

A SOLIDS-FREE THICKENED BRINE COMPRISING CATIONIC
ACRYLAMIDE EMULSION POLYMERS AND THE PREPARATION THEREOF

This invention relates to thickened brine for use in aqueous well drilling and servicing fluids and to the preparation of such brine.

In the drilling of subterranean wells, aqueous fluids containing 5 no suspended solids have been used extensively in completion and work-over operations in order to minimize damage to the production stratum caused primarily by fluid and solids invasion. After high solids drilling muds have been employed, these fluids are flushed through the well in order to remove any moveable solids which may cause clogging and in 10 turn prevent oil from freely flowing into the producing zone. The fluids also function to control subsurface pressure and maintain hole stability while remaining stable at working temperatures. The fluids are concentrated water solutions of metal salts including, for example, KCl, NaCl, NaBr, CaCl₂, CaBr₂, ZnCl₂ and ZnBr₂. The salt or salts 15 selected and the concentration employed are determined by the desired density and crystallization temperature of the fluid. Modern research has led to the development of a number of useful brines with densities ranging up to 2.3 kg./l. (19.2 ppg. - pounds per gallon).

Additives are used in the brine solutions to control and increase 20 their viscosity which in turn enhances the cuttings carrying capacity of the brines, reduces fluid loss, and conditions and minimizes caving and water damage of the water-sensitive formation. Polysaccharide gums such as xanthan gum, guar gum, locust bean gum, carrageenan, and

hydroxyethyl cellulose (HEC) have been employed to thicken brine systems. These additives, normally supplied in dry powder form, require special preparation and/or mixing and dispersing equipment when added to the brine systems. HEC and other polysaccharide additives surface-hydrate too rapidly and nonuniformly, resulting in clumps referred to as "fish eyes" which can cause clogging and formation damage. Many of these polysaccharide additives hydrate only after elevating the temperature of the brine. As these additives dissolve upon exposure to higher downhole temperatures, they cause brine viscosities to fluctuate resulting in unpredictable and undesirable latent viscosities. Moreover, many of the polysaccharides tend to also form separate gummy polymer layers in the higher density brines.

Various attempts have been made involving additional time and expense to overcome the dissolution problems described above. For example, in U.S. Pat. No. 4,392,964 issued on July 12, 1983 to R. House et al., a polymer composition prepared by mixing 5-30 parts of HEC with at least 40 parts of isopropanol is mixed with 3-40 parts water in order to thoroughly wet the HEC prior to addition to the brine system. In U.S. Pat. No. 4,415,463 issued on November 15, 1983 to B. Mosier et al., natural polysaccharide gums such as carageenan and locust bean are treated with a basic nitrogen reagent to wet the polymer prior to addition to the brine system. In U.S. Pat. Nos. 4,435,564 and 4,439,333 issued on March 6, 1984 and March 27, 1984, respectively, to R. House, HEC is first activated such that the HEC will disperse and hydrate in heavy brines. The activation process comprises admixing HEC in a solution of either an amino or phenolic compound and a water soluble organic liquid prior to brine addition. Some of the additives also become in-

effective when added to brine systems having densities above about 1.4 kg./l. (12 ppg.). In U.S. Pat. No. 4,420,406 issued on December 13, 1983 to R. House et al. it was disclosed that heavy brine solutions having a narrow density range of 1.7 to 1.9 kg./l. (14.2 to 15.6 ppg) could be effectively thickened with HEC depending on the presence or absence of CaCl_2 and the specific amount of ZnBr_2 in the brine.

Other problems still exist when the polysaccharides described above are added to brine solutions. Many of the polysaccharides are subject to incompatibility problems in the brines after a period of time. The polysaccharides also become thermally unstable when subjected to down-hole temperatures above about 82°C (180°F). Furthermore some of the polysaccharides employed are subject to bacterial attack. For these reasons the subterranean well drilling industry is searching for other means to effectively thicken brine solutions.

There is therefore a need for brine thickeners which will easily dissolve, be compatible in the brines, be thermally resistant, and not be subject to bacterial attack.

The present invention provides a thickened aqueous brine solution having a density of at least 1.7 kg./l. (14.4 ppg) and a cationic water-in-oil emulsion polymer of acrylamide or methacrylamide and a cationic monomer having an intrinsic viscosity (I.V.) measured in 1.0 N KCl of 1 to 7.0 dl./g. The cationic polymers have acrylamide or methacrylamide to cationic monomer molar ratios of about 60:40 to 95:5. Preferably the cationic monomers are selected from the group consisting of dimethyldiallyl ammonium chloride, methacrylamidopropyltrimethyl ammonium chloride, trimethylaminoethyl methacrylate and dimethylaminopropyl methacrylamide.

