

STRUCTURE-PROPERTY RELATIONSHIP OF POLYELECTROLYTES AND ITS APPLICATION IN STABILIZING DRILLING-MUD IN PRESENCE OF SALTS*

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ABSTRACT

A new polyelectrolyte (SPU) has been prepared. It can depress the water-loss of drilling-mud much more effective than the commonly used acrylic polyelectrolytes even in 30% NaCl solution. SPU has phenyl group in the backbone with $-\text{SO}_3^-$ in the side chain while the acrylic polyelectrolytes have $\text{C}-\text{C}$ and $-\text{COO}^-$ respectively. There exists an intrinsic relationship between the structure of polymer and its tolerance to salts. It has been found: 1) The adsorption amount of polymer on clay is related closely to the flexibility of polymer chain. 2) The salt-tolerance of $-\text{SO}_3^-$ is superior to $-\text{COO}^-$. 3) Both SPU-mud and HPAN-mud are plastic fluids. The dependence of yield point on salts relates to the molecular weight of polymer and hydration of ionogenic group, which is quite different for SPU-mud and HPAN-mud. 4) The extent of raising zeta-potential of base-mud by SPU is greater than by HPAN, but the extent of dropping zeta-potential of SPU-mud by NaCl is smaller than HPAN-mud. According to these results we suppose the salt-tolerance of SPU-mud is attributed mainly to hydration of $-\text{SO}_3^-$ and that of HPAN-mud mainly to network structure formed in the drilling-mud.

Many kinds of polyelectrolytes have been used widely as stabilizing agents for petroleum drilling-mud, keeping the mud in stable colloidal state with low water-loss under the complicated conditions of high temperature, high pressure and high salt-content in the drilling process. A lot of researches have been reported of their syntheses and applications, but only a limited number of investigations^[1-3] have been performed to elucidate the structure-property relationship of polyelectrolytes in stabilizing the drilling-mud. In the recent years, we have prepared a new water-soluble polyelectrolyte, urea-modified sulfonated phenol-formaldehyde condensation polymer (SPU), which can reduce the water-loss of drillingmud much more effective than the commonly used acrylic polyelectrolytes in presence of salts as compared in Table 1.

The main difference in structure of SPU and the acrylic polymers lies in: the former has phenyl group in the backbone with $-\text{SO}_3^-$ as the functional group in the side chain while the latter have $\text{C}-\text{C}$ and $-\text{COO}^-$ respectively. It is obvious there exists an intrinsic relationship between the structure of polyelectrolytes and their stabilizing effect for muds. In this paper a brief review of our research in this field will be presented. It is found that the adsorption of polymer on clay, the dehydration of polymers by salts, the rheological behavior of treated-muds and the effect of polyelectrolytes on zeta-potential of clays are quite different in presence of salts for SPU and for the acrylic polyelectrolytes.

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Table 1 Water-loss of muds treated by various polyelectrolytes

Medium	Base-mud		SPU-mud			HPAM-mud			HPAN-mud			HPMMA-mud		
	B ₃₀	B ₇₀	%	B ₃₀	B ₁₈₀	%	B ₃₀	B ₁₈₀	%	B ₃₀	B ₁₅₀	%	B ₃₀	B ₁₈₀
Water	33	44	3.5	4	5.4	0.5	5	16.4	1	4	12	0.5	6	53
NaCl (35%)	113	128	3.5	7	9	0.5	floc.		0.5	23	floc.	1	floc.	

Note: 1) % corresponds to the amount of polyelectrolyte used (g/100 mL).
2) B corresponds to the water-loss (mL/30min) of the mud which have been treated for 12 hr at the temperature indicated by the subscript.
3) HPAM, HPAN and HPMMA refer to the hydrolysate of polyacrylamide (PAM), polyacrylonitrile (PAN) and polymethyl methacrylate (PMMA).
4) Characterization parameters for the polyelectrolytes used in Table 1

	(SPU)	HPAM	MPAN	HPMMA
M. W. $\times 10^{-4}$	2.1	45	47	139
Degree of hydrolysis (%)	—	55.7	55.5	57.7
Content (% mole):				
phenol-unit	77			
urea-unit	23			
-SO ₃ ⁻	69			

1. Effect of salts on the adsorption of SPU and polystyrene sulfonate (PSSNa) on clays

Since the stabilization effect relates directly to adsorption, it is of significance to study the adsorption behavior of polyelectrolyte on clay in aqueous medium. We chose PSSNa to compare with SPU, because they have the same ionic group -SO₃⁻ but different backbone structure, then it is easier to highlight in studying the effect of chain flexibility on adsorption.

