Effect of Added Salt on Properties of Aqueous SMP Solution

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SYNOPSIS

Sulfomethylated phenolic resin (SMP) is a drilling mud additive having good fluid loss and dispersion characters and may be resistant to the action of high temperature and high salt frequently encountered in well drilling, especially in deep wells. SMP is one kind of polyelectrolyte. There are dissociable groups ($-CH_2SO_3^-Na^+$) along the chain of SMP. The conformations and properties of SMP in solution are affected greatly due to electrostatic attraction and repulsion. From the experimental results of viscosities and fluorescence spectra of polyelectrolyte SMP in pure water and aqueous solutions containing added salt, the effects of added salt on molecular conformations of SMP in aqueous solution and properties of reducing fluid loss of water base drilling mud are discussed. © 1995 John Wiley & Sons, Inc.

INTRODUCTION

Drilling muds are used in circulating systems with rotary well drilling mechanisms in which they are forced by pumping down the follow drill stem, through the bit lubricated and cooled by the mud, and then back to the surface to a setting pit. Thus, the mud washes out the cuttings that have been made from the hole and the cuttings are carried outside the drill stem to the surface where the coarse particles are removed and the mud used again in a continuous circulating process.

It has been common practice in the oil well drilling industry to employ starches, starch derivatives, and water-soluble gums to reduce the filtration rate of water base muds. Derivatives of cellulose, such as sodium carboxy methylcellulose and hydroxy ethylcellulose, have also been used as organic colloid additives for reduction of fluid loss of drilling materials. Although these materials reduce the fluid loss of drilling muds, they have other undesirable properties. For example, it is well known that some of the additives mentioned above increase the viscosity of drilling muds undesirably. These materials are not thermally stable when the treated muds are subjected to extreme thermal environments. A synthetic organic polymer such as hydrolyzed sodium polyacrylate has been extensively used for fluid loss control in drilling muds. This sodium polyacrylate is quite susceptible to contaminates such as calcium or magnesium ions and becomes ineffective as a fluid loss control agent. This material is also not heat stable and inhibits the hydration of clays.

Sulfomethylated phenolic resin (SMP) is a drilling mud additive having good fluid loss and dispersion characters and may be resistant to the action of high temperature and high salt frequently encountered in well drilling, especially in deep wells. As viscosity and fluid loss control agents in water base muds, it resists flocculation due to contamination and high temperature more effectively than most other agents used for this purpose.[1]

Water-soluble sulfomethylated phenolic condensate is obtained from the reaction of phenol, formaldehyde, and anhydrous sodium sulfite. There are dissociable groups ($-CH_2SO_3^-Na^+$) along the chain of SMP. Therefore, SMP is one kind of polyelectrolyte. Polyelectrolytes combine the properties of both usual neutral polymers and electrolytes. Polyelectrolytes may be dissociated into polyions with a certain charge and counterions with opposite charge in polar solvents. The conformations and properties of the aqueous SMP solution are affected greatly due to electrostatic attraction and repulsion.

From experimental results of viscosities and fluorescence spectra of polyelectrolyte SMP in pure water and the aqueous solution containing added salt, the effects of added salt on molecular conformations of SMP in aqueous solutions and properties of reducing fluid loss of water base drilling mud are discussed.

EXPERIMENTAL

In a three-necked flask equipped with a mechanical stirrer, a thermometer and a reflux condenser were placed in 1.0 mol distilled phenol, 0.25 mol anhydrous sodium bisulfite, 0.25 mol anhydrous sodium sulfite, and 2 mol formaldehyde. The mixture was heated to about 70°C that initiated an exothermic reaction that caused the temperature to reach about 120°C. The mixture was then refluxed until a thick, light brown syrup resulted. The viscosity of 10% aqueous SMP solution was about 120 cp at 25°C. The product was dried and ground.[1,2]

SMP was dissolved in distilled, deionized water. The solution was precipitated by absolute ethanol, then filtered. The sample was dried under vacuum.

Solutions were prepared by weighing SMP into volumetric flasks and diluting with solvents (distilled deionized water or brine). Sufficient time (> 24 h) was allowed for dissolution.

With the method of dilution in constant concentration of added salt, viscosities of SMP in aqueous solution containing added salt were measured at 25 ± 0.1°C in an Ubbelohde Viscometer.

Fluorescence spectra of the aqueous SMP solution were measured by a Hitachi Model M-850 Fluorescence Spectrometer made in Japan.