In the method herein, the cationic emulsion polymer is added to an aqueous brine solution in an amount sufficient to thicken a well drilling or servicing fluid.

The cationic emulsion polymers useful herein are obtained by the polymerization of acrylamide or methacrylamide with a cationic monomer.

The cationic monomers which are applicable for use herein, are: dialkylaminoalkyl (meth)acrylamides, tri-alkylaminoalkyl (meth)acrylamides, trialkylaminoalkyl (meth)acrylates and dialkyldiallyl ammonium halides.

10 Most preferably the monomers are selected from the group consisting of dimethyldiallyl ammonium chloride and methacrylamidopropyltrimethyl ammonium chloride, hereinafter referred to as DMDAAC and MAPTAC respectively. Other cationic monomers preferably employed include dimethyl-aminopropyl methacrylamide (referred to as DMAPMA) and the quaterniza-
15 tion products of dimethylaminoethyl methacrylate with methyl chloride (referred to herein as trimethylaminoethyl methacrylate or TMAEMA) and dimethylaminoethyl methacrylate with dimethyl sulfate. In addition, minor amounts of other polymerizable monomers may be employed in the preparation of the cationic emulsion polymer; however, no improvement
20 over a polymer prepared with only acrylamide or methacrylamide and a cationic monomer is expected.

The cationic polymers will ordinarily have an acrylamide (ACM) or methacrylamide to cationic monomer molar ratio of about 60:40 to 95:5. The preferred molar ratio range for a given polymer will vary depending
25 on the cationic monomer employed and the density of the brine to be treated. For instance, the preferred molar ratio for ACM:TMAEMA copolymer is about 70:30 to 80:20, whereas ACM:DMDAAC and ACM:MAPTAC copolymer

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preferably have molar ratios of about 80:20 to 91:9.

The cationic polymers may be prepared according to any number of conventional emulsion polymerization techniques known to those skilled in the art. Suitable processes include those taught in U.S. Pat. Nos. 53,284,393 (issued November 8, 1966 to J. Vanderhoff et al.), 3,826,771 (issued July 30, 1974 to D. Anderson et al.) and 4,077,930 (issued March 7, 1978 to S. Lim et al.). The polymers will generally be present in the emulsion in amounts of about 25-50% solids by weight.

It should be noted that any emulsion polymerization technique may be employed as long as the resultant polymers are of sufficiently high molecular weight, as represented by intrinsic viscosities measured in 1.0 N KCl of about 1 to 7.0 preferably 3.5 to 6.5, and most preferably 5.0 to 6.0. It has been found that as the intrinsic viscosity of the cationic polymer increases above about 7.0, there is a tendency in some brine systems for such a polymer to not only thicken the brine solution but also to cause the solution to become dilatant. Such a physical trait may be noted by evaluating the rheological data obtained from a treated brine solution. If the apparent viscosity of the solution (the Baroid reading at 600 rpm divided by 2) is greater than the Baroid reading taken at 300 rpm, the solution is said to be dilatant to some extent. As the difference between these two values increases, the fluid is pumped with less ease which in turn puts an added strain on the pumping equipment. Large fluctuations in viscosity readings are observed in a very dilatant system. When describing the brine solutions herein, a solution referred to as being stringy does not connote the same meaning as being dilatant. A solution is referred to as stringy if it exhibits a slightly cohesive texture upon visual

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observation under non-shear conditions. It should be noted that a stringy solution does not pose pumping problems to the same degree as a fluid which is dilatant.

The quantity of the cationic polymers utilized will vary with 5 circumstances depending on such factors as the density and composition of the brine solution to be treated. The cationic emulsion polymers are extremely effective as thickeners for heavy brine solutions, having densities of at least 1.7 kg./l. (14.4 ppg), which comprise aqueous solutions of a water soluble salt of a multivalent metal 10 including CaCl_2 , CaBr_2 , ZnCl_2 , ZnBr_2 , and mixtures thereof. We have found the cationic emulsion polymers to be especially effective in the denser, more difficult to thicken zinc-containing brines having densities of 1.9 kg./l. (16.0 ppg) and greater. Other factors influencing the treatment levels of the polymers employed include the 15 formation strata type encountered, drilling depths, and temperatures and pressures encountered. Ordinarily the polymers will impart a viscosifying effect to heavy brine solutions when used in amounts (based on dry solids) of about 0.0006-0.0119 kg./l., i.e., 0.25 to 5.0 pounds per 42-gallon barrel -ppb). Preferably the polymer is added at 20 the 0.0012-0.0071 kg./l. (0.5 to 3.0 ppb) treatment level. The exact amount to be added can be determined by simple routine tests known to those skilled in the art at the time the addition is made.