The amount of polymers adsorbed on Na-kaolin has been determined in aqueous NaCl solution by the spectrophotometric method^[4-5]. The dependence of relative adsorption amount ($=\Gamma_{NaCl}/\Gamma_0$ where Γ_{NaCl} and Γ_0 are the adsorption amounts in presence and in absence of NaCl respectively) on the concentration of NaCl is shown in Fig. 1 (a) and (b) . It is seen the amounts of SPU and PSSNa adsorbed are enhanced as concentration of NaCl increases, which is in consistency with many other polyelectrolytes^[6-9]. One of the explanations for this

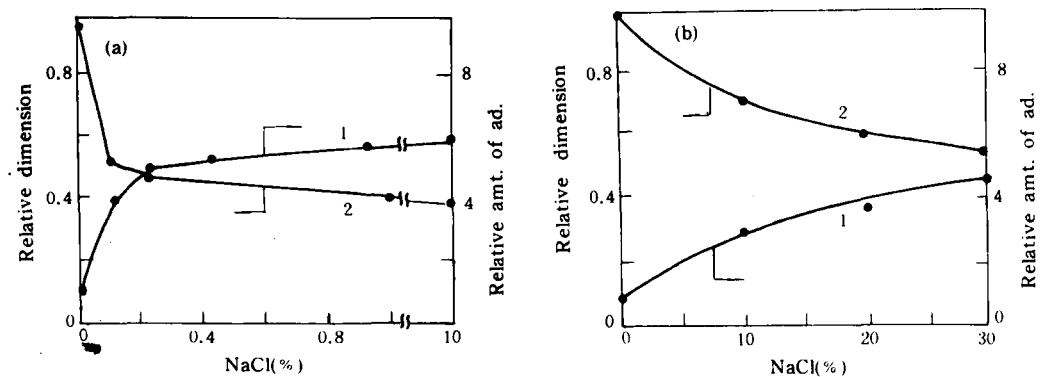


Fig. 1 Dependence of adsorption amounts and macroion dimension on concn. of NaCl. (a) PSSNa , (b) SPU.

phenomenon is that the charges of the polyion and the adsorbent are partly neutralized by the counterions resulting in the reduction of electrostatic repulsion between them. We tried to measure the zeta-potential of the clay in various concentrations of clay and NaCl. the results in Table 2 show clearly that the ξ -decrease ($\Delta\xi$) equals 3.1 for $\text{NaCl}/\text{clay} = 0.66$, and $\Delta\xi$ increases merely to 4 for $\text{NaCl}/\text{clay} = 3$. The effect of NaCl on ξ of clays is not so pronounced as expected. It demonstrates Na^+ can neutralize the negative charge of clay to some extent but far from enough to raise the adsorption amount by 5—6 times as indicated in Fig. 1.

Table 2 Effect of NaCl on zeta-potential of clay

Clay (%)	NaCl (%)	NaCl/clay	ξ (mv)	$\Delta\xi$
1.5	0	0	-23.1	3.1
	1	0.66	-20.0	
	0	0	-27.3	
10	30	3	-23.0	4.0

Is it possible the enhancement of adsorption amount due to the interlayer absorption inside the clay or (and) due to the multilayer adsorption on the surface of the clay? The answer is "No". The X-ray analysis^[4,10] shows $d(001)$, which corresponds to the interlayer distance along the C-axis of clay, does not vary practically before and after adsorption as seen in Table 3, similar to adsorption of sodium polymethacrylate on montmorillonite^[6].

Table 3 $d(001)$ of clay before and after adsorption of polymer

Kaolin		Montmorillonite				
No	+	No	+ SPU	+ SPU	+ SPU	+ SPU
Polymer	PSSNa	polymer	+ NaCl	+ MgCl_2	+ CaCl_2	+ SrCl_2
7.407 Å	7.407 Å	16.3 Å	15.4 Å	16.2 Å	16.2 Å	16.5 Å

Figs.2 and Fig. 3 are adsorption isotherms for SPU-salt-montmorillonite system^[10] and PSSNa-NaCl-kaolin system^[4] respectively, both of which do not show multilayer adsorption. Conversely the curves tend to declining down instead of raising up after a definite concentration of polymer.

