Inhibiting shale hydration and dispersion with amine-terminated polyamidoamine dendrimers

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ABSTRACT

Dendrimers have been paid increasing attention in the area of drilling fluid recently due to their unique structure and properties. The inhibitive properties of amine terminated polyamidoamine (PAMAM) dendrimers ranging from G0 to G5 were evaluated by relative inhibition rate, shale cuttings hot-rolling dispersion test and particle size distribution measurement respectively. Meanwhile the inhibitive capacity of the polymers under various pH value conditions was studied. The interaction between sodium bentonite and PAMAM dendrimers was characterized by zeta potential measurement and X-ray diffraction (XRD). The results indicated that, G0 and G5 are superior to polyether diamine, while G1, G2, G3 and G4 perform better than KCl. PAMAM dendrimers from G0 to G5 can decrease the zeta potential of clay particles from -39 mV to about -22.6 mV at natural pH values and reverse the charge when the pH value is adjusted to 9. When intercalated into the clay interlayer in aqueous solution, the candidate PAMAM dendrimers can form monolayer arrangement at lower concentrations and reduce the interlayer spacing of hydrated clay from 1.95 nm to 1.38-1.63 nm, which is the direct evidence of inhibiting shale hydration. With the increase of

concentration, mixed phase and bilayer orientation are formed in the interlayer. The multi-terminal amine groups of dendrimers can effectively bind the adjacent layers together with electrostatic attraction and hydrogen bonding, and expel the water molecules out of the interlayer, contributing to the suppression of clay swelling and dispersion. The pH value reduction of aqueous solution improves the protonation of terminal-amine group, which can intensify the interaction between the polymers and clay, inducing the decrease of hydrated interlayer spacing and the zeta potential of clay particles, thus enhancing the inhibitive properties.

Keywords: polyamidoamine; dendrimers; shale hydration; interlayer spacing; protonation

1. Introduction

It is always a worldwide challenge for well drilling in shale formations due to the wellbore instability problems induced by the interaction between shale and aqueous filtration including tight hole, sloughing, washout, caving and so on (Al-arfaj et al., 2014; Stelger and Leung, 1998). Oil-based drilling fluids are the first choice for most shale formations because of the outstanding shale stability, however, the drawback of high cost and stringent environmental legislation make them a much less attractive alternative than before (He et al., 2014; Stamatakis et al., 1995; Suter et al., 2011). Consequently, much research has been transferred to improve the inhibitive properties of water-based drilling fluids with the eventual goal of replacing oil-based drilling fluids, which is also a hallmark of high performance water-based drilling fluid (Galindo et al., 2015).

Based on the understandings of shale hydration mechanisms and the physical-chemical interactions between shale and drilling fluid, lots of work has been carried out to evaluate and

seek solutions to mitigate and control the reactive shale formations during the past decades (Van Oort et al., 1994; Van Oort, 1997). Numerous chemicals including inorganic salts, formates, organic amine compounds, polymers, silicates and polyglycerols have been used with different mechanisms such as hydration inhibition, reduction of pore pressure transmission, or cuttings encapsulation (Galindo et al., 2015; Patel et al, 2007; Reid et al., 1995; Van Oort, 2003; Xuan et al., 2013; Zhang et al., 2001). Based on these chemical inhibitors, several inhibitive water-based drilling fluids have been established and utilized in the field (Donham and Young, 2009; Patel and Gomez, 2013; Stamatakis et al., 1995; Young and Ramses, 2006). Nevertheless, it is not completely successful for these fluids to inhibit the hydration and dispersion of reactive shales with various performance limitations (Patel et al., 2002). Therefore, developing new highly inhibitive and environmentally friendly shale inhibitors is still an ongoing endeavor and research hotspot.

