

Viscosity Study of Salt Tolerant Polymers

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ABSTRACT: The rheological characteristics of copolymers of acrylamide (AM) with sodium salt of 2-acrylamido-2-methylpropane sulfonic acid (PAMS), and of hydrolyzed polyacrylamide (HPAM) have been studied in both NaCl solutions and synthetic seawater. PAMS may possible have high salt tolerance and thereby find use in enhanced oil recovery processes for high salinity reservoirs. The viscosity and solubility effect of the PAMS copolymers have been systematically studied with variations in sulfonation degree and molecular weight. Emphasis has been studies as a function of shear rate, polymer concentration, NaCl and divalent ions concentration in aqueous phase. Shear rate dependence of PAMS varies with sulfonation degree, and PAMS with higher sulfona-

tion degree is found to be less shear rate dependent. PAMS with high sulfonation degree are more salt tolerant also compared to HPAM. Also the effect of divalent ions on viscosity of PAMS is lower compared to HPAM. Two parameters will increase the solubility effect of the PAMS copolymers in mix brine, one is sulfonation degree and the other is in the presence of NaCl. Both parameters have a direct effect on the solubility of PAMS copolymer in mixed brine. In all cases the PAMS copolymers are more salt tolerant than HPAM. © 2010 Wiley Periodicals, Inc. *J Appl Polym Sci* 117: 1551–1557, 2010

Key words: sulfonated polyacrylamide polymers; rheology; viscosity; HPAM; divalent ions

INTRODUCTION

Polymers are used for several oilfield applications, e.g., drilling, chemical flooding, and profile modifications. In water flooding processes water is injected into the reservoir to maintain pressure and displace oil. Because oil typically has higher viscosity than water this may however lead to unstable displacement. Increasing the viscosity of injected water by addition of polymer improve the displacement instability during water flooding process. This improvement can be explained by several mechanisms, e.g., mechanism description of mobility ratio, (M), which is defined as a combination of relative permeability and viscosities of oil and water as given below:

$$M = K_w \mu_o / K_o \mu_w \quad (1)$$

Where K_o and K_w are the relative permabilities to oil and water, and μ_w , μ_o are the viscosity of water and oil, respectively.^{1,2}

For a given reservoir situation, the oil recovered before water break through to the producing well decreases as M increases, Based on eq. (1), polymer will by increasing the water viscosity and reducing

the relative permeability to water, improve oil recovery by decreasing the mobility ratio of oil. This also means that in the portion of the reservoir where polymer penetrates flow resistance will build up, and injected water will subsequently divert into unswept or poorly swept areas.^{1,2}

Viscosity, filterability, and chemical stability of several polymers like polyacrylamide (PAM), hydrolyzed polyacrylamide (HPAM), biopolymers, copolymers of acrylamide with different comonomers, different water soluble terpolymers and water soluble hydrophobically associating polymers have been extensively studied.^{3–9} For example, hydrophobically associating polymers which contain a small hydrophobic group can associate to minimize their exposure to the solvent, and it results in an increase in the hydrodynamic size of the polymer which can increase solution viscosity.¹⁰ This phenomenon can help these associative polymers as mobility control agents in reservoir brine of high salinity and high divalent ion concentration.^{11,12}

HPAM as a synthetic polymer is used in enhanced oil recovery processes, e.g., in Daqing and Bohai oil fields with low salinity and divalent ion concentrations.^{13,14} HPAM has shown good results for low salinity reservoir condition but has some limitations at high salinity reservoirs, and are also readily shear degraded. Degree of hydrolysis, polymer concentration, molecular weight, and temperature has been shown to have important effect on the shear thinning behavior of polyacrylamide and HPAM polymers.⁵

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TABLE I
Polymers Characteristics

Polymer ^a	Molecular weight (mDa)	Sulfonation degree (mol %)
AN105	6	5
AN113	8	13
AN125VLM	2	25
AN125	8	25
AN125VHM	12	25
AN132	8	32
HPAM	8	–

^a All studied polymers were supplied by SNF FLOERGER.