On the other hand, the decrease of relative adsorption amount and the increase of relative dimension of the polymer ($= (\eta_{sp}/C)_{\text{NaCl}} / (\eta_{sp}/C)_0$) with the concentration of NaCl corresponds to each other quite well (cf. curve 1 and curve 2 in Fig.1). Similar results have been found for PAANa-NaBr-Pt system^[11]. In the case of SPU, the contraction of coil and the enhancement of adsorption occur by degrees only with the addition of NaCl in consequence of the rigidity of the main chain due to the presence of phenyl group. Whereas, in the case of PSSNa, the changes take place abruptly in presence of even small amount of NaCl due to the flexibility of $-\text{C}-\text{C}-$ chain. This fact reveals that the increase of adsorption amount in presence of added salt relates closely to the flexibility of the polymer chain, and this relationship is brought about by the contraction of coil as a result of the suppression of the polyelectrolyte effect by the salts. The decrease of Γ with

increasing C_f in both Fig. 2 and Fig. 3 also reveals the effect of less coiling of polymer on the adsorption amount since the suppression of polyelectrolyte effect by definite amount of NaCl would decrease as C_f increases.

The adsorption amount of polymer increased by salts is advantageous to stabilization of mud; but, on the other hand, the dehydration of polymer, the disruption of network-structure inside the mud and the depression of zeta-potential of clay by salts are very disadvantageous to stabilization of mud. All these effects will be discussed in the following sections.

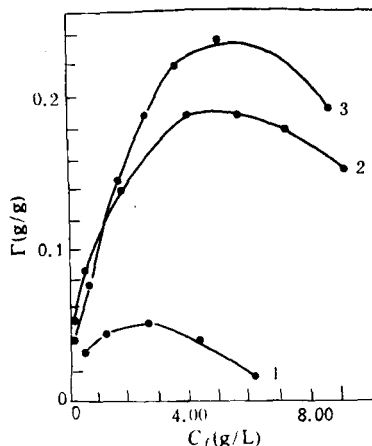


Fig. 2 Adsorption isotherm for SPU-clay-montmorillonite at 30°C, 1) NaCl (0.34N), 2) CaCl₂ (0.1N), 3) SrCl₂ (0.1N), pH 10

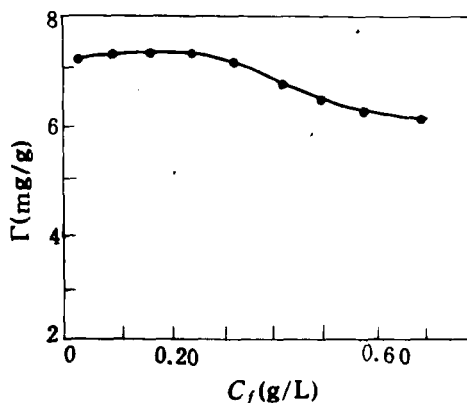


Fig. 3 Adsorption isotherm for PSSNa-NaCl-kaolin at 30°C, NaCl 1%, pH 9

2. Effect of salts on the hydration of $-\text{SO}_3^-$ and $-\text{COO}^-$

If it is common knowledge that the hydration of polyelectrolyte plays an important role in stabilizing mud. But, in presence of salts, dehydration will take place due to the condensation of counterions on the polyion and will lead to the coagulation of mud. Here we chose PSSNBu₄ and PAANBu₄ as model compounds to compare the salt-tolerance of $-\text{SO}_3^-$ and $-\text{COO}^-$ by the differential refractometric method.

The number of water molecules dehydrated by salts per unit volume of solution (S') can be calculated by the following relationship^[12]:

$$S' = - \frac{100}{11} \frac{\rho_0}{M_0} \frac{6n_0 N_A \Delta n}{(n_0^2 + 2)(n_0^2 - 1)}$$

and

$$\Delta n = (n_{s+p} - n_0) - (n_p - n_0) - (n_s - n_0)$$

where n_0 , n_s , n_p and n_{s+p} refer to the refractive index of water, salt solution, polyelectrolyte solution and mixture of salt and polyelectrolyte respectively, ρ_0 and M_0 the density and molecular weight of water, N_A the Avogadro's number. Dependence of S' on the concentration of salts is depicted in Fig. 4(a) and (b). It is seen the number of dehydrated water S' for $-\text{SO}_3^-$ is much smaller than for $-\text{COO}^-$ either by M^+ or M^{2+} .