In the examples which follow, all percentages are given by weight unless otherwise indicated. All physical property measurements were 25 made in accordance with testing procedures set forth in Standard Procedure For Testing Drilling Fluids API Recommended Practice, 13B, May 1982, Sections 2 and 3.

In formulating the brine solutions, the following salt solutions were employed:

Brine Density		Brine Composition
kg./l.	ppg	
5 1.4	11.6	aqueous solution containing 37.6% CaCl_2 and 1.65% CaBr_2
1.7	14.4	aqueous solution containing 30.7% CaBr_2 and 35.8% CaCl_2
10 1.9	16.0	aqueous solution containing 6.35% ZnBr_2 , 14.5% CaCl_2 , and 45.9% CaBr_2
2.3	19.2	aqueous solution containing 26.7% ZnBr_2 and 43.03% CaBr_2

EXAMPLE 1

This example illustrates the ability of ACM:DMDAAC copolymers to effectively thicken various heavy brine solutions. The copolymers evaluated are described below:

	Copolymer	ACM:DMDAAC Molar Ratio	Intrinsic Viscosity dl./g.
20	A	80:20	3.8
	B	80:20	5.2
	C	90:10	5.0
	D	90:10	7.8
	E	95:5	10.8

The copolymers were evaluated in 1.4 and 1.9 kg./l. (11.6 and 16.0 ppg) dense brine solutions. To 350 ml. of each brine was added 0.5 or 1.0 g. (based on dry solids) of each copolymer. This is equivalent to treatment levels of 0.0012 and 0.0024 kg./l. (0.5 and 1.0 ppb). The treated brines were mixed with a Hamilton Beach Multimixer for 20 minutes, qualitatively evaluated for compatibility, then sealed in glass jars and statically aged at 82°C (180°F) for 16 hours. The flow properties and gel strengths of the samples were measured at 82°C (180°F), 46°C (115°F), and room temperature. The apparatus used to evaluate the treated brine solutions was a Baroid Viscometer Model

#286-76163. Readings were taken at 600 and 300 rpm. HEC (Natrosol* 250 MR obtained from Hercules) was also evaluated for comparison in this example as well as all subsequent examples. The results may be found in Tables I and II.

5 The results of Tables I and II indicate there is a significant difference in compatibility between the ACM:DMAAC copolymers and HEC in the brines. The cationic copolymers dissolved easily in the brines while HEC provided an undesirable gummy polymer layer in the 1.4 kg./l. (11.6 ppg) brine and grainy insolubles in the 1.9 kg./l. (16.0 ppg) brine. It
10 was noted that the ACM:DMAAC copolymers thickened both brine solutions while being more effective in the denser brine. Copolymer E, the 95:5 molar ratio ACM:DMAAC copolymer having an IV of 10.8 caused the brines to be dilatant. It was noted that as the molecular weight and molar ratio of AMC to DMAAC increased, the brines treated therewith became
15 more dilatant.

EXAMPLE 2

This example illustrates the ability of ACM:MAPTAC and ACM:TMAEMA copolymers to effectively thicken various heavy brine solutions. The copolymers evaluated are described below:

20	Copolymer	Comonomer	ACM:Comonomer Molar Ratio	Intrinsic Viscosity
				dl./g.
	F	MAPTAC	70:30	2.3
	G	MAPTAC	70:30	4.2
	H	MAPTAC	80:20	4.15
25	I	MAPTAC	91:9	4.15
	J	MAPTAC	91:9	6.05
	K	TMAEMA	70:30	6.2
	L	TMAEMA	80:20	7.3

30 The copolymers were evaluated in 1.7 and 2.3 kg./l. (14.4 and 19.2 ppg) dense brine solutions by the procedure described in Example 1. The fluid loss of the treated brines at room temperature was also measured.

The results may be found in Tables III and IV.

