Eng. Sci., 2024, **31**, 1262

Engineered Science
DOI: https://dx.doi.org/10.30919/es1262

Rheological Study of Salted Water-Based Drilling Fluid Formulations Developed Using a Novel Amphoteric Terpolymer

Nurbatyr Mukhametgazy,[1, 2,*] Iskander Sh. Gussenov,[1, 2] Kuanysh Togizov,[2] Miras E. Sanatbekov,[2] Raikul Smabaeva,[2] Yernar Kanagat[3] and Sarkyt E. Kudaibergenov[1,*]

Abstract

This research presents a comparative study of the rheological properties of amphoteric terpolymer (ATP-I) and high-viscosity polyanionic cellulose (PAC-HV) as rheology modifiers across various salinity levels. Thermogravimetric analysis shows ATP-I has better high-temperature resistance than PAC-HV. The viscosity of ATP-I doubles from 0.02 to 0.04 Pa·s at 100 s^{-1} as salinity increases from 23.2 to 25%, at concentrations between 0.5 and 2.0 wt.%, ATP-I, and PAC-HV have similar viscosities, both polymers demonstrating high salinity tolerance. Although, in a 35 wt.% NaCl solution, the viscosity of 2.0 wt.% ATP-I is 44% higher than that of 2.0 wt.% PAC-HV. The viscoelastic properties of ATP-I improve with increasing salinity from 1 to 35 wt.% NaCl: shear stress rises from 0.6 to 1.34 Pa and from 38.5 to 90 Pa with increasing shear rates from 1 to 1000 s^{-1}, respectively. PAC-HV shows lower shear stress under similar conditions, indicating lower viscoelasticity. Polymer formulations with bentonite (BT) exhibit decreased viscosity, gel strength, and flow behavior at low salinity. However, when NaCl concentration exceeds 15 wt.%, the ATP-I/BT formulation shows improved properties. These findings highlight the significant differences in the rheological behavior of these polymer formulations for use in drilling fluids across a wide salinity range.

Keywords: Amphoteric terpolymer (ATP); Rheology; High-viscosity polyanionic cellulose (PAC-HV); Salinity tolerance; Drilling fluids.
Received: 01 August 2024; Revised: 29 September 2024; Accepted: 30 September 2024.
Article type: Research article.

1. Introduction

Different types of polymers, both natural (such as xanthan gum, starch, guar gum, cellulose) and synthetic (polyacrylamide, polyethylene glycol, polyacrylates) as well as semi-synthetic polymers (high viscosity polyanionic cellulose (PAC-HV), carboxymethyl cellulose (CMC), nanocellulose, and nanostars) are employed in the formulation of drilling fluid systems.[1-5] Water-based drilling fluids (WBDFs) are more commonly employed than oil-based drilling fluids (OBDFs) because of their lower environmental impact, ease of handling, relatively lower cost, and effectiveness.[6-8] Apparent and plastic viscosities are fundamental rheological characteristics of drilling fluids. Continuous monitoring of these properties during drilling operations is imperative to preempt any potential drilling challenges and achieve successful drilling operations.[9]

Furthermore, temperature and salinity are the primary factors that influence the stability of WBDFs.[10,11] Water-based mud rheology is controlled by adding Na^+-montmorillonite, also known as bentonite, which provides viscosity, gel strength, and fluid-loss controls. The influence of NaCl and KCl at three low concentration levels 3%, 5%, and 7wt.% and their impact on shear stress rate relation under extremely high pressure and high temperature (HPHT) conditions has been studied.[12,13] The Hershel-Bulkely model exhibited the optimal alignment with the experimental data and proved to be the most accurate in forecasting the observed rheological characteristics of drilling fluids.[14]

Although PAC-HV is widely used for its effective rheology-enhancing properties, it faces challenges such as

---

[1] *Institute of Polymer Materials and Technology, Microregion "Atyrau 1", 3/1, Almaty 050019, Kazakhstan.*
[2] *Satbayev University, 22a Satbaev str., Almaty 050013, Kazakhstan.*
[3] *Eurasian National University, 2 Satbayev str., Astana 10000, Kazakhstan.*
**Email:* Nurbatyr.kaz@gmail.com (N. Mukhametgazy); skudai@mail.ru (S. E. Kudaibergenov)

sensitivity to salinity (due to electrolyte effects), temperature, and contaminants. It is also susceptible to biodegradation and raises environmental concerns. These limitations can reduce its effectiveness in specific drilling conditions, such as deep wells and high-temperature operations, where more robust alternatives or additional additives may be required to overcome these disadvantages.[15,16] In this regard, amphoteric polymers are used as a polymeric additive for drilling fluids in increased salinity conditions, around 15 to 20 wt.% NaCl concentration has received relatively little attention except for some research.[17,18]

Amphoteric polymers can enhance the tolerance of WBDFs to high salinity levels, especially under elevated temperatures.[19,20] In this context, polyampholytes are particularly intriguing due to their capacity to elevate viscosity in response to rising salinity levels.[21,22] Furthermore, amphoteric polymers can attract negatively charged bentonite layers through electrostatic interactions, leading to a decrease in fluid loss.[23] Moreover, a solution containing BT/amphoteric polymer exhibits superior shear-thinning and thixotropic properties, along with reduced fluid loss.[24] Lately, temperature-resistant and salt-tolerant polyampholyte gels have been employed as additives to mitigate fluid loss in WBDFs.[25-28]

In this study, a new AAm/AMPS/APTAC ternary polyampholytes were assessed as a potential rheological enhancer for WBDF across a broad salinity range (1-35 wt.% NaCl). The TPA was designed to enhance salt tolerance compared to PAC-HV, aiming to improve the overall performance of the drilling fluids.

2. Experimental

2.1 Materials

2.1.1 Monomers and chemical reagents

Acrylamide (AAm, 97% purity), 2-acrylamido-2-methylpropanesulfonic acid sodium salt (AMPS, 50 wt.%), (3-acrylamidopropyl) trimethylammonium chloride (APTAC, 75 wt.% in water) were purchased from Sigma-Aldrich Chemical Co. (USA) and used without further purification. Ammonium persulfate (APS, 98% purity), N, N, N', N'-tetramethylethylenediamine (TMEDA, purity 95%), caustic soda (NaOH, purity 97%) were purchased from Sigma-Aldrich Chemical Co. (USA) and used without further purification to control the pH levels of the drilling fluid to approximately 9-9.5.

2.1.2 Brines

Sodium chloride - NaCl, calcium chloride - $CaCl_2$, and magnesium chloride - $MgCl_2$ (purity 99%) were purchased from "Titan Biotech LTD" (Rajasthan, India), which were used in the mass concentration range from 1 to 35 wt.%. Compositions of synthetic brines with different salinities are listed in Table 1.

Table 1. Total salinity and chemical composition of synthetic brine and 1-35 wt.% NaCl brines.

Chemical composition of salts, g	Total salinity, wt.%						
	23.2	25	1	7	15	25	35
NaCl	208.8	225	10	70	150	250	350
$CaCl_2$	11.6	12.5	-	-	-	-	-
$MgCl_2$	11.6	12.5	-	-	-	-	-

2.1.3 Bentonite clay

Bentonite clay (*purity 98%)* was supplied from BENTO LUX LLC, Tatarstan, Russia. It is widely used for drilling wells in the oilfields of Kazakhstan. The chemical composition of bentonite clay is listed in Table 2.

2.2 Methods

2.2.1 Differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA)

10 mg of AAm-*co*-AMPS-*co*-APTAC terpolymer and PAC-HV powder was placed in a cuvette for thermogravimetric analyses (TGA) tested using a synchronous thermal analyzer SKZ1060A (China), at a temperature range of 30 to 500 °C and heating rate of 5 °C/min in air.