RESULTS AND DISCUSSION

Viscometric Behavior of Aqueous SMP Solution[3]

Reduced viscosity is a measure of the size or extension in space of polymers at a given concentration. Basically, a solution viscosity measurement may be taken as a direct method to study the molecular conformation of SMP in solution.

Viscosity and Molecular Conformation of Aqueous SMP Solution in Absence of Added Salt

The correlation between reduced viscosity η_{sp}/C and concentration C of aqueous SMP solution was shown as curve a in Figure 1. Obviously it was different from that of a usual neutral polymer. For a neutral
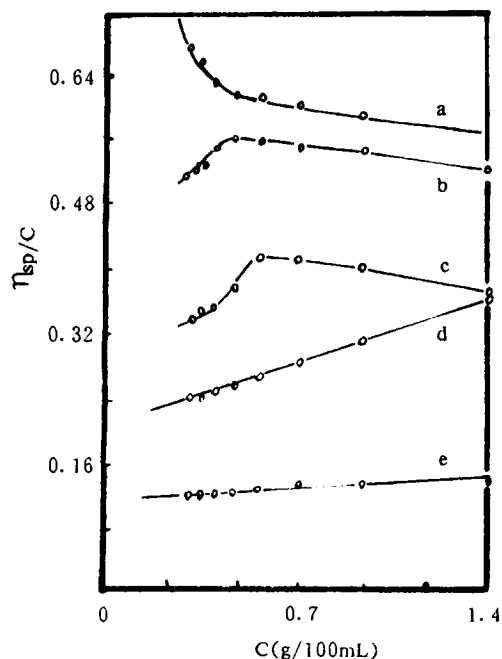

Figure 1 Reduced viscosities of SMP solutions in pure water and aqueous NaCl solutions. (a) H_2O; (b) 0.001N NaCl; (c) 0.01N NaCl; (d) 0.1N NaCl; (e) 1N NaCl.

polymer, $\eta_{sp}/C \sim C$ relationship is in accordance with Huggins equation

$$\eta_{sp}/C = [\eta] + k'[\eta]^2 C.$$

However, for the aqueous SMP solution, η_{sp}/C was not proportional to C. It was impossible to get intrinsic viscosity by virtue of extrapolation to zero concentration with the usual viscosity equation. The dilution of solution curve slope was increased continuously and concave upward. The viscosity of the SMP solution was very sensitive to change in its molecular conformation. When SMP was dissolved in water, it was dissociated to polyions and simple counterions. Meanwhile most equilibrium ions were concentrated around the molecular chain. Due to mutual repulsion between many anions in the polyanion, the conformations of polyanions were more extended than that of neutral polymers. The more dilute the solution, the higher the dissociation degree, the bigger the repulsive force, and the higher the reduced viscosity. With the solution concentration increased, polyanionic chains are close to each other, polyions may be bonded with more counterions, the effective charge density of molecular chains are reduced, and electrostatic repulsion relatively weakened. The size and conformation of a polyelec-

trolyte molecule SMP depend on its net charge along the molecular chain.

Effect of Concentrations of Added Salt

In an aqueous salt-free solution, counterions are all from the dissociation of polyelectrolytes. In the presence of added salt, the viscosity of the polyelectrolyte solution was reduced. As the concentration of added salt increased, the relationship between the reduced viscosity and concentration of polyelectrolyte solution was also changed. For examples aqueous 0.001N NaCl solution was used as a solvent (diluent) in curve b of Figure 1. Because a simple electrolyte (e.g. NaCl) was added to the aqueous SMP solution, the concentration of equilibrium ions in solution increased, and some of them were returned into polyions. Thus, the extention of the molecular chain caused by repulsion between anions decreased, and contraction increased. During the dilution, SMP concentration decreased gradually, while NaCl concentration was kept constant. At high SMP concentration (about 1%), the polyelectrolyte was in excess; reduced viscosity was slightly less than that observed in aqueous salt-free solution. As SMP concentration decreased, it was gradually close to NaCl concentration. When the concentration of cations from SMP was about the same order as the concentration of cations ($[Na^+]$) from the solution, there existed a maximum in the curve of $\eta_{sp}/C \sim C$. When SMP concentration was further reduced, electric charges on the polyions were basically neutralized; repulsion action of static electricity was not evident. At that time, viscometric behavior of the aqueous polyelectrolyte SMP solution was like a neutral polymer; correlation between η_{sp}/C and C was linear. In curve d, aqueous 0.1N NaCl solution was a solvent. During dilution of the SMP solution, the simple electrolyte was always excessive. The curve of $\eta_{sp}/C \sim C$ was a line, similar to a typical neutral polymer. The usual viscosity equation may be applied to calculate $[\eta]$. Comparing curve d with e, as the concentration of added NaCl solution increased, intrinsic viscosity was converged gradually.