*Natrosol is a registered trade mark

TABLE 1

COPOLYMER	TREATMENT LEVEL	COMPATIBILITY	KILOCALORY IN DISKS OF BRADLEY IN 1.4 kg./l. (11.6 ppg) SOLUTION									
			0 82°C (180°F)			0 46°C (115°F)			0 Room Temp.			
			600	300	GS	600	300	GS	600	300	GS	GS
Blank	kg./l. ppg	-	9	5	0.45 (1)	14	7	0.45 (1)	22	11	0.45 (1)	
HEC	0.0012 0.5	gunny polymer layer*	18	10	0.91 (2)	29	16	0.91 (2)	91	48	0.45 (1)	
	0.0024 1.0	gunny polymer layer*	26	14	1.36 (3)	35	19	0.91 (2)	90	55	0.91 (2)	
A	0.0012 0.5	++	12	6	0.91 (2)	25	12	0.45 (1)	42	19	0.91 (2)	
	0.0024 1.0	++	18	10	0.91 (2)	33	16	0.45 (1)	44	23	0.45 (1)	
B	0.0012 0.5	++	12	7	0.45 (1)	20	10	0.45 (1)	30	14	0.45 (1)	
	0.0024 1.0	++	15	8	0.45 (1)	31	15	0.45 (1)	39	19	0.45 (1)	
C	0.0012 0.5	++	10	5	0.91 (2)	19	10	0.91 (2)	26	13	0.91 (2)	
	0.0024 1.0	++	14	7	0.45 (1)	24	12	0.45 (1)	31	16	0.91 (2)	
D	0.0012 0.5	++	19	10	0.91 (2)	45	19	0.91 (2)	48	37	0.91 (2)	
	0.0024 1.0	++ (s)	38	22	0.91 (2)	58	34	0.91 (2)	60	43	0.91 (2)	
E	0.0012 0.5	++	33	18	0.91 (2)	05	38	0.45 (1)	05	48	0.45 (1)	
	0.0024 1.0	++	68	43	0.91 (2)	05	58	0.91 (2)	05	>80	0.91 (2)	

US = 10 second gel strength kg./9.29 m.² (lb./100 ft.²)

* = layer observed upon surface of urine solution

++ = good compatibility (no insolubles)

s = stringy

US = off scale (>320 degrees Baroid)

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TABLE II

COPOLYMER	TREATMENT LEVEL	COMPATIBILITY	RHEOLOGY IN DEGREES BAROID IN 1.4 kg./l. (11.0 ppg) SOLUTION									
			@ 82°C (180°F)			@ 46°C (115°F)			@ Room Temp.			
			600	300	GS	600	300	GS	600	300	GS	GS
Blank	kg./l. - ppb		17	8	0.45 (1)	27	14	0.45 (1)	41	20	0.45 (1)	
HEC	0.0012 0.5	grainy insolubles	17	10	0.91 (2)	30	15	0.91 (2)	48	25	0.91 (2)	
	0.0024 1.0		15	8	0.91 (2)	30	14	0.91 (2)	50	25	0.91 (2)	
A	0.0012 0.5	++ few tiny lumps	23	12	0.45 (1)	58	28	0.91 (2)	88	42	0.45 (1)	
	0.0024 1.0		39	19	0.45 (1)	86	41	0.91 (2)	100	55	0.45 (1)	
B	0.0012 0.5	++	19	9	0.91 (2)	44	22	0.45 (1)	58	27	0.45 (1)	
	0.0024 1.0		31	15	0.45 (1)	66	34	0.45 (1)	78	32	0.45 (1)	
C	0.0012 0.5	++	23	12	0.45 (1)	40	20	0.45 (1)	71	31	0.45 (1)	
	0.0024 1.0		34	18	0.45 (1)	78	35	0.45 (1)	96	45	0.45 (1)	
D	0.0012 0.5	++	58s	30	0.91 (2)	83s	58	0.45 (1)	05	58	0.91 (2)	
	0.0024 1.0		78s	58	0.91 (2)	105s	80	0.91 (2)	05	05	1.36 (3)	
E	0.0012 0.5	++	70s	53	0.45 (1)	05	70	0.91 (2)	05	05	1.36 (3)	
	0.0024 1.0		05	70	0.91 (2)	05	05	0.91 (2)	05	05	1.36 (3)	

GS = 10 second gel strength kg./9.29 m.² (1b./100 ft.²)

++ = good compatibility (no insolubles)

s = stringy

05 = off scale (>320 degrees Baroid)

TABLE III

COPOLYMER	TREATMENT LEVEL kg./l. ppb	COMPATIBILITY	1.7 kg./l. (14.4 ppb) DENSE BRINE SOLUTION RHEOLOGY IN DEGREES BAROID								API Fluid Loss (cc. at 30 min.)
			Ø 82°C (180°F)		Ø 46°C (115°F)		Ø Room Temp.		CFL		
			600	300	600	300	600	300			
Blank HEC	0.0024 1.0	- gummy polymer layer*	18 25	9 13	38 46	19 24	66 90	34 55	5		
F	0.0024 1.0	++	27	13	60	30	108	57	12		
G	0.0024 1.0	++	41	18	75	38	112	58	5		
H	0.0024 1.0	++	30	14	67	33	101	52	12		
I	0.0024 1.0	++	33	17	66	33	118	58	-		
J	0.0024 1.0	++	40	26	72	41	130	70	5		
K	0.0024 1.0	++	42	20	72	37	110	56	2		
L	0.0024 1.0	++	32	14	87	38	130-135	69	2		

CFL = complete fluid loss (>300 cc.)