$-\text{SO}_3^-$ is more salt-tolerant than $-\text{COO}^-$ is presumably related to the

stronger acidity of $-\text{SO}_3\text{H}$. In $-\text{SO}_3\text{H}$ there exists $\text{S} \rightarrow \text{O} \text{ p} - \text{d}\pi$ coordinate bond reinforcing the ability of S to attract electrons from $\text{O}-\text{H}$, resulting in the ease of dissociation of H^+ . Thus the attraction of $-\text{SO}_3^-$ for M^+ or M^{2+} is also weaker as for H^+ . In $-\text{COOH}$, since there is no $\text{C} \rightarrow \text{O} \text{ p} - \text{d}\pi$ coordinate bond, the attraction of $-\text{COO}^-$ for H^+ , as well as for M^+ or M^{2+} , is stronger. Hence M^+ or M^{2+} can penetrate into the $-\text{COO}^-$ hydration layer more easily than into $-\text{SO}_3^-$ hydration layer resulting in the larger S' for $-\text{COO}^-$. Among the divalent cations, Mg^{2+} is the weakest in destroying the hydration layer due to the strong hydration of Mg^{2+} itself. the bulky volume of hydrated Mg^{2+} hinders it from interacting with polyion or the dehydration cannot occur easily even after interaction.

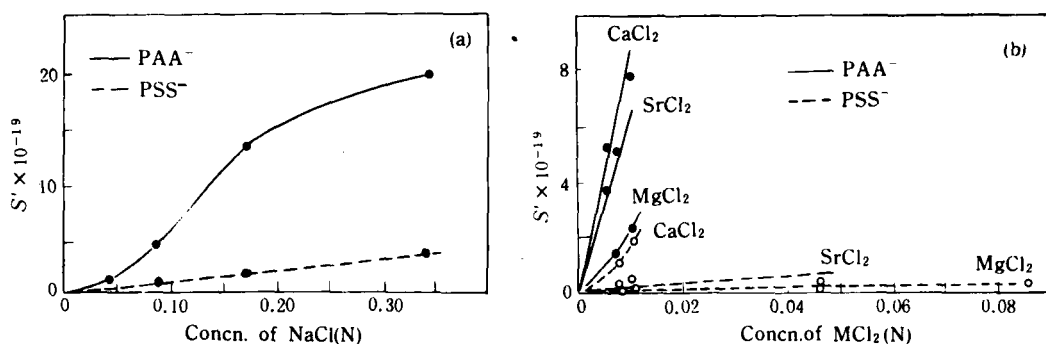


Fig. 4 Dehydration of polyions by salts

3. Effect of salts on the rheological behavior of SPU-mud and HPAN-mud

Fig. 5 depicts the dependence of shear rate upon stress for 5% SPU-mud and 0.5% HPAN-mud. Both are fluids of plastic flow^[5,13] wherein the yield point τ_0 can be found by extrapolation of straight line part of the curve. The value of τ_0 reflects the strength of the network-structure inside the mud.

It is found the rheological behaviors of these two kinds of mud are quite different. First of all, τ_0 of SPU-mud equals 4 even smaller than that of base-mud ($\tau_0 = 10$) while τ_0 of HPAN-mud is 76, indicating that HPAN can reinforce the network-structure but SPU cannot. And secondly, τ_0 of SPU-mud increases with increasing NaCl whereas τ_0 of HPAN-mud decreases. These facts remind us that the mechanisms of salt-resistance of these two kinds of mud may not be the same.

It is evident the high molecular weight of HPAN ($= 40 \times 10^4$) and flexible $-\text{C}-\text{C}-$ main chain render HPAN feasible in forming network-structure with the clay particles^[13]. By adding NaCl the network-structure would be disrupted due to the contraction of the polyions, leading to a marked decrease of τ_0 from 76 to 40. Then it is easy to understand why τ_0 of HPAN-mud decreases with increasing NaCl as shown in Fig. 5(a).

On the contrary, SPU of low molecular weight ($= 2 \times 10^4$) and with phenyl group in the backbone, not only cannot form network structure with the clay particles, but even destroy the networks originally existing in the bulk of base-mud. Therefore the stabilizing effect of SPU may not be resulted from the

network-structure as HPAN, but mainly from the hydration of SPU adsorbed on the surface of clay. in presence of NaCl, on account of the enhancement of adsorption amount and the insensitivity of dehydration of $-\text{SO}_3^-$ to salts, the hydration layer around the clay particles would become thicker leading to increasing τ_0 with the increase of NaCl as shown in Fig. 5(b).