Dendrimers have been paid extensive attention since the first synthesis because of their unique characteristics such as highly ordered structure, narrow size distribution, and uniform dense terminal functional groups, which render the polymers as ideal candidates in a wide range of applications (Abdel Rehim et al., 2010; Mo et al., 2008). Recent studies have shown that dendrimers have potential application in the area of oilfield chemistry (Amanullah, 2013; Kaiser, 2013; Lai et al., 2013; Li et al., 2012; Rivers et al., 2011; Stanciu et al., 2015). As far as drilling fluid is concerned, Amanullah (2013) illustrated a promising potential of developing high performance drilling fluid in future challenging conditions with the use of dendrimers. Miller (2011) applied a patent that poly(propyleneimine) dendrimers and polyamine twin dendrimers can be used as shale hydration inhibition agent and high

temperature resistant to 500°F. Teixeira et al. (2014) synthesized hyperbranched polyglycerols and evaluated their inhibitive performance. The results showed that the polymer has a great potential to be environmentally friendly inhibitor in water-based drilling fluid. In a recent study, elaborated dendritic polymers were designed and synthesized to reduce the fluid loss with temperature resistance of 260 °C in water based drilling fluid (Zhang et al., 2015).

PAMAM dendrimers, first synthesized by the Tomalia et al. (1985), are one of the most widely used dendrimers (Gillies et al., 2005). According to the molecular design rule of the clay swelling inhibitor (Suter et al., 2011), the unique characteristics including high density of terminal amine group and ellipsoidal or spheroidal structure of PAMAM dendrimers make them suitable for shale inhibition. The feasibility of PAMAM dendrimers as shale stabilizers has been investigated in our previous work (Zhong et al., 2015). The purpose of this paper is to further study the effect of PAMAM dendrimers on shale hydration and dispersion suppression under different pH values, and establish a relationship between the molecular structure of PAMAM dendrimers and stabilization of reactive shales.

2. Experimental

2.1. Materials

Different generations (from G0 to G5) of amine terminated polyamidoamine (PAMAM) dendrimers with ethylene diamine as initial core, were purchased from Sigma-Aldrich (Fig. 1). Polyether diamine (PEA) with molecular weight of 230 was provided by BASF Chemical Co. Potassium chloride was purchased from Sinopharm Chemical Reagent Co., Ltd, China with analytical purity. Sodium bentonite was provided by Boyou bentonite Group Co., Ltd, China, and the detailed mineralogical composition was presented in mass percentage as

follows: montmorillonite, 57.6 %, illite, 1.2%, kaolinite, 0.6%, chlorite, 0.6%, quartz, 32%, potassium feldspar, 8%. The cation exchange capacity (CEC) was determined to be 74 mmol/g. Drilling fluid bentonite was obtained from Weifang Huawei Bentonite Group Co., Ltd, China, following the American Petroleum Institute (API) standard. All of the chemicals were used as received without further purification.

The shale cuttings used for shale dispersion tests were provided by Zhundong Drilling Company from Well Yueman 6 of Tahe oilfield. The detailed mineralogical composition of the shale cuttings was identified using X-ray diffraction (XRD) and shown as follows, quartz, 41%, K-feldspar, 5%, plagioclase, 15%, calcite, 17%, iron dolomite, 4%, kaolinite, 1%, chlorite, 1%, illite, 7%, interlayered illite-smectite, 9%.

Fig. 1 Structures of the PAMAM dendrimers to be studied (G3).

2.2. Methods

2.2.1. Relative inhibition rate

Inhibitor solution containing 350 mL fresh water and 3.5 g inhibitor sample was prepared.

Drilling fluid bentonite (35 g) was incorporated into the solution and stirred at 10,000 rpm for

20 minutes. Then the dispersion was hot-rolled at 120°C for 16 hours. After cooling to ambient temperature, the rheological properties of the dispersion were determined by ZNN-D6 rotational viscometer (Qingdao Haitongda Special Instrument Co., Ltd). The relative inhibition rate was calculated according to the following equation.

$$R = \frac{\phi_{100} - \phi_{100'}}{\phi_{100}} \times 100\% \quad (1)$$

where, R is relative inhibition rate, ϕ_{100} and ϕ_{100}' are 100 dial reading of control sample and inhibitor sample respectively.