2.2.2 Viscosity and rheological study

The apparent viscosity (AV), shear stress of 2 wt.% polymer ATP-I/BT and PAC-HV/BT polymer solutions, as well as the viscoelasticity of both polymers with 4 wt.% bentonite dispersions in 1-35 wt.% NaCl brine at 25±1°C was determined using an Anton Paar Rheolab QC rotational rheometer (Austria). The gel strength measurements of ATP- I/BT and PAC-HV/BT fluids were conducted with a cylindrical measuring system (CC39/QC-LTD). Shear stress (τ) and viscosity (η) were determined over a wide range of shear rates (γ= 1-1000 s^{-1}) at 25 °C. The rheological properties of the bentonite and bentonite/polymer formulations were analyzed using the Herschel-Bulkley model.[14,28]

$$\tau = \tau_o + K(\gamma)^n \qquad (1)$$

Table 2. Chemical composition of bentonite clay.

Metal oxides	SiO_2	Fe_2O_3	Al_2O_3	K_2O	CaO	MgO	TiO_2	P_3O_4	FeO	MnO_2
wt. %	25.5	7.92	6.8	3.28	1.57	0.92	0.71	0.46	0.19	0.052
Metal oxides	ZrO_2	SrO	Rb_2O	Cr_2O_3	ZnO	V_2O_5	Ni_2O_3	CuO	Y_2O_3	Ga_2O_3
wt.%	0.032	0.025	0.022	0.016	0.015	0.018	0.007	0.005	0.005	0.004

where K ($Pa\cdot s^n$), n, and τ_o (Pa) are the consistency coefficient, flow behavior index, and yield stress, respectively.[14]

Gel strength (GS) was measured using the API (American Petroleum Institute) standard procedure at a low shear rate of 5.1 s^{-1}. Before measuring the $GS_{10\ s}$, the samples were pre-sheared for 1 min at 510 s^{-1} and left undisturbed for 10 s. Then, the sample was left undisturbed for 10 min before measuring the $GS_{10\ min}$.[28]

2.2.3. Preparation of basic and bentonite/polymer-based drilling fluids

At the initial step, 2 wt.% polymer solutions were meticulously prepared within 1-35 wt.% NaCl brines utilizing a magnetic stirrer. These solutions underwent stirring for 24 hours at 1000 rpm to ensure thorough homogenization. Subsequently, the solutions were subjected to static conditions for an additional 24 hours to facilitate complete polymer hydration. This protocol was implemented to guarantee optimal polymer performance and consistency in subsequent experimental procedures. In the second step, bentonite/polymer dispersions were prepared by gradually introducing 4 wt.% of bentonite powders into the polymer solutions while stirring. Each bentonite/polymer fluid was then transferred to a covered container and left to stand statically for 24 hours, allowing the bentonite clay to swell fully at room temperature.[14,15] As a result, multiple ATP- I/BT and PAC-HV/BT fluids were prepared using brines with various NaCl concentrations. Additionally, bentonite mixtures (without polymer) were prepared in both deionized water (basic fluid) and a 35 wt.% NaCl brine to compare their rheological properties with those of bentonite/polymer-based drilling fluids. To ensure uniform suspension of bentonite particles in the drilling fluid before rheological testing, the samples were agitated for one hour.[27]

The pH of the bentonite/polymer solutions was adjusted with NaOH to 9.5±0.04, which is unfavorable for stabilizing the drilling fluid system. This is attributed to the negative charges of both bentonite particles (-16 mV, as per zeta-potential measurements) and PAC-HV, categorized as an anionic polyelectrolyte. However, in the case of the ATP-I/bentonite formulation, the presence of 10 mol.% of the positively charged monomer APTAC may improve stability due to the anti-polyelectrolyte effect. The positively charged APTAC component can help stabilize the bentonite particles.

2.2.4. Fluid loss tests

Fluid-loss tests were performed according to the laboratory methods for each test that followed the API RP 13I standard (2009).[29] The results were expressed as the mean for each formulation, assessed in triplicate. The standard deviation of the experimental data quantified the reproducibility of the tests, which is the standard procedure for evaluating DFs [30].

3. Results and discussion

The impact of synthetic polyampholyte and semi-synthetic polyanionic cellulose on the gel stability and rheology of polymer/bentonite suspensions in brine through comparative experiments was examined. The linear polymer dispersed in the slurry stabilizes the dispersion of clay particles. The resulting weak gel formed by the polymer and mud in brine enhances the viscosity and stability of the bentonite suspension, preventing the accumulation and settling of bentonite particles.

3.1 Synthesis of AAm/AMPS/APTAC terpolymer

The synthesis and characterization of the AAm/AMPS/APTAC terpolymer, consisting of AAm (80 mol.%), AMPS (10 mol.%), and APTAC (10 mol.%) were comprehensively described previously in Fig. 1[27,28]. This terpolymer was used as a polymeric additive in SWDF.

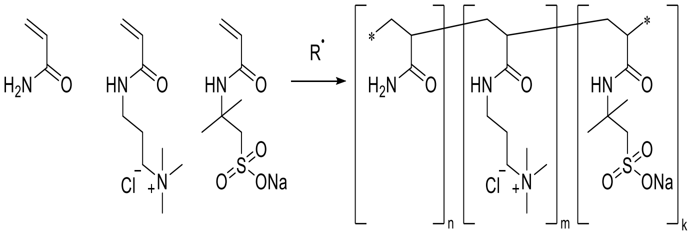

Fig. 1 Synthetic protocol of amphoteric terpolymer (ATP-I=80:10:10 mol.%).

3.2 PAC-HV (Polyanionic cellulose high viscosity)

PAC-HV purchased from Yutian Chemical Co., Ltd, Feicheng as an OBM drilling fluid additive, with a degree of substitution (DS) is 0.85, viscosity is 1600 mPa·s was used without further purification as a polymeric additive to prepare SWDF. The repeating monomeric unit of PAC is shown in Fig. 2.

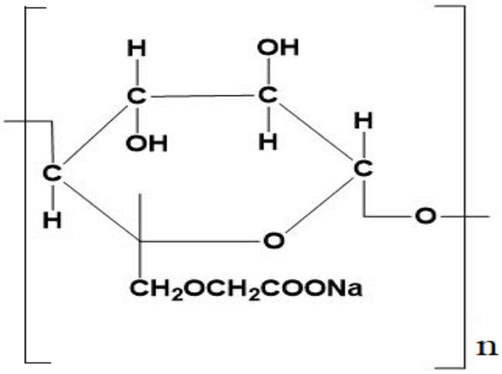

Fig. 2 Repeating monomeric unit of polyanionic cellulose. Reproduced with permission from [31], copyright 2020 Elsevier Ltd.

3.3 Thermogravimetric Analysis (TGA) and Differential Scanning Calorimetry (DSC) of polymers

Figure 3 displays the TGA and DSC curves of the ATP-I (blue line) and PAC-HV (red line) recorded under a nitrogen atmosphere. The mass loss of the polymers is broken down into several stages indicated by downward arrows (Fig. 3 (a)). In the first stage, the PAC-HV sample shows a steady decrease in mass loss, while the ATP-I sample experiences a rapid

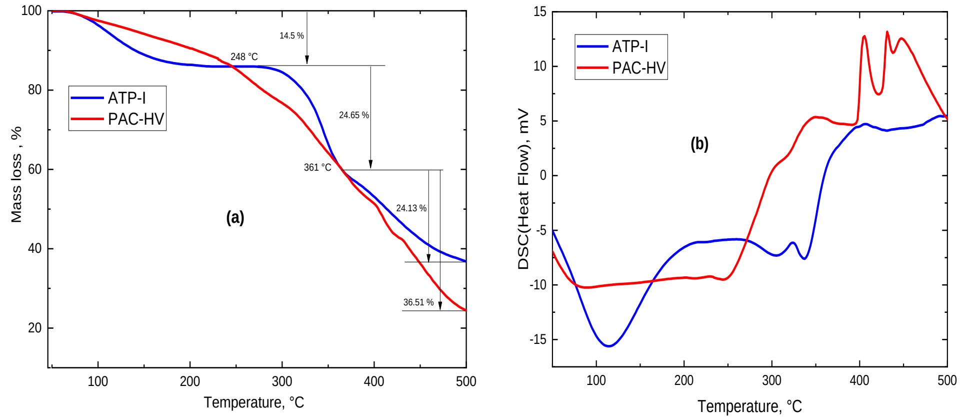

Fig. 3 The TGA (a) and DSC (b) curves versus temperature of the ATP-I (blue line) and PAC-HV (red line).

decrease, with a total mass loss of 14.5% between 29 and 248 °C, attributed to the evaporation of moisture in the samples. In the second stage, between 248 and 361 °C, the polymer flakes exhibit a significant mass loss of about 24.65 %. However, during this stage, the ATP-I sample shows a lower mass loss rate compared to the PAC-HV sample, suggesting greater stability. This may correspond to the cleavage of the amide group in the amphoteric terpolymer. In the third stage, as the temperature increases from 361 to 500 °C, the mass loss for ATP-I and PAC-HV samples decreases by two different values, resulting in a 24.13 % weight loss for ATP-I and 36.51 % for PAC-HV. This may be linked to the decomposition of sulfonic groups and the C-C main links of the polymer chain, leading to complete carbonization. It can be concluded that ATP exhibits significantly higher thermal stability compared to PAC-HV. Therefore, it is likely suitable as a temperature-resistant polymer additive to prepare water-based drilling fluids.