++ = good compatibility (no insolubles)

* = layer observed upon surface of brine solution

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TABLE IV

2.3 kg./l. (19.2 ppb) DENSE BRINE SOLUTION									
RHEOLOGY IN DEGREES BRAKID									
COPOLYMER	TREATMENT LEVEL	COMPATIBILITY	68°C (180°F)		94°C (211°F)		Room Temp.		API Fluid Loss (cc. at 30 min.)
			600	300	600	300	600	300	
Blank	kg./l. ppb	-	16	8	31	16	53	27	CFL
HEC	0.0012 0.5	gummy polymer layer*	44	24	64	36	108	62	-
	0.0024 1.0	gummy polymer layer*	28	15	54	28	89	48	4
F	0.0012 0.5	++	27	14	48	25	72	37	11
G	0.0024 1.0	few tiny lumps	52	27	75	39	143	74	60
H	0.0012 0.5	++	26	14	38	20	75	39	9
I	0.0012 0.5	++	28	15	45	24	87	45	-
J	0.0012 0.5	++	38 ^s	16	55	30	107	54	5
K	0.0024 1.0	++	35	18	57	29	114	56	31
L	0.0024 1.0	++	80-90 ^s	45-50	110-160 ^s	65-85	120-180 ^s	120-140	13

++ = good compatibility (no insolubles)

* = layer observed upon surface of brine solution

s = stringy

CFL = complete fluid loss (>300 cc.)

As can be seen in the tables, the cationic copolymers effectively thickened and were compatible with both the 1.7 and 2.3 kg./l. (14.4 and 19.2 ppg) brines while HEC produced gummy polymer layers which had the appearance of gels on top of the brines. The cationic copolymers were seen to provide good to excellent fluid loss control in the 1.7 kg./l. (14.4 ppg) brine and many provided good fluid loss control in the 2.3 kg./l. (19.2 ppg) brine as well. Sample L, an 80:20 ACM:TMAEMA copolymer having an I.V. of 7.3, was noted to thicken the brines; however, the fluctuations in Baroid rheology observed in the 2.3 kg./l. (19.2 ppg) brine indicated the solution to be very dilatant.

EXAMPLE 3

An 80:20 and a 90:10 molar ratio ACM:DMDAAC emulsion copolymer (samples B and C respectively of Example 1) were evaluated in four brine solutions at treatment levels of 0.0012 to 0.0048 kg./l. (0.5 to 2.0 15 ppb). Excellent results were obtained. The data is given in Table V.

EXAMPLE 4

This example illustrates the ability of an ACM:DMPMA copolymer to effectively thicken various heavy brine solutions. The cationic acrylamide emulsion copolymer employed contained 20 mole percent of the 20 cationic tertiary amine comonomer and had an I.V. of 1.35 dl./g. The treated brines were evaluated by the procedure described in Example 1. Rheology data may be found in Table VI.

In addition to being compatible in all the brines, the results showed that the ACM:DMPMA copolymer did thicken each as well. The 25 copolymer was seen to be especially effective in the 2.3 kg./l. (19.2 ppg) zinc-containing brine.

TABLE V

COPOLYMER	BRINE DENSITY kg./l. ppq	TREATMENT LEVEL kg./l. ppb	COMPATIBILITY	RHEOLOGY IN DEGREES BAROID									
				@ 82°C (180°F)			@ 46°C (115°F)			@ Room Temp.			
				600	300	GS	600	300	GS	600	300	GS	
Blank	1.4	11.6	-	9	5	0.45 (1)	14	7	0.45 (1)	22	11	0.45 (1)	
HEC	1.4	11.6	*	18	10	0.91 (2)	29	16	0.91 (2)	91	48	0.45 (1)	
	1.4	11.6	*	26	14	1.36 (3)	35	19	0.91 (2)	90	55	0.91 (2)	
	1.4	11.6	*	35	19	1.36 (3)	42	24	1.36 (3)	124	78	1.36 (3)	
	1.4	11.6	*	40	22	1.36 (3)	67	38	1.36 (3)	152	99	1.81 (4)	
B	1.4	11.6	++	12	7	0.45 (1)	20	10	0.45 (1)	30	14	0.45 (1)	
	1.4	11.6	++	15	8	0.45 (1)	31	15	0.45 (1)	39	19	0.45 (1)	
	1.4	11.6	++	29	14	0.91 (2)	35	18	0.45 (1)	75	39	0.91 (2)	
	1.4	11.6	++	40	20	0.91 (2)	54	28	1.36 (3)	95	52	1.81 (4)	
C	1.4	11.6	++	10	5	0.91 (2)	19	10	0.91 (2)	26	13	0.91 (2)	
	1.4	11.6	++	14	7	0.45 (1)	24	12	0.45 (1)	31	16	0.91 (2)	
	1.4	11.6	++	20	10	0.91 (2)	30	15	0.91 (2)	43	23	0.91 (2)	
	1.4	11.6	++	24	12	1.36 (3)	42	22	0.91 (2)	56	30	1.36 (3)	
Blank	1.7	14.4	-	18	9	0.45 (1)	38	19	0.45 (1)	66	34	0.45 (1)	
HEC	1.7	14.4	*	27	14	0.91 (2)	4	22	0.91 (2)	92	52	0.91 (2)	
	1.7	14.4	*	25	13	0.91 (2)	46	24	0.91 (2)	88	46	0.91 (2)	
	1.7	14.4	*	23	12	0.91 (2)	36	18	0.91 (2)	100	53	0.91 (2)	
	1.7	14.4	*	30	14	0.91 (2)	44	24	0.91 (2)	104	57	0.91 (2)	
B	1.7	14.4	++	23	12	0.45 (1)	47	24	0.45 (1)	64	32	0.45 (1)	
	1.7	14.4	++	33	16	0.45 (1)	70	35	0.45 (1)	97	47	0.45 (1)	
	1.7	14.4	++	62	32	0.91 (2)	104	53	0.91 (2)	134	80	1.36 (3)	
	1.7	14.4	++	71	36	0.91 (2)	126	65	0.91 (2)	150	92	1.81 (4)	