2.2.2. Shale cuttings hot-rolling dispersion test

This test was designed to evaluate the dispersion of shale cuttings after exposing to a formulated fluid in a rolling oven cell at setting temperatures. In this test, mass of 40 g shale cuttings from Well Yueman-6 and 280 mL aqueous solution containing 2w/v% inhibitor samples were added to the roller oven cell. After hot rolling at 77°C for 16 hours, the fluid and shale were cooled to ambient temperature and screened with 40 mesh sieve. The remaining shale cuttings were washed and recovered. After dried at 105°C for 4 hours, the recovered shale cuttings were weighed and the percentage recovery of the shale cuttings was determined.

2.2.3. Particle size distribution measurement

Particle size distribution measurement can be used to assess the inhibition ability of shale inhibitors (Liu et al., 2004). Mass of 16 g sodium bentonite was added into 400 mL deionized water and stirred vigorously for 1 hour. Then the dispersion was incubated for at least 24 hours. After that, 4 g shale inhibitors were added into the dispersions and stirred for 24 hours. The particle size distribution of the dispersion was measured by Bettersize 2000 particle size

analyzer (Bettersize instruments Ltd., China).

2.2.4. Zeta potential measurement

Zeta potential was measured with a Zetasizer Nano ZS90 (Malvern instrument, United Kingdom). Inhibitor solution containing 1 g inhibitor and 97 mL deionized water was prepared. Then 3 g Boyou sodium bentonite was added into the solution and vigorously stirred for 24 hours. Before the measurement, the dispersion was diluted to make the particles visible under the microscope. The zeta potential of each sample was tested three times and their average was taken as the final result. After adjusting the pH value to about 9 with hydrochloric acid, the pH value of the dispersion was measured with pH meter and the related zeta potential was derived.

2.2.5. Measurement of interlayer spacing with X-ray diffraction (XRD)

Firstly, sodium bentonite dispersion containing 7 g sodium bentonite and 350 mL deionized water was prepared first. Then PAMAM dendrimers were added into the dispersion with the content of 0.35, 0.70, 1.75, 2.80 and 7.00 g respectively. The dispersion was stirred for another 24 hours to establish adsorption equilibrium. The pH value of the dispersion was adjusted by 0.1 mol/L hydrochloric acid. Then the mixture was centrifuged at 8000 r/min for 20 min and washed three times to remove the un-adsorbed polymers. After centrifugation, the sedimentation was collected. One part of the sample was tested by X-ray diffraction directly to obtain the interlayer spacing, while the other part of the precipitation was dried at 105 °C and ground to fine powders. XRD patterns were recorded using an X'pert PRO MPD diffractometer with CuK α radiation operating at 45 kV and 40 mA. The interlayer spacing was analyzed by using Bragg's equation. The value for $n=1$ was calculated from $2d\sin\theta=n\lambda$.

3. Results and discussion

In this section, the inhibitive properties of PAMAM dendrimers of different generations were evaluated at different pH values firstly. Then the inhibitive mechanism of PAMAM dendrimers was analyzed by zeta potential measurement and XRD. Finally a plausible model was proposed to illustrate the interaction between PAMAM dendrimers and clay.

3.1. Inhibitive properties evaluation

In order to compare the inhibitive properties between candidate PAMAM dendrimers and PEA and potassium chloride, typical inhibitive evaluation experiments including relative inhibitive rate measurement and shale cuttings hot-rolling dispersion test were performed. Meanwhile the interaction between shale inhibitors and clay particles will influence the colloidal properties of clay particles, therefore, particle size distribution measurement was also carried out to probe the inhibition of PAMAM dendrimers.

3.1.1. Relative inhibitive rate

The effect of different inhibitors on yielding tendency of sodium bentonite was investigated by rheological tests. In fresh water system, clay particles will imbibe water rapidly in the process of surface hydration and osmotic hydration. After thorough hydration, even individual lamellar layers will form dimensional networks in the system, resulting in an increase of the viscosity of the dispersion. On the contrary, the system incorporating various inhibitors exhibited a lower 100 dialing readings, indicating a lower rheological profile compared to the control sample, corresponding to a higher relative inhibition rate which can be identified by equation 1. As shown in Fig. 2, the relative inhibition rate of PAMAM dendrimers was higher than that of potassium chloride, approaching to that of PEA,

demonstrating that PAMAM dendrimers showed superior inhibitive performance to potassium chloride.