Biopolymers (e.g. Xanthan gum) also has been used in classical polymer flooding.³ In contrast to HPAM, xanthan gum is a rigid polysaccharide which is not easily shear degraded, and also is more salt and divalent ions tolerable. However, the main problems of using biopolymers are biodegradation and injectivity problems.¹⁵

A study of a copolymer of acrylamide with sodium salt of 2-acrylamido-2-methylpropane sulfonic acid (PAMS) with a specific sulfonation degree, has showed the decrease in viscosity at high salinity by addition of calcium is less for PAMS copolymers than for HPAM.³ For different associating polymers and also for one specific PAMS it has been reported that they are shear stable at flow rate up to 1000 ft/day in Berea sandstone and do not exhibit any injectivity problems.³ Hydrolytic stability of this specific copolymers of AM and PAMS containing 40 mol % AMPS is better than that of HPAM at the same temperature (93°C) for the same ageing time (100 days).¹⁶

So far, systematic studies of sulfonated copolymers (PAMS) of different sulfonation degree and molecular weight have not been reported. In this work a rheological study of sulfonated polyacrylamide polymers as a function of their sulfonation degree and molecular weight is performed, especially focusing on their salt tolerance. The rheological properties of HPAM are also studied in order to make a comparison with the properties of PAMS under the same conditions.

EXPERIMENTAL

Materials

Polymers

Six different sulfonated polyacrylamide polymers with a range of different sulfonation degree and molecular weight, and HPAM with 25–30 mol % hydrolysis were used in this research. The characteristics of the studied polymers are given in Table I. All the polymers used were supplied by SNF Floerger. The molecular structure of sulfonated polyacrylamide polymers and HPAM are given in Figure 1.

Bulk solutions

The solvents used were NaCl-solutions of different concentrations ranging from 0.1 to 20 wt % in water. To study the effect of divalent ions on the viscosity of polymers, simplified synthetic seawater containing the main cations and of similar salinity as seawater,¹⁷ as given in Table II, has been used. The temperature here is constant at 20°C.

Methods and measurements

Solution preparation

The NaCl solutions or SSW was stirred by propeller stirrer at 720 rpm and dry polymer powder was slowly introduced into the side of the vortex to avoid formation of fisheyes which can be formed if the powder is not wetted evenly. The solution was then stirred slowly for almost 90 min to ensure complete dissolution. A standard polymer solution (5000 ppm) was made. By diluting this standard sample final polymer concentration ranging from 100 to 3500 ppm was obtained.

Viscosity measurement

The viscosity measurement was performed by using a rotary rheometer, Anton Paar Physica MCR 300, with two different constructions; cone and plate measuring system for viscous samples (e.g., viscosity higher than 10 mPa s), and parallel plate system for samples with low viscosity (e.g., viscosity lower than 10 mPa s).

Shear viscosity were measured at 20°C on polymer samples in both directions from shear rate of 10 to

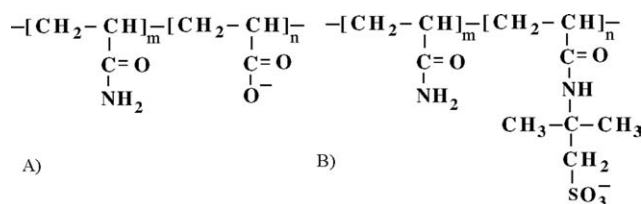


Figure 1 (A) HPAM molecular structure and (B) molecular structure of Sulfonated polyacrylamide polymers.

TABLE II
Simplified Seawater Composition Containing the Main Ions with the Same Salinity of Seawater – Grams of Salt in 1 kg Solvent

Salt	Amount in g/kg solvent
NaCl	25.0
MgCl ₂ ·6H ₂ O	11.1
CaCl ₂ ·2H ₂ O	1.7
KCl	0.7

1000 s⁻¹ and vice versa. For all solutions studied no shear rate hysteresis was observed.

RESULT AND DISCUSSIONS

Shear rate dependence of viscosity

The shear rate dependence of the viscosity for one of the studied sulfonated polyacrylamide polymers, e.g., AN125, at 5 wt % NaCl solvent for different polymer concentrations is shown in Figure 2. Figure 2 shows the shear rate dependence for the polymer with 25 mol % sulfonation degree, at different polymer concentrations in 5 wt % NaCl solvent, and qualitatively this illustrated the results observed for all the studied polymers. Overall the shear rate dependence of the PAMS are found to be in line with those typically observed for polyelectrolyte solutions, e.g., HPAM solutions.⁵ As seen in Figure 2, at low polymer concentrations e.g. less than 1000 ppm, the polymer solutions behave like Newtonian fluids, i.e., the viscosity is shear-independent, within the range of shear rate studied. For higher polymer concentrations, however, the viscosity is found to decrease with shear rate as for pseudo-plastic (shear thinning) fluids. The phenomenon of shear thinning behavior is related to the orientation of macromolecules along the stream line of the flow.^{18–21}