GS = 10 second gel strength kg./9.29 m.² (lb./100 ft.²)

+ = good compatibility (no insolubles)

* = layer observed upon surface of brine solution

S = stringy

TABLE V - (cont'd)

RHEOLOGY IN DEGREES BAROID												
				82°C (180°F)		84°C (115°F)		Room Temp.				
				600	300	600	300	600	300			
				GS		GS		GS				
COPOLYMER	BRINE DENSITY	TREATMENT LEVEL	COMPATIBILITY									
	Kg./l. pp9	Kg./l. ppb										
C	1.7 14.4	0.0012 0.5	++	22	11	0.45 (1)	40	21	0.45 (1)	63	32	0.91 (2)
	1.7 14.4	0.0024 1.0	++	28	15	0.45 (1)	74	39	0.91 (2)	67	34	0.45 (1)
	1.7 14.4	0.0036 1.5	++	46	25	0.45 (1)	88	46	1.36 (3)	102	53	0.91 (2)
	1.7 14.4	0.0048 2.0	++	55	29	0.45 (1)	47	24	0.45 (1)	124	64	0.91 (2)
Blank HEC	1.9 16.0	-	-	17	8	0.45 (1)	27	14	0.45 (1)	41	20	0.45 (1)
	1.9 16.0	0.0012 0.5	*	17	10	0.91 (2)	30	15	0.91 (2)	48	25	0.91 (2)
	1.9 16.0	0.0024 1.0	*	15	8	0.91 (2)	30	14	0.91 (2)	50	25	0.91 (2)
	1.9 16.0	0.0036 1.5	*	14	7	0.91 (2)	34	15	0.91 (2)	48	24	0.91 (2)
B	1.9 16.0	0.0048 2.0	*	15	8	0.91 (2)	34	16	0.91 (2)	52	26	0.91 (2)
	1.9 16.0	0.0012 0.5	++	19	9	0.91 (2)	44	22	0.45 (1)	58	27	0.45 (1)
	1.9 16.0	0.0024 1.0	++	31	15	0.45 (1)	66	34	0.45 (1)	78	32	0.45 (1)
	1.9 16.0	0.0036 1.5	++	51	25	0.45 (1)	64	32	0.91 (2)	98	47	0.91 (2)
C	1.9 16.0	0.0048 2.0	*	66	32	0.91 (2)	67	35	0.91 (2)	118	60	0.91 (2)
	1.9 16.0	0.0012 0.5	++	23	12	0.45 (1)	40	20	0.45 (1)	71	31	0.45 (1)
	1.9 16.0	0.0024 1.0	++	34	18	0.45 (1)	78	35	0.45 (1)	96	45	0.45 (1)
	1.9 16.0	0.0036 1.5	++	34	18	0.91 (2)	50	27	0.91 (2)	144	80	0.91 (2)
Blank HEC	1.9 16.0	0.0048 2.0	*	42	22	0.91 (2)	58	30	1.36 (3)	158	52	0.91 (2)
	2.3 19.2	-	-	16	8	0	31	16	0.45 (1)	53	27	0
	2.3 19.2	0.0012 0.5	*	44	24	0.45 (1)	64	36	0.45 (1)	102	62	0.45 (1)
	2.3 19.2	0.0024 1.0	*	24	12	0.45 (1)	42	24	0.45 (1)	104	89	1.36 (3)
	2.3 19.2	0.0036 1.5	*	24	12	0.45 (1)	42	24	0.45 (1)	215	133	1.81 (4)
	2.3 19.2	0.0048 2.0	*	26	13	0.45 (1)	42	25	0.45 (1)	242	157	3.18 (7)