Figure 3 (b) shows the DSC scan (1.62 °C/min) for ATP-I (blue line) and PAC-HV (red line) samples that were melted from the crystal at the normal rate and cooled. The plot ATP-I (blue line) illustrates the exothermic and endothermic thermal events during temperature scans from 29 to 500 °C. The endothermic step change (glass transition) first occurs in the scan at 114, 304, and 337 °C. Due to "cold" the exothermic peak appears from 114 to 304 °C. The endothermic peak due to heating is continuously observed from 337 to 500 °C.

The scan plot for the PAC-HV samples (red line) shows a predominantly endothermic condition during temperature scans from 29 to 500 °C. An endothermic step change (glass transition) first occurs in the scan from 29 to 89 °C, followed by an exothermic peak due to "cold" at 405 and 431 °C, and then another exothermic peak at 421 °C due to a slight cooling. It can be observed that the endothermic property of the PAC-HV sample is higher than that of the ATP-I sample.

3.4 Rheological properties of polymer solutions in synthetic brine

Figure 4 shows the changes in viscosity across a wide range of shear rates for the amphoteric terpolymer ATP-I and PAC-HV samples in two different synthetic brines with concentrations of 23.2 and 25 wt.% at room temperature. As shown in Fig. 4(a), the viscosities of the ATP-I and PAC-HV with a concentration of 0.5 wt.% are generally similar across a wide range of shear rates (1-1000 s^{-1}), with only slightly higher viscosity values ranging from 0.04-0.01 Pa·s, at an all-shear range. However, when the salinity is 25 wt.%, ATP-I aqueous solutions under similar conditions show significantly higher viscosity values, from 0.06-0.02 Pa·s, in the 10-1000 s^{-1} shear rate range. These measurements indicate that the viscosity of the amphoteric terpolymer solution gradually increases as the salt concentration rises from 23.2 to 25 wt.%.

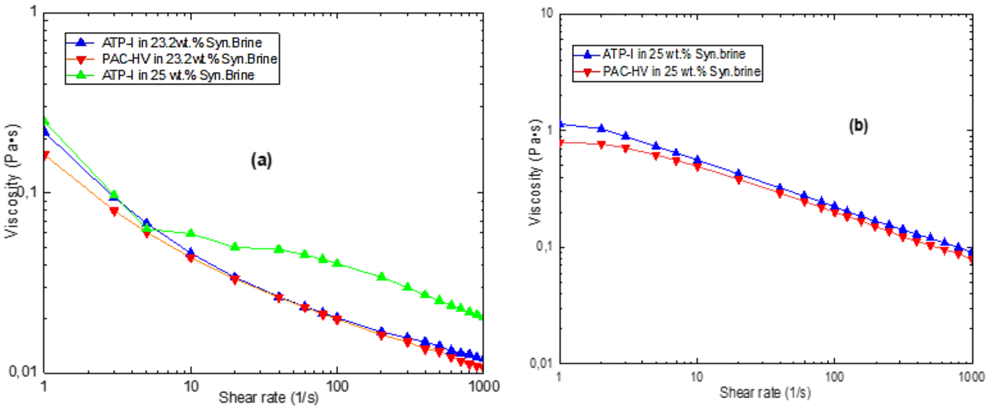

Fig. 4 Viscosity changes of ATP-I and PAC-HV solutions at 0.5 wt.% (a) and 2.0 wt.% (b) versus shear rate in synthetic brines at 25 °C.

To optimize the results, the polymer concentration was increased from 0.5 % to 2 wt.% for both ATP-I and PAC-HV polymers in 25 wt.% synthetic brine, as shown in Fig. 4(b).

This adjustment ensured minimal differences in viscosity changes at concentration 2.0 wt.%, ATP-I ranged from 0.275 to 0.091 Pa·s and PAC-HV from 0.248 to 0.079 Pa·s across a wide shear rate range of 1-1000 s^{-1}, which is approximately 10 times higher than that observed at 0.5 wt.% polymer concentrations. However, a slight increase in viscosity values was observed only for the ATP-I aqueous solution. Based on these results, the viscosity and rheological properties of a homogeneous NaCl solution with a high salinity of up to 35 wt.% were studied internally to evaluate the salt resistance of two different polymers.

3.5 Rheological properties of polymer solutions in NaCl brine

As shown in Fig. 5(a), the viscosity of ATP-I solutions in 1 and 7 wt.% NaCl brines increase from 0.08 to 0.2 Pa·s with the increase of NaCl concentration in the range of 15-35 wt.%. The viscosity of PAC-HV solution is also seen to increase with salinity especially within the low shear rate range (1-10 s^{-1}). For example, the increase of NaCl concentration from 1 to 35 wt.% results in the increase of apparent viscosity of PAC-HV from 0.09 to 0.8 Pa·s (11.25fold increased) at a shear rate of 1 s^{-1}. However, at a high shear rate of 1000 s^{-1}, there is only a 2-fold increase in viscosity (from 0.04 to 0.08 Pa·s) with the increase in salinity. In 35 wt.% NaCl brine at a shear rate of 1 s^{-1}, there is a substantial difference in viscosity values between the polymer solutions, ranging from 1.14 to 0.79 Pa·s for ATP-I and PAC-HV, respectively. These results demonstrate that in high salinity conditions (in 35 wt.% NaCl) the viscosity of ATP-I is notably higher than those of PAC-HV at low and high shear rates.

The flow curves (shear stress versus shear rate) of ATP-I and PAC-HV polymer solutions are depicted in Fig. 6(a) and Fig. 6(b). At a constant shear rate of 5.1 s^{-1} (API standard procedure), the PAC-HV exhibits lower shear stress compared to the ATP-I, the shear stress values of ATP-I and PAC-HV in a 35 wt.% NaCl brine is equal to 3.67 Pa and 3.2 Pa, respectively. Over a wide range of shear rates (1-1000 s^{-1}), the shear stress values observed for ATP-I solutions prepared in 1-35 wt.% NaCl brines show a consistent increase as the salinity of the brine increases (see Fig. 6(a)). Specifically, the shear stress at shear rates of 1 and 1000 s^{-1} were equal to 0.6 and 38.5 Pa, 0.38 and 34.7 Pa for 1 and 7 wt.% NaCl brines, respectively. When the salinity increased up to 35 wt.%, the shear stress of the amphoteric polymer solution at the shear rates of 1 and 1000 s^{-1} reached 1.34 and 90.9 Pa, respectively, showing a substantial increase compared to low salinity (1 and 7 wt.% NaCl). This finding indicates that the viscoelastic properties of amphoteric terpolymers improve with the salinity. The shear stress values observed for PAC-HV polymer solutions prepared in brine, with varying salinity levels and at the same shear rates as ATP-I, show a consistent increase as the salinity increases (see Fig. 6(b)). When the salinity reaches 35 wt.% NaCl, the shear stress of the PAC-HV at shear rates of 1 and 1000 s^{-1} reaches 0.79 and 79 Pa, respectively. The observed shear stress values for these high salinity solutions (35 wt.% NaCl) are significantly lower than those observed for amphoteric terpolymer solutions prepared with similar high salinity. Notably, this indicates that the viscoelastic properties of the PAC-HV are lower compared to the amphoteric terpolymer.