Fig. 2. Relative inhibition rate of various inhibitor systems.

3.1.2. Shale cuttings hot-rolling dispersion test

In order to investigate the effect of pH value on the inhibitive performance of PAMAM dendrimers, shale cuttings hot-rolling dispersion test and particle size distribution test were carried out under various pH values. As shown in Fig. 3, in comparison to the control sample, the shale cuttings recovery was improved greatly for PAMAM dendrimers of various generations, PEA and KCl. High recovery is an indication of low dispersion of shale cuttings and highly effective inhibition. When the pH value of testing solution was 11, the shale cuttings recovery of the candidate fluids followed the sequence of $G5 > G0 > PEA > G1 > G2 > G3 > KCl$, demonstrating that G5 could be used as an efficient shale dispersion suppressant. When the pH value of the aqueous solution was adjusted to 9, both the shale cuttings recovery of PAMAM dendrimers and PEA further increased obviously. However, G5 still exhibited the best inhibitive performance. For KCl, the shale cuttings recovery was less influenced by the pH value.

Fig. 3. Shale cuttings recoveries of different inhibitors at pH value of 11 and 9 respectively.

3.1.3. Particle size distribution measurement

Clay particles, mainly composed by montmorillonite, would disperse into fine particles and even single unit layers after thorough hydration. However, when shale inhibitors of cationic type are incorporated, the particle size would be obviously changed because of the interaction between the shale inhibitors and clay particles. The increase of particle size of the composites could be correlated to the occurrence of agglomeration. The effect of PAMAM dendrimers, PEA and KCl on the particle size of clay particles at natural pH value and 9 were determined and shown in Fig. 4 and Fig. 5, respectively. It could be obviously seen that, when the pH value of the dispersion was not adjusted, the control sample contained a large amount of small particles and a small part of great particles. The addition of inhibitors shifted the distribution curves to the right, corresponding to the increase of particle size. However, potassium chloride didn't have apparent effect on the particle size of clay. The distribution curves changed relatively little. When the pH value was adjusted to 9, the particle distribution curves shifted to even more right, demonstrating greater particles formed, namely, the inhibitive properties were improved with the decrease of aqueous pH value. As shown in

Table 1, when the pH value of the dispersion was adjusted to 9, the value of median size increased and specific surface area decreased for PAMAM dendrimers and PEA.

There are a number of amine groups on the outer surface of PAMAM dendrimers, which can be adsorbed onto the negative clay surface with multi-sites. This multi-adsorption can lead to the increase of particle size with two modes. On one hand, the positively charged PAMAM dendrimers neutralize the negative sites of clay surface and decrease the repulsion between clay particles. On the other hand, PAMAM dendrimers with numerous amine groups can be anchored on adjacent clay particles and bind the particles together. Thus the particles easily flocculate and become larger. When the pH value is reduced, the protonation of amine groups of PAMAM dendrimers intensifies this behavior, reflecting a further increase of particle size. Because there are only two amine groups at the terminal for PEA, it can't change the particle size as effectively as PAMAM dendrimers. Potassium ions just exchange with the hydrated sodium cations and have little effect on particle size.

Fig. 4. Particle size distribution of different inhibitor systems at natural pH value.

Fig. 5. Particle size distribution of different inhibitor systems at pH value of 9.

Table 1 Particle size distribution of different inhibitor systems.