CS = 10 second gel strength kg./9.29 m.² (lb./100 ft.²)

++ = good compatibility (no insolubles)

* = layer observed upon surface of brine solution

(2)

TABLE V - (cont'd)

COPOLYMER	BRINE DENSITY	TREATMENT LEVEL	COMPATI- BILITY	RHEOLOGY IN DEGREES BAROID							
				82°C (180°F)		115°F		Room Temp.			
				600	300	600	300	600	300	600	300
B	kg./l. pp9	kg./l. ppb		CS		CS		CS			
	2.3 19.2	0.0012 0.5	*	23	12	53	27	71	36	0.45 (1)	
	2.3 19.2	0.0024 1.0	*	41	21	69	35	98	51	0.45 (1)	
	2.3 19.2	0.0036 1.5	*	73	38	103	51	168	98	0.91 (2)	
C	2.3 19.2	0.0048 2.0	*	90	49	126	81	182	126	1.81 (4)	
	2.3 19.2	0.0012 0.5	*	30	16	41	22	75	38	0.45 (1)	
	2.3 19.2	0.0024 1.0	++	35	18	80	42	104	53	0.45 (1)	
	2.3 19.2	0.0036 1.5	++	66	37	76	42	143	79	0.91 (2)	
	2.3 19.2	0.0048 2.0	++	69	37	81	46	180	98	1.36 (3)	

GS = 10 second gel strength kg./9.29 m.² (lb./100 ft.²)
 ++ = good compatibility (no insolubles)
 * = layer observed upon surface of brine solution

BRINE
DENSITY
kg./l.
(ppg)

TREATMENT LEVEL OF
80:20 ACM:DMAPMA
kg./l.
(ppb)

TABLE VI
Rheology in Degrees Baroid

		@ 82°C (180°F)		@ 42°C (115°F)		@ Room Temp.	
		600	300	600	300	600	300
		CS		CS		CS	
1.4 (11.6)	Blank 0.0071 (3.0)	9	5	14	7	22	11
		16	9	24	13	34	18
		0.45 (1) (0)		0.45 (1) (0)		0.45 (1) (0)	
1.7 (14.4)	Blank 0.0071 (3.0)	18	9	38	19	66	34
		35	19	60	30	93	44
		0.45 (1) (1)		0.45 (0)		0.45 (1) 0.45 (1)	
1.9 (16.0)	Blank 0.0071 (3.0)	17	8	27	14	41	20
		27	15	42	21	61	30
		0.45 (1) (0)		0.45 (1) (0)		0.45 (1) <0.45 (<1)	
2.3 (19.2)	Blank 0.0024 (1.0)	16	8	31	16	53	27
		25	13	45	24	72	37
		0 (0) (0)		0 (0) (0)		0 (0) 0.45 (1)	
	0.0071 (3.0) (3.0)	32	17	60	31	102	52
		0 (0) (0)		0 (0) (0)		0.45 (1)	

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EXAMPLE 5

This example illustrates the improved solubility of the copolymers described herein in comparison to other polymers which are commonly used as brine thickeners.

A 1.7 kg./l. (14.4 ppg) dense brine solution was treated with 5 various polymers at the 0.0024 kg./l. (1.0 ppb) addition level. Samples were aged at 82°C (180°F) for 16 hours and evaluated as described in Example 1. A duplicate series of samples was aged at room temperature and evaluated for comparison. As can be seen by the data in Table VII, the viscosity, measured at room temperature, of the sample containing 10 Copolymer G (described in Example 2) after 82°C aging was very similar to the viscosity of the room temperature aged sample. This indicates the copolymer was fully dissolved in the brine at room temperature. The viscosities of the heat-aged brines treated with the hydroxyethyl cellulose and xanthan gum, however, were almost doubled that of the 15 room temperature-aged samples. The latent viscosities of these samples indicate that the polysaccharide gums did not completely dissolve in the brines at room temperature. Such viscosity fluctuations caused by exposure to heat are undesirable in well servicing operations.