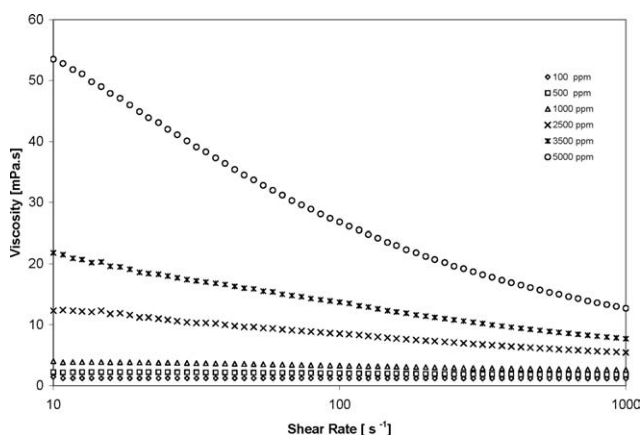


Figure 2 The viscosity of sulfonated polyacrylamide polymers as a function of shear rate for AN125 in 5 wt % NaCl at different polymer concentrations, at 20°C.

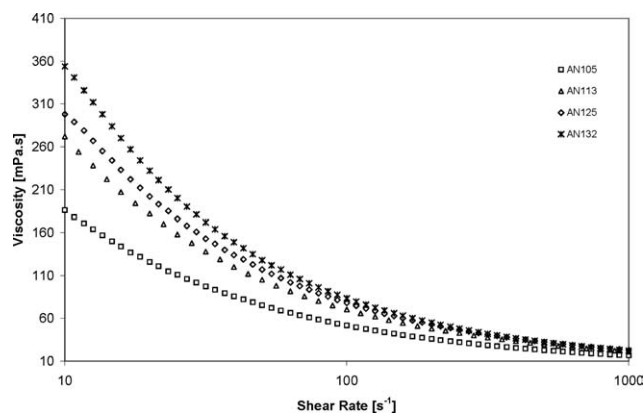


Figure 3 The effect of sulfonation degree on the viscosity changes of sulfonated polyacrylamide polymers as a function of shear rate in 0.1 wt % NaCl and 5000 ppm polymer concentration, 20°C.

As seen in Figure 2, at higher polymer concentration the viscosity is higher and more shear-rate dependent because entanglements of macromolecules chains increase and then extend shear thinning region.¹⁹

The effect of sulfonation degree on the shear rate dependence, expressed as the difference between the viscosity at low shear rate, e.g., 10 s⁻¹ and high shear rate e.g., 1000 s⁻¹, is shown in Figure 3. By increasing the sulfonation degree the shear rate dependence decreases. The reason for this is that the introduction of a sulfonic acid unit in the molecular chain probably increases the rigidity of the chain and then induced better resistance to shear.²¹

With regard to effect of salinity on the shear rate dependence, a result for one of the sulfonated polymers is shown in Figure 4. As seen, if salinity increases the solutions behave more like Newtonian fluids. This is inline with the rheological properties

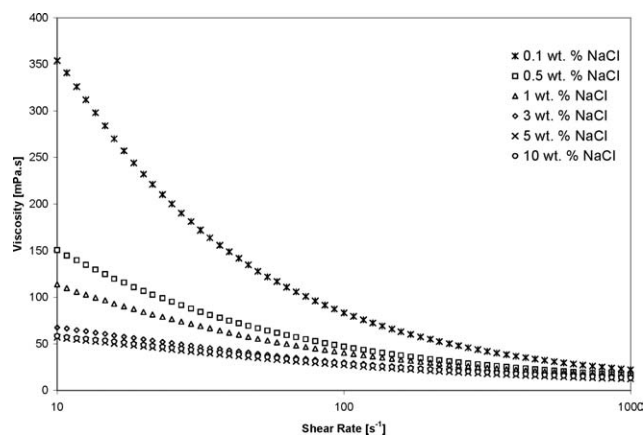


Figure 4 The effect of salinity on the viscosity of the sulfonated polyacrylamide polymers as a function of shear rate for the polymer with 32 mol % sulfonation degree, 5000 ppm polymer concentration, 20°C.

of PAM and HPAM studies other authors.⁵ The results are likely due to the charges on the polymer chain are screened and the entanglement decreases at high salt concentrations.