3.6 Rheological properties of Polymer/Bentonite-based drilling fluids

Before describing the rheological behavior of each formulation in detail at a low shear rate, the overall effect of bentonite on the rheology of ATP-I and PAC-HV is demonstrated in Fig. 7. As can be seen, under low salinity conditions, the addition of bentonite increases the viscosity of both polymers: from 200 to 1560 mPa·s for ATP-I and from 160 to 2040 mPa·s for PAC-HV. With the salinity increases, there is a substantial decrease in viscosity for both polymer formulations containing bentonite. However, for the ATP-I/BT formulation, the viscosity decrease is observed only up to 15 wt.% NaCl; beyond this point, further increases in salinity

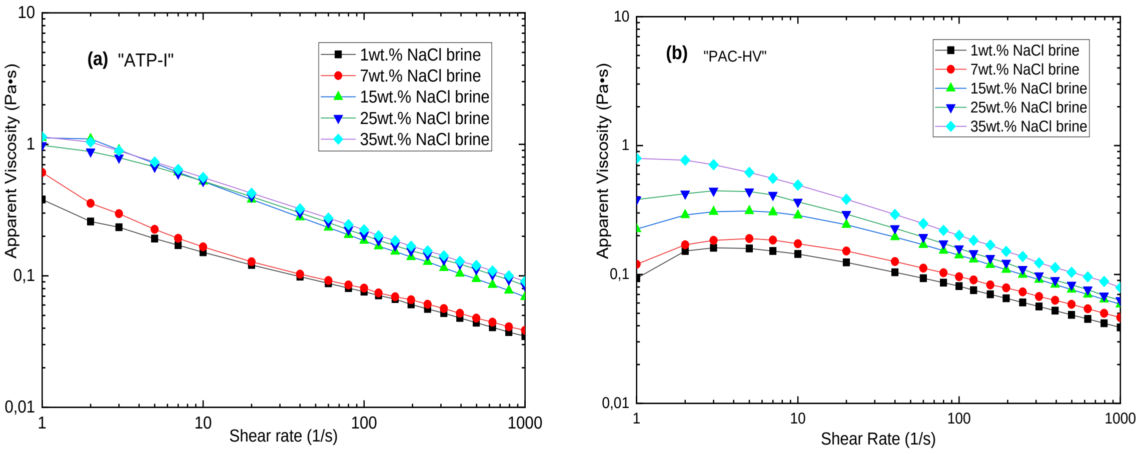

Fig. 5 Apparent viscosity of 2 wt.% ATP-I (a) and PAC-HV (b) solutions versus shear rate in 1-35 wt.% NaCl brine at 25 °C.

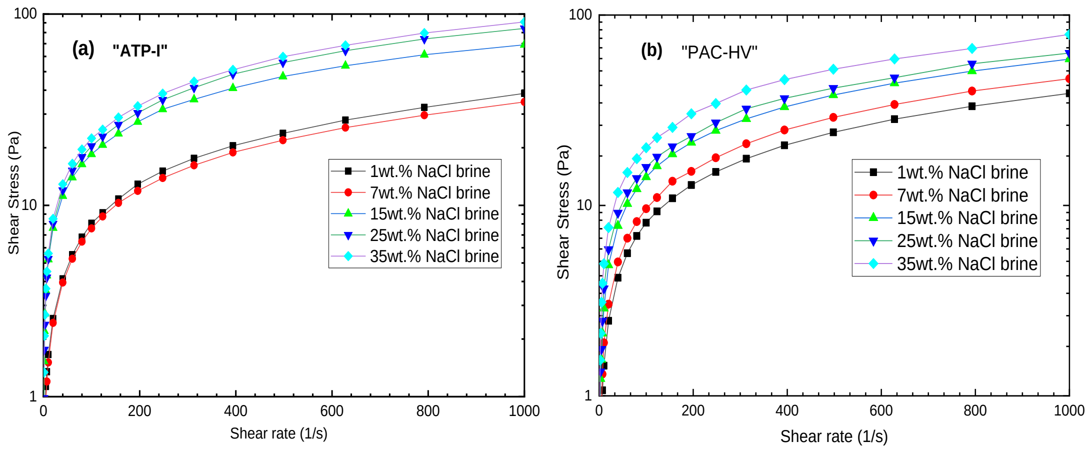

Fig. 6 Flow curves of ATP-I (a) and PAC-HV (b) aqueous polymer solutions (shear stress versus shear rate) in 1-35 wt.% NaCl brine at 25 °C.

result in a reversal of this trend. In contrast, the PAC-HV/BT formulation shows a consistent decrease in viscosity across the same salinity range.

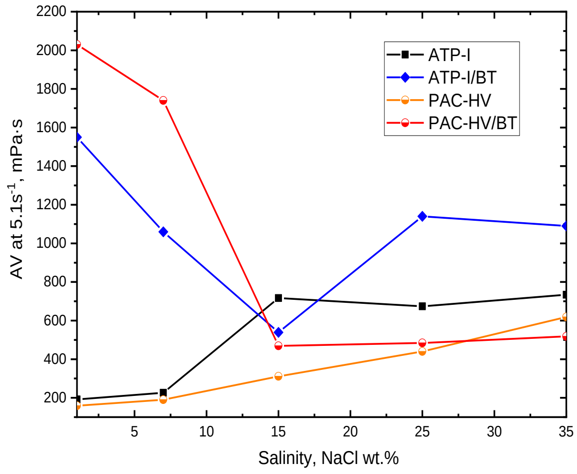

Fig. 7 Apparent viscosity of 2 wt.% ATP-I and PAC-HV depending on NaCl salinity and 4 wt.% bentonite presences at a low shear rate (at 5.1 s^{-1}).

The comparative shear stability of ATP-I and PAC-HV polymer solutions with ATP-I/BT and PAC-HV/BT drilling fluid formulations was examined at 25 °C, over a wide range of salinity at a high shear rate, as shown in Fig. 8. At low salinity from 1 to 15 wt.% and high shear rate, the viscosity of both bentonite-free polymers increases with increasing salinity, from 34.8 to 90 mPa·s for ATP-I and from 38.8 to 79 mPa·s for PAC-HV. As salinity increases, the apparent viscosity of both polymer formulations with bentonite decreases significantly, from 56.3 to 14.7 mPa·s for ATP-I/BT and from 75 to 47 mPa·s for PAC-HV/BT. However, for ATP-I/BT, a decrease in viscosity is observed only up to 15 wt.% NaCl; beyond this point, further increases in salinity reverse this trend, reaching an apparent viscosity value of 86.1 mPa·s at the highest salinity of 35 wt.%. In contrast, PAC-HV/BT does not show a significant increase in viscosity in the range of 15-35 wt.% salinity.

Figure 9(a) illustrates the steady shear viscosity of ATP-I/BT dispersion as a function of shear rate. A detailed comparison between Figs. 5(a) and 9(a) reveal that incorporating of bentonite into the ATP-I solution significantly increases the viscosity of the formulations in a 35 wt.% NaCl brine at a shear rate of 1 s^{-1}, from 1.14 to 3.83 Pa·s. Comparing Figs. 5(b) and 9(b), at a shear rate of 5.1 s^{-1} in a 35 wt.% NaCl solution, the apparent viscosity was equal to 0.62 Pa·s (PAC-HV polymer solution) and 0.4 Pa·s (PAC-HV/BT), indicating that PAC-HV did not significantly affect the viscosity of the bentonite; rather, the viscosity values of the drilling fluid decreased. As shown in Fig. 9(b), the viscosity fluctuated across a wide range of shear rates from 7.19 to 0.75 Pa·s at 1 wt.% salinity and from 6.9 to 0.73 Pa·s at 7 wt.% salinity, with the highest values observed at lower salinity. It is evident that as salinity and shear rate increase, the viscosity rapidly decreases, indicating that, compared to the ATP-I/BT drilling fluid, it is less tolerant to high salinity and shear stress.