Fluorescence Spectra of Aqueous SMP Solution[4]

Fluorescence spectra in the solutions of polymers with chromogenic groups on side chains or main chains always appear as monomer fluorescence spectrum bands and excimer spectrum bands. Fluorescence emission can reflect sensitively the special local conformations of polymers,[5-14] especially vinyl aromatic polymers. Most recent fluorescence re-

search of aqueous polyelectrolyte solutions by use of some chromogenic probes were limited to vinyl polymers. Fluorescence spectra of SMP in pure water and aqueous solutions containing the added salt confirmed the formation of the intermolecular excimer of polyelectrolyte SMP, in which the chromogenic groups were on the main chains. It was possible to use the intermolecular excimer of SMP as a probe to study the molecular morphological changes of SMP.

Formation of SMP Intermolecular Excimer

The fluorescence of the aqueous SMP solution with different concentrations are shown in Figure 2. The excitation wave length was 282 nm. The emission spectra consisted of monomer spectrum bands (λ_{max} = 315 nm) and excimer spectrum bands (λ_{max} = 425 nm). These spectra were all normalized at λ_{315nm}, the peaks of monomers, to the same height (Fig. 3). The fluorescence spectra of all these concentrations was not coincident, and their fluorescence intensities along long wavelengths increased with the concentrations. Therefore, it could be confirmed that intermolecular excimers in aqueous SMP solution were formed.[12]

Concentration Dependence of SMP Fluorescence

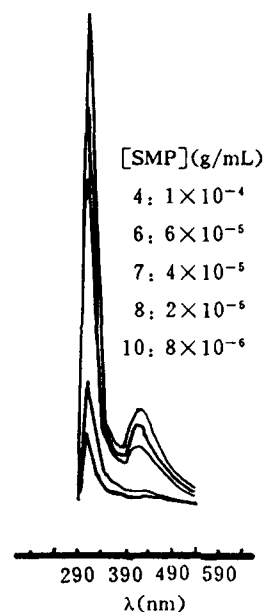When the emission wavelength was 282 nm, a suitable concentration range to measure fluorescence

[SMP](g/mL)

4: 1×10^{-4}

6: 6×10^{-5}

7: 4×10^{-5}

8: 2×10^{-5}

10: 8×10^{-6}

290 390 490 590

λ(nm)

Figure 2 Fluorescence spectra of aqueous SMP solutions.

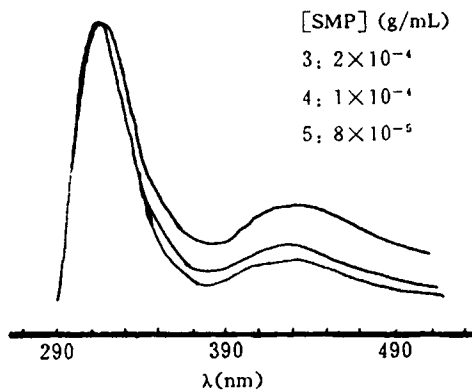**Figure 3** Examples of fluorescence emission spectra of aqueous SMP solutions (normalized at 315 nm).

Figure 5 Examples of fluorescence emission spectra in aqueous solutions of SMP and 0.1N NaCl.

intensities of excimers was $4 \times 10^{-5} \sim 2 \times 10^{-4}$ g/mL. If [SMP] $< 4 \times 10^{-5}$ g/mL, excimer spectrum bands became long tails. When the concentration increased, the fluorescence peaks of excimers were somewhat bathochromatic shifted. However, when [SMP] $> 2 \times 10^{-4}$ g/mL, there were not two peaks between 200 and 500 nm.