Polymer concentration dependence of viscosity

The viscosity as a function of polymer concentration for the different sulfonated polymers and HPAM in 0.1 wt % NaCl at a given shear rate of 100 s⁻¹ is shown in Figure 5.

The critical overlap concentration, (C^*),²² which is defined as the concentration at which individual polymer molecules begin to interact can be calculated from the intrinsic viscosity $[\eta]$ by the equation:²³

$$C^* = \frac{1}{[\eta]} \quad (2)$$

$$[\eta] = \lim_{c \rightarrow 0} \frac{\eta - \eta_s}{\eta_s \times C} \quad (3)$$

where η is the viscosity of the polymer solution (mPa s), η_s is viscosity of pure solvent (mPa s), and C is the polymer concentration (ppm). Increasing the intrinsic viscosity will lower the critical overlap concentration.

The critical overlap concentration, C^* , was calculated from dilute polymer solution in low (0.1 wt %) and high (10 wt %) salinity solutions and the results are presented in Table III.

As seen, at a given NaCl-concentration, the critical overlap concentration, C^* , is found to decrease as the sulfonation degree of the polymers increases. This decrease can be explained by the increase in the charge density of the polymer chain resulting in more extended polymer molecules where fewer polymer molecules (or less concentration) are needed for interaction between the polymer chains.

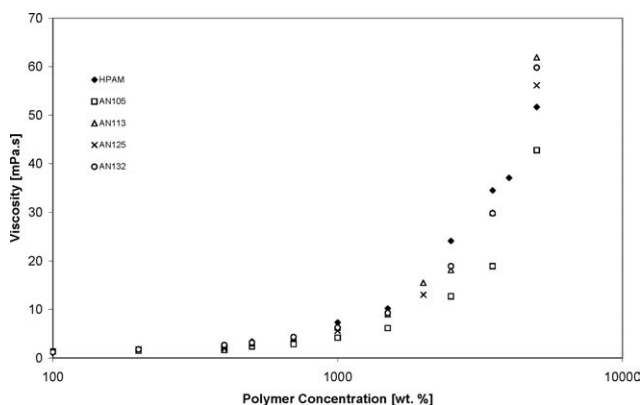


Figure 5 The viscosity of sulfonated polyacrylamide polymers and of HPAM as a function of polymer concentration, in 0.1 wt % NaCl concentration, 100 s⁻¹, 20°C.

TABLE III
Critical Overlap Concentration (ppm) Data as a Function of Salinity for the Studied Polymers at 20°C

Polymers	Solvents	
	0.1 wt % NaCl	10 wt % NaCl
HPAM	167	715
AN105	264	625
AN113	250	556
AN125	244	527
AN132	200	434

As studied by the other authors for HPAM,²⁴ and also observed for these sulfonated polyacrylamide polymers, for each of these polymer an increase in the salinity leads to an increase in the C^* . This is probably due to the shielding of the charges on the polymer chain, which is increasing, and it leads to decrease in the degree of expansion and coiling of the polymers.

NaCl concentration dependence of viscosity

Figures 6 and 7 present the viscosity of the studied polymers as a function of salinity.

In Figure 6 sulfonated polymers of the same molecular weight, but different sulfonation degree are presented. In Figure 7 polymers with the same sulfonation degree, but different molecular weight are given (also included HPAM). In all cases the polymer concentration is 5000 ppm and the shear rate is 100 s⁻¹.

As described earlier, by adding NaCl to the polymer solution the charges on the polymer chain are shielded, and the molecules coil up. Differences between the viscosity at low salinity e.g. 0.1 wt %, and at high salinity e.g. 10 wt % for the polymer with the lowest sulfonation degree compare to the