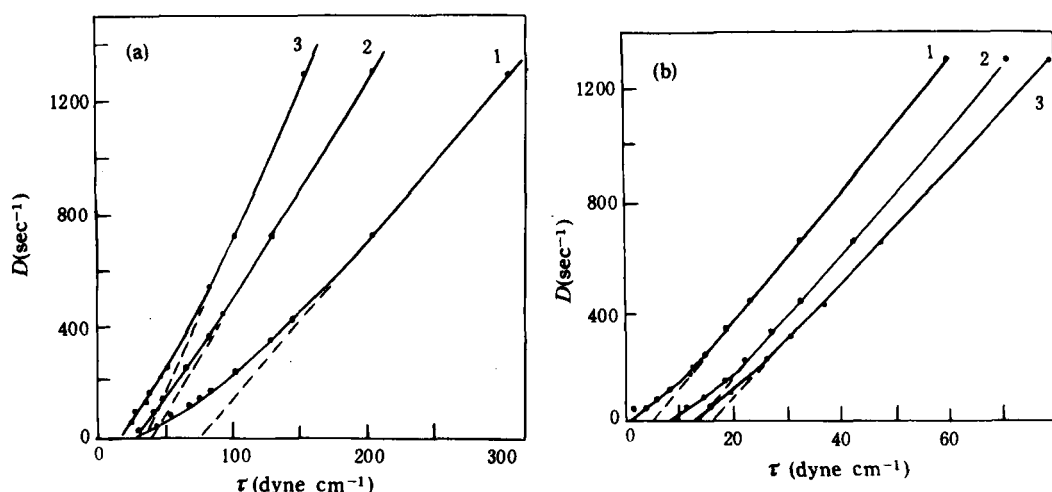


Fig. 5 Plot of strain (D) vs. stress (τ) for muds.

(a) HPAN-mud, NaCl added: 1) 0, 2) 7.5%, 3) 20%;

(b) SPU-mud, NaCl added: 1) 0, 2) 10%, 3) 30%

4. Effect of salts on the zeta-potential of muds

The results are tabulated in Table 4. It is seen the extent of ascent of zeta-potential of base-mud by SPU (-29.0) is greater than by HPAN (-26.3), but the descent of zeta-potential of SPU-mud by NaCl (5.5) is smaller than HPAN (9.2). Obviously this is very favorable for SPU-mud to have a stronger tolerance towards salts.

Table 4 Zeta-potential (ξ) of muds

Clay (%)	pH	NaCl(%)	SPU(%)	HPAN(%)	ξ (mv)	$\Delta\xi$
10	9	0	0	0	-27.3	0
10	9	30	0	0	-23.0	4.0
10	9	0	0	0.5	-53.6	0
10	9	30	0	0.5	-44.4	9.2
10	9	0	3.5	0	-56.3	0
10	9	30	3.5	0	-50.8	5.5

From the above experimental facts and discussions, it is clear that the salt-tolerance of SPU-mud is due to the hydration of $-\text{SO}_3^-$ and the great increase of zeta-potential of clay particles mainly, even in saturated NaCl solution, since SPU is a condensation polymer with rather low molecular weight, it cannot bridge with clay particles forming network-structure as the acrylic polyelectrolyte does. If SPU and acrylic polyelectrolyte are used concurrently, so that the functions

of hydration, zeta-potential and network-structure can be brought into play together, the stabilizing effect should be improved, This is the case as shown in Table 5. It can be expected that a polyelectrolyte with some phenyl groups in the backbone which does not contract too much in presence of salts, with molecular weight high enough to render the chain flexible and with $-SO_3^-$ as the ionogenic group, will be more effective in stabilizing the drilling-mud.

Table 5 Water-loss of muds (mL/30 min) at room temperature

NaCl (%)	Base - mud	+SPU (3.5%)	+HPAN		+SPU(1%)
			(0.5%)	(1%)	+HPAN (0.5%)
0	33	4.0		4.0	4.0
10	86	6.0			4.0
20	68	5.0			4.0
30	113	3.0	23		4.0

Keywords:
Polyelectrolyte; Water-soluble polymer; Drilling-mud

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