Testing sample	Parameter	D50(μm)		Specific surface area(m^2/g)	
		Natural pH	pH=9	Natural pH	pH=9
4% bentonite dispersion		5.114	5.220	0.805	0.799
4% bentonite dispersion +1%(w/v)G0		31.63	33.81	0.163	0.136
4% bentonite dispersion +1%(w/v)G1		29.31	30.51	0.169	0.152
4% bentonite dispersion +1%(w/v)G2		24.79	30.20	0.190	0.165
4% bentonite dispersion +1%(w/v)G3		26.66	31.35	0.162	0.155
4% bentonite dispersion +1%(w/v)G4		27.98	32.42	0.165	0.145
4% bentonite dispersion +1%(w/v)G5		24.40	32.66	0.169	0.140
4% bentonite dispersion +1%(w/v)PEA		11.45	25.36	0.423	0.208
4% bentonite dispersion +1%(w/v)KCl		5.812	5.311	0.781	0.796

3.2. Interaction between PAMAM dendrimers and bentonite

3.2.1. pH value of aqueous solution

The pH values as a function of PAMAM dendrimers concentration is presented in Fig. 6. Concentration critical point (about 0.5g/L) can be easily detected in this Figure. The pH value increased significantly with the increase of concentration below this critical point, while increased smoothly when the concentration is above the point, indicating a pH buffering effect.

Fig. 6. Variation of pH values with the increase of PAMAM concentrations.

3.2.2. Zeta potential

The zeta potential of montmorillonite particles in aqueous dispersion was measured to investigate the effect of inhibitors on the electrokinetic properties of the clay particles at natural pH values and pH value of 9 respectively. Generally, colloidal particles with the zeta potential absolute value greater than 30 mV is considered stable (Garea et al., 2014). Highly negative zeta potential of clay particles have the trend to swell and disperse. As illustrated in Fig. 7(a), the zeta potential of pristine sodium bentonite was about -39mV, reflecting stable dispersion. The addition of inhibitors decreased the zeta potential of clay particles to different degrees. PAMAM dendrimer from G0 to G5 could decrease the zeta potential from -39 mV to about -22.6 mV. PEA reduced the zeta potential to a lower value of about -18.7 mV, and KCl could decrease the zeta potential to about -11.5 mV. According to Mohan and Fogler (1997), reduction of layer charge by 20% is adequate to prevent swelling of the clay completely. Also Riddick established a stability scale of particles in terms of zeta potential, that zeta potential ranging from -16 mV to -30 mV is the threshold of weak dispersion, and zeta potential in the

range of -10 to -15 mV indicates the occurrence of particle binding (Ritter and Gerault, 1985).

Thus it can be inferred that the addition of PAMAM dendrimers, PEA and KCl effectively decrease the zeta potential of clay particles and prevent clay swelling.

Regarding the PAMAM dendrimers, the terminal primary and tertiary amines make the polymers exhibit a weak polyelectrolyte behavior. Their charge density can be tuned by varying the pH value of the solution. For PAMAM dendrimers, the pKa of terminal primary amine groups and the tertiary amine groups is between 9-10 and 4-5, respectively (Shi et al., 2005; Garea et al., 2014). For polyether amine, the pKa is estimated to approximate that of 1, 6-hexanediamine, whose pKa1 and pKa2 values are 9.83 and 10.93, respectively (Wang et al., 2010). According to Horton and Jones (1998), when the pH value is equal to pKa, the ratio of protonated to non-protonated amine is exactly 1. For each drop of 1 pH unit, the ratio of protonation to non-protonated amine is increased 10 fold. Hence a decrease of pH value will improve the protonation degree of amine groups and lead to an increase of charge. As shown in Fig. 7(b), the zeta potential of clay particles became positive for PAMAM dendrimers incorporation when the pH value was adjusted to about 9, whereas the zeta potentials of the system adding PEA and KCl were still negative. The zeta potential reverse indicated that special adsorption existed between PAMAM dendrimers and clay particles, which will be characterized in the following part of X-ray diffraction.

When at the natural pH values, only part of terminal amine groups are protonated, which neutralize the negative sites of clay surface and result in the decrease of zeta potential to some degrees. The decrease of pH value promotes the protonation of amine groups and lead to the special adsorption of PAMAM dendrimers onto clay surface, thus charge reverse of

clay particles occurs. While the difference of charge density for PAMAM dendrimers caused the different extent of zeta potential change. G0 is the most effective in decreasing the zeta potential among all generations. PEA always forms a monolayer arrangement in the interlayer of clay whether for dry or wet sample (Zhong et al., 2011). Therefore no charge reverse occurred.