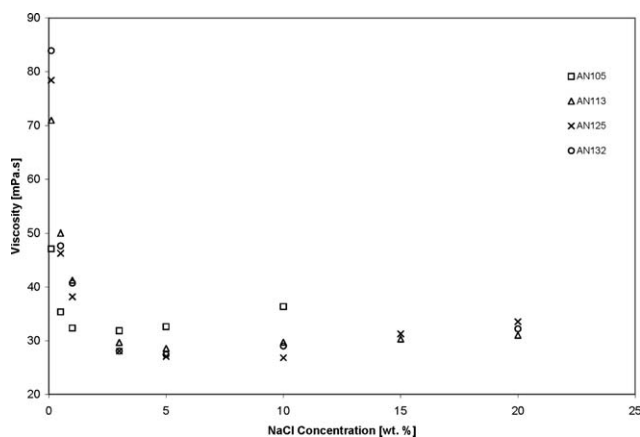


Figure 6 The viscosity of sulfonation polyacrylamide polymers samples with the same molecular weight e.g. 8 MDalton, with different sulfonation degree, as a function of NaCl concentration, 5000 ppm polymer concentration, 100 s⁻¹, 20°C.

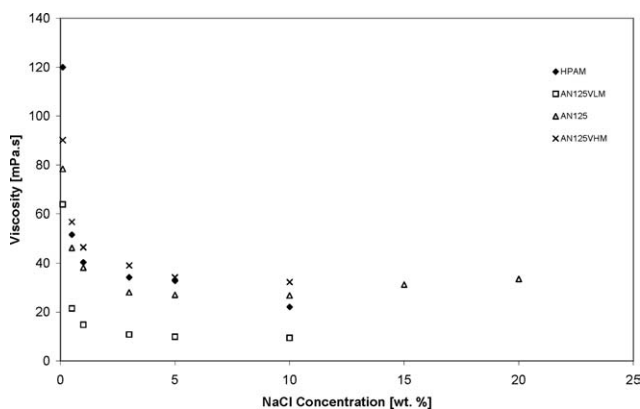


Figure 7 The viscosity of sulfonation polyacrylamide polymers samples with the Sulfonation degree e.g. 25 mol %, with different molecular weight, and HPAM as a function of NaCl concentration, 5000 ppm polymer concentration, 100 s^{-1} , and 20°C .

others is lower. This is due to the charge density on the polymer chain which is lower for this polymer then shielding of charges on the chain is less and NaCl effect on decreasing the viscosity will be less.^{19,20}

As shown in Figure 7, for all sulfonated polyacrylamide polymers, except the sample with the lowest molecular weight, the viscosity at 10 wt % NaCl concentration is higher than HPAM. This may confirm that both molecular weight and sulfonation degree are important.

It should be mentioned that after certain salinity the viscosity decreasing rate levels off, because all the charges on polymer chain has been screened by the NaCl ions (Figs. 6 and 7). As studied for some of these polymers any additional NaCl, even up to 20 wt % NaCl, will only slightly affect the viscosity due to the increase viscosity of the solvent, i.e. they are almost the same for all samples with a very small difference.

HPAM at low salinity (less than 3 wt % NaCl) has the highest viscosity while the sulfonated polymers have higher viscosities at higher salinities. This shows that the sulfonated group in PAMS polymers instead of carboxylate group in HPAM, stabilizes the polymer at high NaCl concentrations, and makes it more interesting for high salinity applications.

Further as shown in Figure 6, at low NaCl concentration e.g. less than 1 wt %, the polymer with the highest sulfonation degree has highest viscosity. For

NaCl concentrations above 3 wt %, the polymer with the lowest sulfonation degree gives the highest viscosity.

As described above, at low salinity the polymer with the lowest sulfonation degree and thereby the lowest charge density is less extended than the ones with higher sulfonation degree (Fig. 6). However, at higher salinity as presented in Figure 6, the viscosity increases with the decreasing of sulfonation degree. This can be explained by the decreasing charge density on the polymer chains which lead to less shielding of ionic groups.^{18,19} Concentration dependence also differs with sulfonation degree (Fig. 5), the polymer with lowest sulfonation degree e.g. 5 mol % has a higher critical concentration. It might be considered that the polymer with lower sulfonation degree compare to the others is more hydrophobic (Fig. 1), and possibly a part of these behaviors is due to more hydrophobicity of this polymer.^{11,12}

As shown in Figure 7 the viscosity increases if molecular weight increases as normally observed for HPAM and PAM polymers.⁵

Influence of divalent ions concentrations on viscosity and redissolution of precipitated polymer

In order to look into the influence of divalent ions on the viscosity of the polymers, viscosity measurements were also performed in SSW. The ionic strength of SSW is equal to 5 wt % NaCl-solution and a comparison of the viscosity of the polymers in these two solvents is presented in Table IV.