Intrinsic emission intensities of monomer and excimer, $I_M/$[SMP] and $I_E/$[SMP], decreased with polymer concentration (Fig. 4). This meant that the emission quantum yield also decreased with the concentration.[13] When SMP concentration was low $(2 \times 10^{-5}$ g/mL $< C < 8 \times 10^{-5}$ g/mL), the ratio of fluorescence intensities of excimer to monomer was not dependent on polymer concentration. When polymer concentration was higher $(C > 8 \times 10^{-5}$ g/
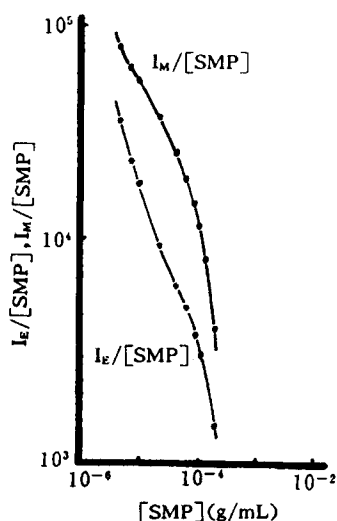
mL), I_E/I_M increased with the concentration. As discussed above, there exists repulsion between anions on polyanion chains of SMP, so that the conformations of polyanions are more extended than that of neutral polymers. This would not be beneficial to near arrangement to form intermolecular excimers. With SMP concentration increased, polyanionic chains were close to each other; the molecule chains were more contracted, which was beneficial to energy migration of intra- and intermolecules; I_E/I_M increased with the concentration.

Fluorescence Quenching of Polyanions in Aqueous Added Salt Solution

The morphological change of SMP was further investigated by adding a simple electrolyte to adjust the solution environment. Under constant concentrations of added salt (1N, 0.1N, 0.01N), the fluorescence spectra of SMP-brine solutions with different SMP concentrations were measured first. Before and after simple salt was added, relations of I_E/I_M, I_E, and I_M of the systems to polymer concentrations had the same trends. After simple salt was added, I_E/I_M of the system increased (Fig. 5). Then, the fluorescence spectra of SMP-brine solutions with different concentrations of added salt were measured under constant concentration of SMP. Experimental results showed that when the concentration of added salt increased, I_E/I_M increased obviously (Fig. 6). As the concentration of equilibrium ions increased, some of them returned into polyions; repulsion between anions was reduced; polyanions also transformed from highly extended to contracted. This state was also beneficial to the formation of intermolecular excimers.
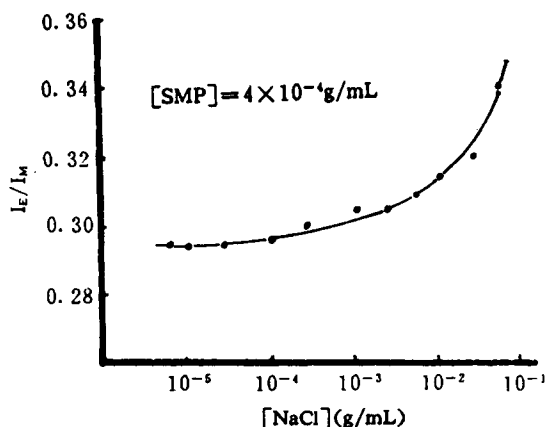

Figure 4 Relationship between $I_E/$[SMP], $I_M/$[SMP], and [SMP].

Figure 6 Fluorescence quenching of polyanions in aqueous solutions of SMP and NaCl.

Reducing Fluid Loss Properties of SMP

Water loss relates to the sealing off of the wall of the drilling hole by building up a filter cake of mud on the wall, thus preventing loss of water from the mud.

In water base drilling mud treated by SMP, there is a large amount of negative charge of $-CH_2SO_3^-$ in the SMP chain. They may be absorbed on the clay surface to raise its ζ potential; increase the thickness of hydration film; protect the colloid thus ensuring or heightening the ratio of colloidal particles in drilling mud; enhancing their ability to plug holes; then improving the quality of filter cake; reducing the coefficient of penetration and filtration; and reducing fluid loss.[15] The situation in which SMP is absorbed on the clay surface is relative to the conformation of SMP in aqueous solution. When the molecular chain of SMP is more extended, more SMP is absorbed on the clay surface and the reduction of fluid loss is better. As discussed above, the conformation of SMP is affected by sim-

ple electrolytes encountered in the drilling well. In brine drilling mud treated by SMP, negative charge density on molecular chain is reduced, the molecular chain contracted, and the ζ potential on the clay surface decreased. Therefore, fluid loss properties of drilling mud dropped under these experimental conditions.

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