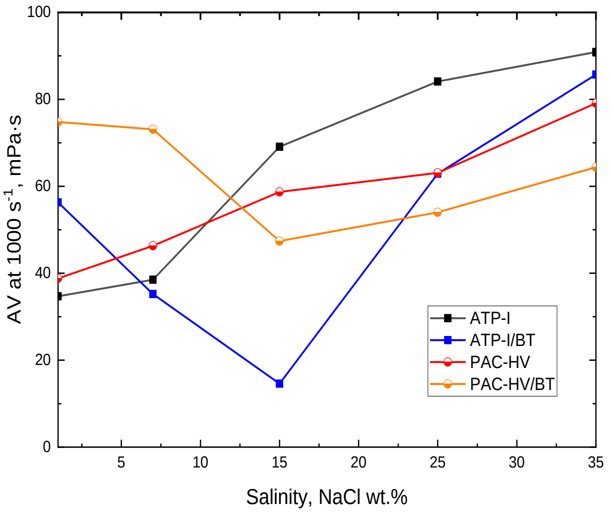

Fig. 8 Apparent viscosity of 2 wt.% ATP-I and PAC-HV depending on NaCl salinity and 4 wt.% bentonite presence at a high shear rate (at 1000 s^{-1}).

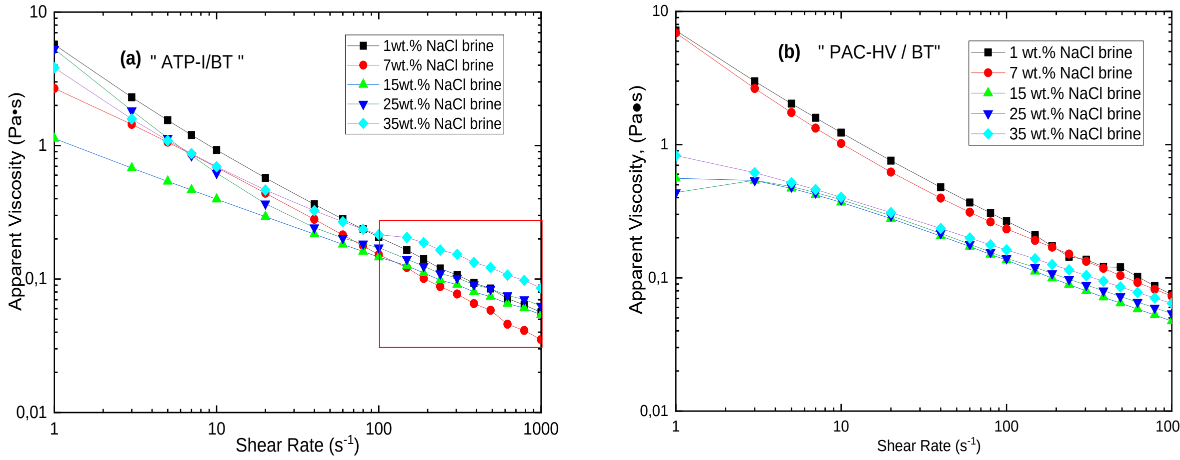

Fig. 9 Apparent viscosity of 2 wt.% ATP-I/BT (a) and PAC-HV/BT (b) dispersions over a wide range of shear rates and NaCl concentrations at 25 °C.

The viscoelastic properties of ATP-I/BT and PAC-HV/BT suspensions at 25 °C are shown in Figs. 10(a) and 10(b), respectively. All graphs display non-Newtonian (pseudoplastic) shear thinning behavior. The shear stress of ATP-I/BT terpolymer dispersions is significantly higher compared to PAC-HV/BT dispersions. Notably, in the ATP-based drilling fluid, the shear stress increases with higher shear rates in 25 and 35 wt.% NaCl brines. Conversely, in the PAC-HV-based drilling fluid, the shear stress is higher at lower salinity levels of 1 and 7 wt.%, whereas its viscoelastic properties decrease significantly at higher salinity levels from 15-35 wt.% NaCl salinity.

The rheological parameters obtained using the Herschel-Bulkley model for bentonite/polymer dispersions are detailed in Table 3. The consistency coefficient K reflects the relationship between shear stress and shear rate, the interactions among the drilling fluid components, and its cleaning efficiency. With regards to the K, in the case of ATP-I/BT, the increase of salinity from 1 to 15 wt.% NaCl resulted in the decrease of K from 1.54 to 0.54 Pa·s^n. However, there was a further increase in salinity of up to 35 wt.% NaCl resulted in the increase of K to the value of 1.1 Pa·s^n. Of note, in the case of PAC-HV/BT, it was observed that the K value varied significantly across different salt concentrations, showing higher values of 2.0 and 1.7 Pa·s over 1 and 7 wt.% salt, respectively. However, as the salinity increased up to 35 wt.%, the "K" value decreased to 0.51 Pa·s. Meanwhile, the

Table 3. Parameters of Herschel-Bulkley model for bentonite/polymer-based drilling fluids prepared in different brines at 25 °C.

Concentration of brine, wt. %		1	7	15	25	35
ATP-I/BT	YS (pa)	4.08	1.68	1.13	5.29	2.99
	K(pa·s^n)	1.54	1.06	0.54	1.14	1.1
	n	0.53	0.75	0.65	0.35	0.50
PAC-HV/BT	YS (pa)	4.41	5.08	-0.89	-1.31	-0.32
	K(pa·s^n)	2.0	1.7	0.46	0.48	0.51
	n	0.65	1.06	1.20	1.26	1.06

*YS - yield stress, K - consistency coefficient, n - flow behavior index, GS - gel strength.

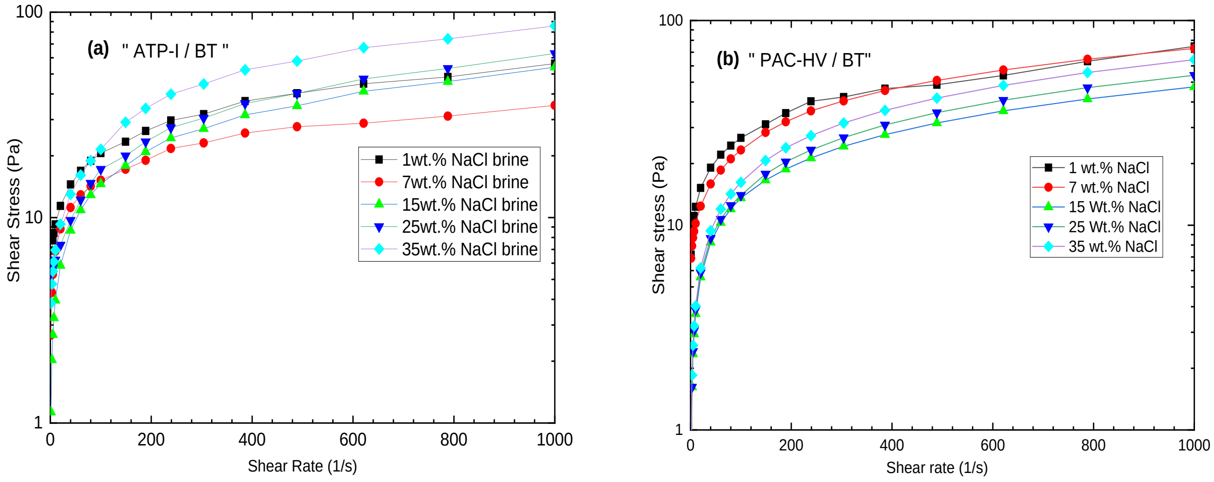

Fig. 10 Viscoelastic (flow) behaviors of the ATP-I/BT (a) and PAC-HV/BT (b) polymer dispersions across a wide range of shear rates and NaCl concentrations at 25 °C.

flow behavior index (n) increased linearly from 1 to 35 wt.% salt, reaching from 0.65 to 1.06. The yield stress (YS) values at zero shear rate for ATP-I/BT suspensions were observed to be highest at 5.29 Pa and 2.99 Pa in 25 and 35 wt.% NaCl solutions, respectively. In contrast, PAC-HV/BT suspensions showed notably low YS values of -1.31 and -0.32 Pa in the same salinity (Table 3).

