ein Verfahren zur Inhibierung der Ausfällung und Ablagerung von anorganischen Salzen in einem wässrigen System, umfassend den Zusatz zu dem wässrigen System, von mindestens einem Polyampholyten mit Carboxylfunktionen oder von einem Salz eines derartigen Ampholyten, hergestellt aus:

- (i) 5 bis 90 Gew.-% mindestens eines Monomeren mit Carboxyl-Funktion mit der Formel:



worin jedes R, das gleich wie das oder verschieden von dem anderen sein kann, Wasserstoff, Phenyl, C₁₋₃-alkyl oder —COOX ist, R¹ eine gerade oder verzweigte Kette mit 0 bis 12 Kohlenstoffatomen ist, und X Wasserstoff oder ein Alkali- oder Erdalkalimetall ist;

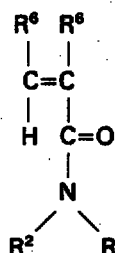
- (ii) 0,5 bis 20 Gew.-% mindestens eines eine kationische Gruppe enthaltendem Monomeren; und
 (iii) gegebenenfalls mindestens einem nicht-ionischen Monomeren.

2. Ein Verfahren wie in Anspruch 1 beansprucht, bei dem der Polyampholyt mit Carboxylfunktionen ein Terpolymeres ist, hergestellt aus:



(i) einem Monomeren mit Carboxylfunktion der in Anspruch 1 angegebenen Formel, wobei jedoch R nicht —COOX ist;

(ii) mindestens einem nicht-ionischen Monomeren der Formel:



worin jedes R^6 , das gleich wie das oder verschieden von dem anderen sein kann, Wasserstoff, Phenyl oder C_{1-3} -Alkyl ist, und jedes R^2 , das gleich wie das oder verschieden von dem anderen sein kann, Wasserstoff oder C_{1-3} -Alkyl ist, und

(iii) einem Kation-enthaltenden Monomeren, das ein quaternäres Ammonium-, Phosphonium- oder Sulfonium-ion enthält.

3. Ein Polyampholytpolymeres mit einer intrinsik Viskosität von 0,05 bis 4,5 in 1,0 m NaCl und hergestellt aus:

(a) 32,5 bis 90 Gew.-% Acrylsäure und/oder Methacrylsäure;

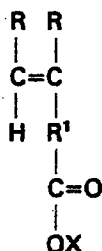
(b) 1,5 bis 65 Gew.-% Acrylamid; und

(c) 0,5 bis 20 Gew.-% Dimethyl-diallyl-ammoniumchlorid und/oder Diethyl-diallyl-ammoniumchlorid.

Revendications

1. Procédé d'inhibition de la précipitation et de la déposition de sels minéraux dans un système aqueux comprenant l'addition au système aqueux d'au moins 0,1 ppm d'un polyampholyte à fonction carboxylique ou d'un sel de ce polyampholyte, préparé à partir de:

(i) 5 à 90 pour cent, en poids, d'au moins un monomère à fonction carboxylique de formule:



dans laquelle chacun des R, qui peuvent être identiques ou différents l'un de l'autre, est l'hydrogène, le phényle, un alkyle en C_{1-3} ou —COOX, R^1 est une chaîne droite ou ramifiée de 0 à 12 atomes de carbone et X est l'hydrogène ou un métal alcalin ou alcalino-terreux;

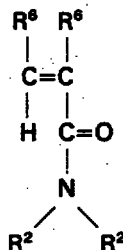
(ii) 0,5 à 20 pour cent en poids d'au moins un monomère contenant un groupe cationique; et

(iii) éventuellement, au moins un monomère non ionique.

2. Procédé selon la revendication 1, dans lequel le polyampholyte à fonction carboxylique est un terpolymère préparé à partir de:

(i) un monomère à fonction carboxylique répondant à la formule de la revendication 1, sauf que R n'est pas —COOX;

(ii) au moins un monomère non ionique de formule:



dans laquelle chacun des R^6 , qui peuvent être identiques ou différents l'un de l'autre, est l'hydrogène, le phényle ou un alkyle en C_{1-3} et chacun des R^2 , qui peuvent être identiques ou différents l'un de l'autre, est l'hydrogène ou un alkyle en C_{1-3} , et



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(iii) un monomère contenant un groupe cationique contenant un ion ammonium quaternaire, phosphonium ou sulfonium.

3. Polymère polyampholyte ayant une viscosité intrinsèque de 0,05 à 4,5 dans le NaCl 1,0 M et préparé à partir de

(a) 32,5 à 90% en poids d'acide acrylique et/ou d'acide méthacrylique;

(b) 1,5 à 65% en poids d'acrylamide; et

(c) 0,5 à 20% en poids de chlorure de diméthyldiallylammonium et/ou de chlorure de diéthylallylammonium.

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This Sheet Has Been Replaced

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* C L N S *