The presence of divalent ions lowers the viscosity for these polymers. Viscosity for all the sulfonated polyacrylamide polymers decreases to a small extent by changing the solvent from 5 wt % NaCl to SSW. For HPAM however the effect is more pronounced compare to sulfonated polyacrylamide polymers (Table IV). This is due to the introducing of the sulfonated group in a polyacrylamide chain which makes it more insensitive to divalent ions.²⁵

Studies made and also data from the literature show that the viscosity of HPAM, however, is affected substantially by divalent ions and it is generally accepted that strong binding between divalent ions and the carboxylate group of HPAM is the main precipitation mechanism in hard brines.^{3,4,6,9,25}

The effect of divalent ions on the polymer precipitation is important. Literature studies have shown

TABLE IV
Viscosity (mPa s) for 5000 Ppm Sulfonated Polyacrylamide Polymers and HPAM, in Two solutions with the Same Ionic Strength E.G. Synthetic Sea Water and 5 wt % NaCl

Polymers	AN105	AN113	AN125	AN125VHM	AN132	HPAM
5 wt % NaCl	32.6	28.6	27.1	34.2	27.4	33.5
Synthetic seawater	29.7	27.9	27.0	31.1	24.6	24.4

that Mg^{2+} is a poorer precipitant than Ca^{2+} based on the precipitation test results for HPAM.²⁶ This is one reason of using $CaCl_2$ to study the cloud point.

Our results on the precipitation study, detected as cloud point, for two of the sulfonated polyacrylamide polymers with 13 mol % and 32 mol % sulfonation degree and HPAM, at high NaCl concentration, e.g. 15 wt % NaCl and 20 wt % NaCl, is shown in Table V. The results for the PAMS copolymer with sulfonation degree of 13 mol %, showed that at high NaCl concentrations, an increase in Na^+ concentration shift the cloud point to higher $CaCl_2$ concentration. These results are in agreement with the literature results on redissolution of precipitated HPAM by NaCl.^{6,26} Generally by adding NaCl the solubility of the polymer in hard brine ($CaCl_2$) is improved. Higher NaCl concentration e.g. 20 wt % gives higher polymer solubility than at lower NaCl concentration.

The results also showed that cloud point will increase with sulfonation degree, which means that the sulfonated polyacrylamide polymer with the highest sulfonation degree is more soluble in mixed brine than the other sulfonated polyacrylamide polymers. However for all cases the cloud point is found to be higher for sulfonated polyacrylamide polymers than HPAM.

CONCLUSION

In this paper the effect of salinity, polymer concentration and sulfonation degree on the viscosity and solubility effect of the PAMS copolymers were studied, and the conclusions are listed as below:

PAMS copolymers with high sulfonation degree are less shear rate dependent. With regards to the salinity effect on the shear rate dependence, like most polyelectrolyte solution, PAMS copolymers at high NaCl concentration behave like Newtonian fluids.

Further study of PAMS copolymer showed that as sulfonation degree increases then critical overlap concentration decreases. Again like most polyelectrolyte solution, C^* of PAMS copolymers has a direct relation with salinity.

TABLE V
 $CaCl_2$ Concentration at Cloud Point for Sulfonated Polyacrylamide Polymers and HPAM, 5000 ppm Polymer solution, 20°C

Polymer	$CaCl_2$ concentration (ppm) at cloud point	
	15 wt % NaCl	20 wt % NaCl
HPAM	50280	
AN113	63000	98000
AN132	94000	

At low salinity e.g. less than 3 wt % NaCl, the highest sulfonation degree gives highest viscosity, opposite trend was obtained at high salinity.

Generally polymer solution viscosity decreases in the presence of NaCl. This decrease rate after a certain NaCl concentration levels off, a small increase rate due to the increase viscosity of the solvent was seen up to 20 wt % NaCl concentration.

The study of divalent ions effect on the viscosity reduction showed less reduction in the viscosity as a function of divalent ions for PAMS compared to HPAM.

The solubility of the PAMS copolymers like HPAM in the presence of NaCl in hard brine is improved. This improvement is a direct function of NaCl concentration which means high NaCl concentrations give higher solubility of PAMS copolymers in Mixed Na/Ca Brine.

Another important parameter which increases the solubility of the PAMS copolymers is polymer sulfonation degree. As was seen here PAMS with high sulfonation degree was more soluble in mixed brine.

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