A high YS value is an important factor for the application of drilling fluid in drilling well operations, as it facilitates the easy transport of shale cuttings to the surface of the hole and improves the efficiency of cleaning the drilling well. A higher consistency coefficient (K) is advantageous for drilling operations because drilling fluids with elevated K values exhibit excellent hole-cleaning efficiency. Additionally, a reduction in the flow behavior index (n) suggests that the developed drilling fluid formulation demonstrates enhanced shear thinning properties at elevated temperatures (Table. 3). This characteristic is confirmed by the viscosity versus shear rate graph for the developed drilling fluid formulations in high salinity brine (see Fig. 9(a)), which shows a reduction in viscosity at higher shear rates. This might be attributed to the flexible segments of the ATP-I with bentonite composite in the drilling fluid formulations, which demonstrate shear-thinning flow behavior. With increasing shear rate, the microstructure aligns completely with the flow direction, which decreases local drag. Conversely, at lower shear rates, polymer entanglement and the formation of aggregates due to hydrogen bonding increase shear viscosity. The shear thinning characteristic is beneficial for drilling fluids exposed to fluctuating shear rates, enabling them to effectively handle diverse tasks across varying shear conditions.[31,32] While being mixed and pumped, drilling fluid ideally exhibits low viscosity; upon return from the borehole to the surface, it should manifest high viscosity under low shear conditions to effectively carry drilled cuttings to the surface. Moreover, a lower flow index (n) signifies a uniform annular velocity profile, which is advantageous for drilling fluids to ensure thorough hole cleaning.

Gel strengths (GS) of ATP-I/BT and PAC-HV/BT formulations prepared in 1, 7, 15, 25, and 35 wt.% brines are shown in Fig. 11. As depicted in Fig. 11(a), both the 10-second and 10-minute gel strength (GS) values decrease as salinity increases from 1 to 15 wt.% NaCl. However, salinity was further increasing to 35 wt.% NaCl causes an increase in GS values. Notably, the ATP-I/BT formulation did not meet the GS requirement specified by the API standard only at 15 wt.% NaCl. In contrast, the GS values were approximately five-fold higher than the standard requirements for the other NaCl concentrations from 1-35 wt.%. Fig.11(b) shows that the GS of PAC-HV/BT measured under similar conditions across a wide range of salinity changes as GS_{10s} 9.99 and 10.3 Pa, and as GS_{10min} 11.51 and 10.3 Pa at initial low salinity of 1 and 7 wt.%, respectively. There was a slight increase in the gel strength index between 2.21-2.48 Pa in the range of 15-35 wt.% salinity, which did not exceed the API standard value. This result confirms that PAC-HV/BT formulations exhibit high gel strength at low salinity, but show decreased performance at higher salinity (in 15-35 wt.% NaCl brine).

Table 4. Effect of the amphoteric terpolymer on the rheological property of a developed base fluid system (2.0 % ATP-I with 4 wt.% bentonite in 1-35 wt.% NaCl brine).

Fluid types	2 % ATP-I solutions					2 % ATP-I/ 4 % BT drilling fluids				
Salinity NaCl, wt.%	1	7	15	25	35	1	7	15	25	35
d, g/cm^3	-	-	-	-	-	1.04	1.05	1.09	1.11	1.13
pH	-	-	-	-	-	9.5	9.5	9.5	9.5	9.5
* AV, mPa·s	192	226	717	674	734	1550	1060	540	1140	1090
SS (τ), Pa	0.9	1.1	3.6	3.4	3.7	7.74	5.29	2.69	5.69	6.1
YS (pa)	0.41	0.12	0.11	-0.7	-0.1	4.08	1.68	1.13	5.29	2.99
GS_{10s}, Pa	-	-	-	-	-	18.8	1.14	3.54	10.7	20.5
GS_{10min}, Pa	-	-	-	-	-	25.8	1.1	3.68	11.1	21.0

Table 5. Effect of the polyanionic cellulose polymer on the rheological property of a developed base fluid system (2.0 % PAC-HV with 4 wt.% bentonite in 1-35 wt.% NaCl brine)

Fluid types	2 % PAC-HV solutions					2 % PAC-HV/4 % BT drilling fluids				
Salinity NaCl, wt.%	1	7	15	25	35	1	7	15	25	35
d, g/cm^3	-	-	-	-	-	1.03	1.05	1.07	1.09	1.11
pH	-	-	-	-	-	9.5	9.5	9.5	9.5	9.5
AV, mPa·s	152	185	304	414	557	2.03	1.74	0.47	0.48	0.52
SS (τ), Pa	0.7	0.95	1.55	1.76	3.1	10.2	8.68	2.35	2.42	2.59
YS (pa)	-0.25	-0.44	-1.13	-1.12	-0.77	4.41	5.08	-0.89	-1.31	-0.32
GS_{10s}, Pa	-	-	-	-	-	9.99	10.3	2.21	2.28	2.42
GS_{10min}, Pa	-	-	-	-	-	11.51	7.92	2.34	2.36	2.48

Note: All the rheological measurements were performed using a 28-35 mm cylinder rotary rheometer (Rheolab QC, Anton Paar) at a constant 5.1 s^{-1} shear rate (using Herschel-Bulkley model) and 25 ± 1 °C temperature.

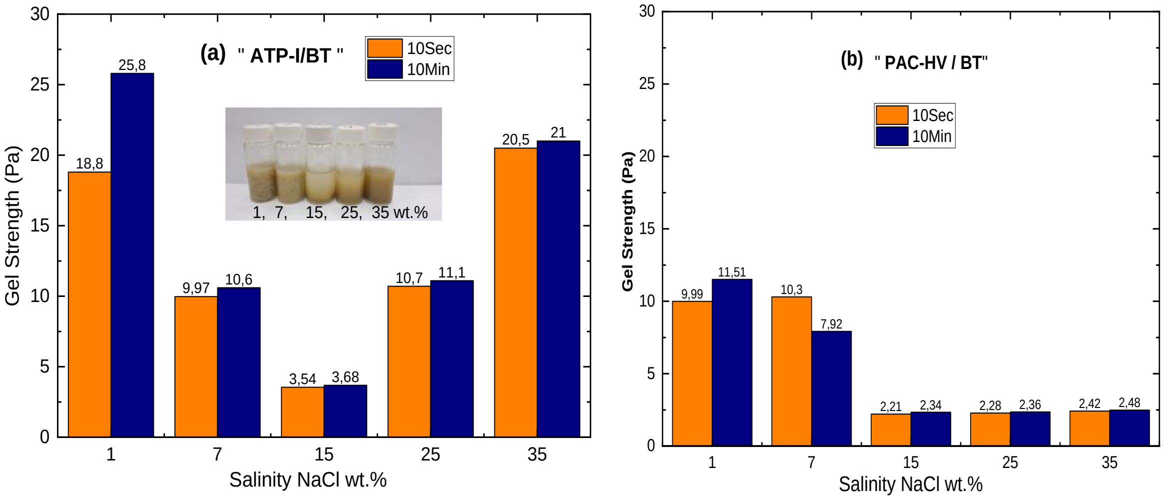

Fig. 11 The gel strength of ATP-I/ BT (a) and PAC-HV/ BT (b) drilling fluid systems under a wide range of NaCl concentration at 25 °C. (*According to the industry standard, the GS should be 2.35 Pa at 10s and 4.7 Pa at 10 min (https://www.drillingmanual.com/gel-strength-drilling-mud/)).

The effect of ATP-I and PAC-HV in salinity and density (D) and the rheological parameters apparent viscosity (AV), Shear stress (SS) yield stress (YS), gel strength (GS) of developed drilling fluid formulations is shown in Tables 4 and 5.

Indeed, the value of the n indicates that all ATP-I/BT formulations exhibit shear-thinning (pseudo-plastic) behavior within the salinity range of 1-35 wt.% NaCl. This confirms that the bentonite/terpolymer composites display shear-thinning behavior at high concentrations of NaCl. These rheological properties make the ATP suitable for use in combination with bentonite as a rheology modifier in brine salt-resistant WBDFs. The ability to control the rheological behavior of drilling fluids is crucial for efficient drilling operations, and the incorporation of ATP can contribute to achieving the desired flow characteristics under high salinity and temperatures.