TABLE VII

Polymer	Treatment Level kg./l. ppb	RHEOLOGY IN DEGREES BAROID AT ROOM TEMP.			
		After Aging 16 Hours @ 82°C (180°F)		After Aging 16 Hours @ Room Temp.	
		600	300	600	300
Blank	-	60	29	67	32
HEC	0.0024 1.0	149	81	67	30
Xanthan gum	0.0024 1.0	112	57	63	29
Copolymer G	0.0024 1.0	128	67	125	64

EXAMPLE 6

This examples illustrates the ability of the copolymers described herein to effectively thicken brine solutions after exposure to high temperatures.

Four dense brine solutions were treated at a 0.0024 kg./l. (1.0 5 ppb) addition level with a 90:10 molar ratio copolymer of ACM:DMDAAC or an 80:20 molar ratio copolymer of ACM:MAPTAC (copolymers C and H respectfully) and aged at 149°C (300°F) for 16 hours. The solution rheologies were evaluated at room temperature. The results may be found in Table VIII.

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TABLE VIII

		Rheology in Degrees Baroid at Room Temp. After Aging 16 Hours @ 149°C (300°F)					
15	Brine Density		Copolymer	600	300	GS	
	kg./l.	ppg					
	1.4	11.6	Blank	22	11	0.45	(1)
			HEC	18	9	0	(0)
			C	20	10	0	(0)
			H	20	10	0	(0)
20	1.7	14.4	Blank	66	34	0.45	(1)
			HEC	75	38	<0.45	(<1)
			C	120	56	0.45	(1)
			H	80	39	0	(0)
25	1.9	16.0	Blank	41	20	0.45	(1)
			HEC	50	25	0	(0)
			C	51	25	0	(0)
			H	60	31	0	(0)
	2.3	19.2	Blank	53	27	0	(0)
			HEC	58	28	0	(0)
25			C	57	28	0	(0)
			H	160	83	0	(0)

The results show that the cationic copolymers described herein thicken as well as and often better than HEC after exposure to high temperatures in various dense brine systems.

Summarizing, the cationic emulsion polymers herein have been found to be useful as thickeners in dense brine solutions. Treated brines useful as drilling and servicing fluids in drilling operations are obtained when the cationic emulsion polymers are employed as brine thickeners.



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CLAIMS

1. A thickened, solids-free non-dilatant aqueous brine having a density of at least 1.7 kg./l. (14.4ppg) comprising an aqueous solution of at least one water-soluble salt of a multivalent metal and a viscosifying amount of a cationic water-in-oil emulsion polymer of acrylamide or methacrylamide and a cationic monomer, which is a dialkylaminoalkyl acrylamide or methacrylamide, a trialkylaminoalkyl acrylamide or methacrylamide, a trialkylaminoalkyl acrylate or methacrylate or dialkyldiallyl ammonium halide, the polymer having an intrinsic viscosity in 1.0 N KCl of 1 to 7.0 dl./g, and the molar ratio of acrylamide or methacrylamide to cationic monomer being from 60:40 to 95:5.

2. The aqueous brine of Claim 1, wherein the cationic monomer is dimethyldiallyl ammonium chloride and the acrylamide or methacrylamide to cationic monomer molar ratio is 80:20 to 91:9.

3. The aqueous brine solution of Claim 1, wherein the cationic monomer is methacrylamidopropyltrimethyl ammonium chloride, the quaternization product of dimethylaminoethyl methacrylate with methyl chloride or dimethyl sulfate, or dimethylaminopropyl methacrylamide.

4. The aqueous brine of Claim 3, wherein the cationic monomer is methacrylamidopropyltrimethyl ammonium chloride and the cationic emulsion polymer has the intrinsic



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viscosity of 3.5 to 6.5.

5. The aqueous brine of Claim 3, wherein the cationic monomer is the quaternization product of dimethylaminoethyl methacrylate with methyl chloride or dimethyl sulfate, the acrylamide or methacrylamide to cationic monomer molar ratio is 70:30 to 80:20, and the cationic emulsion polymer has the intrinsic viscosity of 5.0 to 6.0.

6. The aqueous brine of Claim 1 substantially as described in any one of the embodiments in the foregoing Examples.

7. A process for thickening a heavy solids-free non-dilatant aqueous brine having a density of at least 1.7 kg./l. (14.4ppg) comprising an aqueous solution of at least one water-soluble salt of a multivalent metal, which comprises admixing in the said brine a viscosifying amount of a cationic water-in-oil emulsion polymer as defined in any one of Claims 1 to 6.

8. The process of Claim 7, wherein 0.0006 to 0.0119 kg./l. (0.25 to 5.0 ppb) of the cationic emulsion polymer is admixed in the said brine.

9. The process of Claim 7 or 8, wherein the said water-soluble salt is CaCl_2 , CaBr_2 , ZnCl_2 , ZnBr_2 or a mixture thereof.

10. The process of Claim 7 substantially as hereinbefore described.
