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# Novel latex particles and aluminum complexes as potential shale stabilizers in water-based drilling fluids



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## ABSTRACT

In this paper, novel latex particles and aluminum complexes as potential shale stabilizers in water-based drilling fluids were successfully synthesized and characterized in detail. The spherical latex particles were prepared by emulsifier-free polymerization of styrene and methyl methacrylate, and it possessed uni-modal distribution from 80 nm to 345 nm with the D90 value of 276 nm. The aluminum complexes were synthesized through the complexation reaction of humic acid with sodium aluminate and it could be completely soluble under alkaline conditions, and aluminum hydroxide and humic acid flocculate would precipitate from the filtrate under neutral or acidic conditions or interacting with magnesium or calcium ion. The synergistic effect on shale stability of latex particles and aluminum complexes was investigated quantitatively through the pressure transmission and membrane efficiency tests. The pore structure of shale cores before and after testing was also characterized via nuclear magnetic resonance core analysis and scanning electron microscope analysis. The results indicated that the latex particles as physical shale stabilizer could be deformable to internally bridge and seal micro–nano scale pore-throats and fractures of shale, and the aluminum complexes as chemical shale stabilizer would precipitate from the filtrate when exposed to pore–fluids and the precipitation could also plug and seal pore-throats and micro-fractures. The latex particles work synergistically with aluminum complexes to impart shale stability due to superior properties of decreasing shale permeability and increasing shale membrane efficiency. Furthermore, the compatible test results confirmed that novel latex particles and aluminum complexes could be alternatives to standard shale stabilizers in water-based drilling fluids.

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## 1. Introduction

Wellbore instability is one of the most serious problems in the petroleum industry, and it could lead to delays in drilling process, increases in drilling cost and even abandonment of the oil wells (Bradley, 1979; Chen et al., 2010; Zamora et al., 2000). Shale composes approximately 75% of the drilled formations and shale instability is the main cause of over 90% of the wellbore instability problems such as tight hole, stuck pipe, hole collapse, hole enlargement, wellbore fracturing, and lost circulation (Steiger and Leung, 1992). Although shale instability has been investigated for several decades, it has still been a challenge in the petroleum and mining industries (Carminati et al., 1997; Chenevert, 1970; Chenevert and Dwarakanath, 1993). What's more, shale gas, as a clean and unconventional energy, has become progressively important in the energy landscape worldwide in the past decade (Bowker, 2003; Clarkson et al., 2011), but shale instability in the horizontal drilling process significantly restricted its exploration and

development, especially in China (Cui et al., 2011; Lv et al., 2013; Qiu et al., 2013; Stevens et al., 2013).

Geologically, shale is mainly composed of clay-sized ( $< 6 \mu\text{m}$ ) particles, and believed as the low porosity ( $< 10\%$ ) and ultra-low permeability ( $< 10^{-6}$  Darcy) with a significant pore volume in the nano-pore range (Ambrose et al., 2010; Clarkson et al., 2012). Due to its ultra-low permeability, pore pressure of shale formation could not dissipate easily when interacted with the drilling fluids. This phenomenon was denied as “undrained condition” (Detournay and Cheng, 1988). It could raise the near wellbore pore pressure and reduce the effective stress, thus leading to shale failure and wellbore instability (Chenevert and Sharma, 1993; Chen and Ewy, 2002). Historically, oil-based drilling fluids were chosen to drilling the “trouble” shale formation, and the fluid pressure into shale would not occur because of high capillary entry pressure and good osmotic membrane (Ewy and Morton, 2008). However, high costs and environmental pollution limited its wide use (Morton et al., 2005), and an environmentally friendly water-based drilling fluid with similar properties of oil-based drilling fluids has become more demanding (Rosa et al., 2005; Zhong et al.,

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## Nomenclature

API	American Petroleum Institute
AV	Apparent viscosity
CEC	Cation exchange capacity
D90	Particle size that the cumulative amount is 90%
FT-IR	Fourier transforms infrared spectroscopy
HA	Humic acid
HTHP	High temperature and high pressure

NMR	Nuclear magnetic resonance
SDAC	Aluminum complexes
SDLP	Latex particles
PSD	Particle size distribution
PV	Plastic viscosity
SEM	Scanning electron microscopy
TEM	Transmission electron microscopy
TGA	Thermal gravimetric analysis
YP	Yield point

2012). Recent studies concluded that one of the best way to improve shale instability when using the water-based drilling fluids is to prevent the fluid pressure penetration into the shale (van Oort et al., 1996a; van Oort, 1997; Tare and Mody, 2000), which could be achieved by physically or chemically plugging and sealing the micro–nano scale pore-throats and fractures of shale (Liu et al., 2014a).