The amphoteric terpolymer can impart rheological properties to the developed drilling fluid system under high salinity and shear stress conditions. Its performance as a rheology modifier is compared to that of high-viscosity polyanionic cellulose polymer, which is widely used in the oil and gas industry as a drilling fluid additive. Comparative results are presented in Table 4. It is evident from the data that the synthesized amphoteric terpolymer has a greater impact on the rheological parameters of the developed drilling fluid system than PAC-HV polymer. The ATP-I/BT suspension also exhibits superior fluid-loss control properties over PAC-HV polymer. Low fluid loss volume is desirable for drilling fluids when drilling clay-bearing rock formations.

3.7 Fluid loss tests

In all filtration tests, the resulting filtrate was colorless, suggesting it was primarily water. However, the initial fluid-loss filtration test with BT+35 wt.% NaCl brine failed. The filter cake formation was insufficient, causing a complete loss of water from the bentonite/brine dispersion. This failure might be due to the presence of a channel in the center of the filter cake.

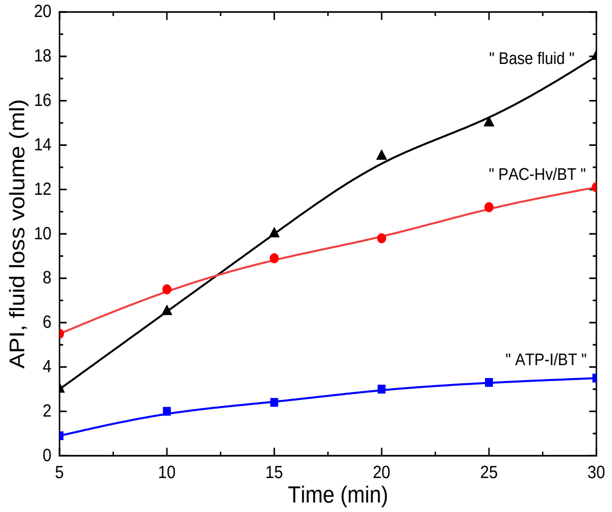

Fig. 12 Fluid loss volume vs time for Base fluid, ATP-I/BT, and PAC-HV/BT drilling fluid systems in 35 wt.% NaCl at 25 °C.

Figure 12 shows the fluid loss over time for different formulations. The results indicate a significantly higher initial filtration rate in the first 5 minutes, due to the lack of a filter cake structure at the start of the filtration process. After this, the filtration rate gradually decreases in 5-minute intervals, suggesting the progressive formation of the filter cake. Among the various formulations, the basic fluid dispersion exhibits the highest fluid loss. This finding implies that adding polymers to the bentonite dispersion improves filtration performance and reduces fluid loss.

In the fluid loss tests with base fluid, the filter cake had small pores and channels, allowing increased water flow and resulting in a high volume of filtrate. However, when polymers were added to the bentonite dispersions, the filtration rate and total fluid loss significantly decreased. This reduction in fluid loss is due to the adsorption of polymer molecules onto the bentonite platelets. The macromolecular chains of the terpolymer prevent water penetration through the filter cake, forming a stable, thin layer that blocks the filter cake pores. This is illustrated in Fig. 12. The filtration performance of the bentonite and bentonite/polymer dispersions showed a distinct trend in fluid-loss values. Specifically, for a filtration duration of 30 minutes, the trend observed was: ATP-I/BT < PAC-HV/BT < Base fluid (4% BT in distilled water).

The ATP-I/BT formulation in a high salinity environment showed a markedly reduced fluid-loss volume of only 3.5 mL, well below the API standard limit. Additionally, the filter cake thickness was 0.09 cm, with a permeability of 1.17 mD. The thin and low-permeability filter cake contributed to the minimal fluid loss. These findings indicate that the novel ATP-I polymer has significant potential for reducing fluid loss in SWBDF under high salinity and shear stress.

4. Conclusions

1. PAC-HV and ATP-I demonstrated high tolerance to high salinity and shear rate. The increase of salinity from 7 to 35 wt.% resulted in the viscosity increase from 190 to 624 mPa·s and from 230 to 735 cp for PAC-HV and ATP-I, respectively, at 5.1 s^{-1}. A similar behavior was observed at 1000 s^{-1}.
2. Adding 4 wt.% bentonite to 2 wt.% polymer solutions in low salinity water increases viscosity from 200 to 1560 cP for ATP-I and from 160 to 2040 cP for PAC-HV at 5.1 s^{-1}. With increasing salinity, both polymer formulations with bentonite show a substantial decrease in viscosity. For the ATP-I/BT formulation, this decrease continues up to 15 wt.% NaCl, after which the trend reverses. Conversely, the PAC-HV/BT formulation exhibits a consistent decrease in viscosity across the same high salinity range.
3. The PAC-HV/BT formulation's 10-second and 10-minute gel strengths slightly exceeded industry standards (GS10sec = 2.35 Pa, GS10min = 4.7 Pa) only at 1 and 7 wt.% NaCl concentrations. Further increases in salinity resulted in an unacceptable decrease in gel strength. In contrast, for all ATP-I/BT formulations, the 10-second gel strength significantly exceeded industry standards across the entire salinity range of 1-35 wt.% NaCl. However, the 10-minute gel strength fell below the industry standard (4.7 Pa), equaling GS10min = 3.68 Pa, only at a 15 wt.% NaCl concentration.
4. In drilling fluid formulation, add 4 wt.% bentonite to 2.0 wt.% ATP-I or PAC-HV solutions resulted in a viscosity decrease of 1.42 and 4 times, respectively, with the salinity change from 1 to 35wt.% NaCl.

In a high salinity condition (35 wt.% NaCl), the ATP-I/BT formulation significantly reduced fluid loss to only 3.5 mL, well below the API standard limit of 12 mL. After 30 minutes of filtration, the fluid loss for the PAC-HV/BT composition increased significantly from 5.43 mL to 12.18 mL. These results indicate that the new ATP-I polymer has significant potential not only as a rheology enhancer for salt water-based drilling fluids under high salinity and shear stress conditions, but also for reducing drilling fluid loss.

Acknowledgments

This research was funded by the Science Committee of the Ministry of Science and Higher Education of the Republic of Kazakhstan under Grant № AP14972771.

Conflict of Interest

There is no conflict of interest.

Supporting Information

Not applicable.

References

[1] Jain, R., Mahto, T. K., & Mahto, V, Rheological investigations of water-based drilling fluid systems developed using synthesized nanocomposite, *Korea-Australia Rheology Journal*, 2016, **28**, 55–65, doi:10.1007/s13367-016-0006-7.

[2] Li, M.-C.; Wu, Q.; Song, K.; Qing, Y.; Wu, Y, Cellulose Nanoparticles as Modifiers for Rheology and Fluid Loss in Bentonite Water-Based Fluids, *ACS Applied Materials and Interfaces,* 2015, **7**, 5006−5016, doi:10.1021/acsami.5b00498.

[3] Dias, F. T. G.; Souza, R. R.; Lucas, E. F, Influence of Modified Starches Composition on Their Performance as Fluid Loss Additives in Invert-Emulsion Drilling Fluids, *Fuel*, 2015, **140**, 711−716, doi: 10.1016/j.fuel.2014.09.074.

[4] Amanullah, M.; Yu, L, Environment-Friendly Fluid Loss Additives to Protect the Marine Environment from the Detrimental Effect of Mud Additives, *Journal of Petroleum Science and Engineering*, 2005, **48**, 199−208, doi: 10.1016/j.petrol.2005.06.013.

[5] A. Ayazbayeva, V. Baddam, A. Shakhvorostov, I. Gussenov, V. Aseyev, M. Yermaganbetov, S. Kudaibergenov, Amphoteric nano-and microgels with acrylamide backbone for potential application in oil recovery. *Polymers for Advanced Technologies*, 2023, **34**, 3826-3837, doi: 10.1002/pat.6182.

[6] A. Aftab, A. R. Ismail, Z. H. Ibupoto, H. Akeiber, M. G. K. Malghani, Nanoparticles based drilling muds a solution to drill elevated temperature wells, *Renewable and Sustainable Energy Reviews,* 2017, **76**, 1301–1313, doi: 10.1016/j.rser.2017.03.050.

[7] G. T. Teixeira, R. F. Lomba, S. A. Fontoura, V. A. Melendez, E. C. Ribeiro, A. D. Francisco, R. S. Nascimento, New material for wellbore strengthening and fluid losses mitigation in deepwater drilling scenario, In SPE Deepwater Drilling and Completions Conference, 2014.

[8] M. C. Li, Q. Wu, K. Song, S. Lee, C. Jin, S. Ren, T. Lei, Soy protein isolate as fluid loss additive in bentonite-water-

based drilling fluids, *ACS Applied Materials and Interfaces*, 2015, **7**, 24799–24809, doi: 10.1021/acsami.5b07883

[9] A. A. Abalymov, B. V. Parakhonskiy, A. G. Skirtach, Colloids-at-surfaces: physicochemical approaches for facilitating cell adhesion on hybrid hydrogels, *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, 2020, **603**, 12585, doi: 10.1016/j.colsurfa.2020.125185.

[10] K. B. Azouz, K. Bekkour, D. Dupuis, Influence of the temperature on the rheological properties of bentonite suspensions in aqueous polymer solutions, *Applied Clay Science*, 2016, **123**, 92–98, doi: 10.1016/j.clay.2016.01.016.

[11] K. Y. Choo, K. Bai, Effects of bentonite concentration and solution pH on the rheological properties and long-term stabilities of bentonite suspensions, *Applied Clay Science*, 2015, **108**, 182–190, doi: 10.1016/j.clay.2015.02.023.

[12] M. Amani, K. J. Hassiba, Salinity effect on the rheological properties of water based mud under high pressures and high temperatures of deep wells, *SPE Kuwait International Petroleum Conference and Exhibition*, 2012, **11**, 163315, doi: 10.2118/163315-ms.

[13] K. Abdiyev, M. Marić, B. Orynbaev, M. Zhursumbaeva, N. Seitkaliyeva, Z. Toktarbay, A novel cationic polymer surfactant for regulation of the rheological and biocidal properties of the water-based drilling muds. *Polymers*, 2023, **15**, 330, doi: 10.3390/polym15020330.

[14] H. M. Ahmad, M. S. Kamal, M. A . Al-Harthi, High molecular weight copolymers as rheology modifier and fluid loss additive for water-based drilling fluids, *Journal of Molecular Liquids*, 2018, **252**, 133-143, doi: 10.1016/j.molliq.2017.12.135.

[15] W. Shan, J. Ma, G. Jiang, J. Sun, Y. An, An inverse emulsion polymer as a highly effective salt- and calcium-resistant fluid loss reducer in water-based drilling fluids, *ACS Omega*, 2022, **7**, 16141-16151, doi: 10.1021/acsomega.2c01476.

[16] M. C. Li, Q. Wu, K. Song, Y. Qing, Y. Wu, Cellulose nanoparticles as modifiers for rheology and fluid loss in bentonite water-based fluids, *ACS Appl. Mater. Interfaces,* 2015, **7**, 5006−5016, doi: 10.1021/acsami.5b00498.

[17] Y. He, G. C. Jiang, W. G. Cui, Salt-responsive AM/AMPS/ATC terpolymers as modifiers for rheology and fluid loss in water-based drilling fluid, *Key Engineering Materials*, 2018, **765**, 106–112, doi: 10.4028/www.scientific.net/KEM.765.106.

[18] L. D. W. Djouonkep, B. Xie, H. Tao, J. Chen, L. Zhuo, N. B. S. Selabi, A. P. Tchameni, L. Zhao, Thermo-thickening/amphoteric polymer nanocomposite incorporating vinyl-functionalized nano-silica as a viscosifier for high-salt and ultra-high temperature water-based drilling fluids, *Journal of Molecular Liquids*, 2024, **404**, 124866, doi: 10.1016/j.molliq.2024.124866.

[19] F. Liu, G. Jiang, S. Peng, Y. He, J.Wang, Amphoteric polymer as an anti-calcium contamination fluid-loss additive in water-based drilling fluids, *Energy Fuels*, 2016, **30**, 7221−7228, doi: 10.1021/acs.energyfuels.6b01567.

[20] G. S. Georgiev, E. B. Kamenska, E. D. Vassileva, I. P. Kamenova, V. T. Georgieva, S. B. Iliev, I, A. Ivanov, Self-assembly, antipolyelectrolyte effect, and nonbiofouling properties of polyzwitterions, *Biomacromolecules,* 2006, **7**, 1329−1334, doi: 10.1021/bm050938q.

[21] O. Toktarbaiuly, A. Kurbanova, G. Imekova, M. Abutalip, Z. Toktarbay, Desert water saving and transportation for enhanced oil recovery: bridging the gap for sustainable oil recovery, *Eurasian Chemico-Technological Journal*, 2023, **25**, 193-200, doi: 10.18321/ectj1522.

[22] B. A. Hamad, M. He, M. Xu, W. Liu, M. Mpelwa, S. Tang, J. Song, A novel amphoteric polymer as a rheology enhancer and fluid-loss control agent for water-based drilling muds at elevated temperatures, *ACS Omega*, 2020, **5**, 8483-8495, doi: 10.1021/acsomega.9b03774.

[23] I. Gussenov, The effect of polymer mixing time on the strength of HPAM-Cr(III) Gels, *Eurasian Chemico-Technological Journal*, 2023, **25**, 157–163, doi: 10.18321/ectj1518.

[24] F. Wang, J. Yang, J. Zhao, Understanding anti-polyelectrolyte behavior of a well-defined polyzwitterion at the single-chain level, *Polymer International*, 2015, **64**, 999−1005, doi: 10.1002/pi.4907.

[25] J. Li, J. Sun, K. Lv, Y. Ji, J. Liu, X. Huang, S. Shi, Temperature-and salt-resistant micro-crosslinked polyampholyte gel as fluid-loss additive for water-based drilling fluids, *Gels*, 2022, **8**, 289, doi: 10.3390/gels8050289.

[26] S. B. Aghdam, A. Moslemizadeh, E. Kowsari, N. Asghari, Synthesis and performance evaluation of a novel polymeric fluid loss controller in water-based drilling fluids: High-temperature and high-salinity conditions, *Journal of Natural Gas Science and Engineering*, 2020, **83**, 103576, doi: 10.1016/j.jngse.2020.103576.

[27] N. Mukhametgazy, I. S. Gussenov, A. V. Shakhvorostov, S. E. Kudaibergenov, Salt tolerant acrylamide based quenched polyampholytes for polymer flooding, *Bulletin of the Karaganda University, CHEMISTRY Series*, 2020, **4**, 119-127, doi: 10.31489/2020Ch4/119-127.

[28] N. Mukhametgazy, A. V. Shakhvorostov, H. Tenhu, M. Abutalip, S. E. Kudaibergenov, Synthesis and characterization of salt tolerant ternary polyampholyte as rheology enhancer and fluid loss additive for water-based drilling fluids, *Engineered Science*, 2023, **26**, 965, doi: 10.30919/es965.

[29] V. C. Kelessidis, R. Maglione, C. Tsamantaki, Y. Aspirtakis, Optimal determination of rheological parameters for Herschel–Bulkley drilling fluids and impact on pressure drop, velocity profiles, and penetration rates during drilling,

Journal of Petroleum Science and Engineering. 2006, **53**, 203–224, doi: 10.1016/j.petrol.2006.06.004.

[30] C. Vipulanandan and A. Mohammed, Effect of drilling mud bentonite contents on the fluid loss and filter cake formation on a field clay soil formation compared to the API fluid loss method and characterized using Vipulanandan models, *Journal of Petroleum Science and Engineering*, 2020, **89**, 107029, doi: 10.1016/j.petrol.2020.107029.

[31] M. Li, S. Gu, J. Jin, Y. Zheng, D. Xie, Research on the influence of polyanionic cellulose on the microstructure and properties of oil well cement, *Construction and Building Materials*, 2020, **259**, 119841, doi: 10.1016/j.conbuildmat.2020.119841.

[32] R. Jain, T. K. Mahto, V. Mahto, Rheological investigations of water-based drilling fluid system developed using synthesized nanocomposite, *Korea-Australia Rheology Journal*, 2016, **28**, 55-65, doi: 10.1007/s13367-016-0.