In the past decade, a variety of approaches were proposed to improve the capability of reducing pore pressure transmission when using the water-based drilling fluids, such as fined calcium carbonate, asphaltenes, and polymers, but the fluid pressure penetration could not be prevented by these standard plugging additives (mainly micrometer-size) because they were too large to bridge and seal narrow pore throats ( $< 0.01 \mu\text{m}$ ) (Ewy and Morton, 2008; Liu et al., 2014b). Therefore, the introduce of nano-scale particles to reduce pressure penetration by physically plugging micro–nano scale pore-throats and fractures holds the potential to remove the major hurdle to apply water-based drilling fluids to drilling shale formation. The commercially available, non-modified silica nanoparticles were introduced for this purpose, but only marginal success has been achieved because of its low coagulation stability in the water-based drilling fluids (Cai et al., 2011; Sensoy et al., 2009). In addition, shale could act as a non-ideal semi-permeable membrane due to its narrow pore-throats and negative surface charge with a low membrane efficiency of 0.15–3.0%, and improving the shale membrane efficiency could be also beneficial to prevent pore pressure transmission (Qiu et al., 2005). Recently, poly-alcohol, silicates and aluminum complexes have been proved to be capable of decreasing fluid pressure penetration and improving shale membrane efficiency (Ramirez et al., 2005). Among these chemicals above, poly-alcohol were confirmed to reduce fluid pressure penetration by cloud point effect while the precipitation reaction made silicates and aluminum complexes possible to decrease pore pressure transmission (van Oort et al., 1996b; Saddok et al., 1997). The new generation aluminum complexes were reported to provide high shale membrane used in the water-based drilling fluids (Ramirez et al., 2006; Zhang et al., 2013), and they were tested to be environment-friendly (Saddok et al., 1997).

On the other hand, to evaluate the effectiveness of additives or drilling fluids to reduce fluid pressure penetration, various laboratory experimental methods have been adopted and they were uniformly referred to as “pressure transmission” or “membrane efficiency” test. Several examples of experimental methods and results could be found in the published literatures (Mody, Hare (1993); van Oort et al., 1995; Ewy and Stankovich, 2000; Stowe et al., 2001; Xu et al., 2005). Depending on experimental methods or devices, one could investigate the osmotic pressure effect only, or the hydraulic pressure effect only, or the combined effects simultaneously. It could be concluded that, to truly improve shale instability problems, the water-based drilling fluids must be effective at both physically plugging micro–nano scale pore-throats and fractures and high osmotic membrane efficiency (Ewy and

Morton, 2008; Qiu et al., 2005).

In this study, we attempted to synthesize the novel latex particles (SDLP) and aluminum complexes (SDAC), and they are introduced as potential physical and chemical shale stabilizers respectively in water-based drilling fluids. The novel latex particles (SDLP) and aluminum complexes (SDAC) could work synergistically to impart shale stability due to superior properties of decreasing shale permeability and increasing shale membrane efficiency.

## 2. Materials and methods

### 2.1. Materials

**Chemical agent.** The styrene (St,  $\text{C}_6\text{H}_5\text{CH}=\text{CH}_2$ ) and methyl methacrylate (MMA,  $\text{CH}_2=\text{C}(\text{CH}_3)-\text{COO}-\text{CH}_3$ ), obtained from Sino-pharm Chemical Reagent Co. Ltd (China), were distilled under vacuum before use. The initiator, potassium persulfate ( $\text{K}_2\text{S}_2\text{O}_8$ ), was obtained from Aladdin Reagent Co. Ltd (China), was recrystallized for purification. Isopropanol ( $(\text{CH}_3)_2\text{CHOH}$ ), sodium chloride (NaCl), sodium aluminate ( $\text{NaAlO}_2$ ), sodium hydroxide (NaOH), calcium chloride ( $\text{CaCl}_2$ ), magnesium chloride ( $\text{MgCl}_2$ ), hydrochloric acid (HCl), AR grade, were all obtained from Sino-pharm Chemical Reagent Co. Ltd (China) and used as received. The humic acid (HA) was extracted from lignite, obtained from Yunnan province of China, by alkali solubilization and acid precipitation method recommended by International Humic Substance Society (IHSS). The distilled water was used throughout the experiments.

**Shale.** The fully preserved outcrop shale used in this study was cored from Longmaxi Formation in the south of Sichuan Basin (China), with activity close to 1, and the reconstituted pore-fluids used is 3% (m/v) sodium chloride (NaCl) solution ( $a_w=0.998$ ). The shale cores were selected for pressure transmission and membrane efficiency tests for its good parallelism. According to the experiment requirement, the fresh shale cores were incised into cylindrical cores with a diameter of 2.54 cm and a length of 0.80 cm and they were not contacted with any aqueous fluids in the whole process. The mineralogical composition is reported in

**Table 1**  
Mineralogical composition of shale cores.

X-ray diffraction		Wt%
Quartz		51
Calcite		12
Dolomite		2
Plagioclase		3
Pyrite		1
Clay		31
Clay	Kaolinite	15
	Chlorite	8
	Illite	56
	Illite/smectite	21

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