Fig. 7. Zeta potential measurement of various inhibitor systems at different pH values. Note: (a) natural pH value, (b) pH=9.

3.2.3. XRD

Clay swelling is mainly controlled by the component of aqueous solutions with which the clays come into contact (Amorim et al., 2007). The swelling can be directly evaluated by the increase of interlayer spacing. The interlayer spacing of pristine bentonite is 1.23 nm, showing a typical X-ray diffraction pattern of sodium bentonite. After thorough hydration, the interlayer spacing increased as high as 1.95 nm. While the incorporation of PAMAM dendrimers of different generations exhibited different intercalation types. For all the PAMAM dendrimers, when the concentration was low, the interlayer spacing decreased dramatically. For example, when the concentration was 0.35 g, the interlayer spacing

decreased from 1.95 nm to 1.38, 1.46, 1.63, 1.52, 1.46 and 1.45 nm for the dendrimers of different generations respectively. This was the direct evidence of inhibiting clay swelling by PAMAM dendrimers. At low concentrations, PAMAM dendrimers intercalated into the interlayer of clay and exchange the hydrated cationic ions, resulting in the expelling of interlayer water molecules and the decrease of interlayer spacing. While with the increase of concentration, PAMAM dendrimers adopted overlapped orientations in the interlayers, leading to the increase of interlayer spacing.

As shown in Fig. 8(a), when the content of G0 is 0.35 g and 0.70 g, the related interlayer spacing was 1.38nm. When the concentration increased as high as 1.75 g, there were two diffraction peaks, indicating mixed phase intercalation existed in the gallery. With the further increase of concentration, only one peak was observed. The value of 1.68 nm indicated bilayer structure was formed in the interlayer. The same trend was also observed for G2. G2 formed monolayer arrangement, mixed phase, and bilayer structures at lower, intermediate, and higher concentration, respectively. For G1, G3, G4 and G5, it was interesting to find that, monolayer adsorption was observed at low concentration of 0.7 g, and bilayer adsorption was formed at high concentrations, which was different from previous results. According to our former XRD test from dry samples, G0 always formed monolayer structure in the whole range of concentration, G1, G2, G3 and G4 formed monolayer orientation at low concentration, but mixed-phase at higher concentrations. G5 showed limited intercalation because of steric hindrance. This difference can be interpreted as that, the dendrimers assume a changed conformation in the lattice in the process of drying at high temperatures. In addition, the bilayer adsorption explains the charge reverse of clay particles at pH value of 9

as discussed above.

The hydrodynamic diameter of dendrimers in solution estimated from molecular models is 1.4, 2.2, 2.9, 3.6, 4.5, and 5.4 nm for the PAMAM dendrimers from G0 to G5, respectively (Shi et al., 2005). However, the maximum value of interlayer spacing was about 2 nm for the dendrimer modified bentonite, much less than that of their diameters in aqueous solution (Fig. 9). Lower generation (G0 - G3) PAMAM dendrimers with ethylenediamine core have an ellipsoidal shape, whereas the higher generation (G4 - G5) dendrimers have a roughly spherical shape (Liyanage et al., 2013). This rather small interlayer spacing in comparison with that of polymers indicated that polymers intercalated into the gallery with highly oblate or flattened conformation. This strongly distorted structure can be related to the intrinsic characteristics of PAMAM dendrimers. Electrostatic attraction between protonated terminal amine group and negative clay surface, and hydrogen bonding between amine group and siloxane contribute to the strong interaction between PAMAM dendrimers and clay. Meanwhile, PAMAM dendrimers are very soft and do not preserve their shape in condensed state in the interlayer. Moreover, the absence of macromolecular entanglements in comparison with linear polymers makes PAMAM dendrimers easy to be compressed (Tsukruk et al., 1997), thus explaining the rather small interlayer distance.

Fig. 8. X-ray diffraction patterns of PAMAM dendrimers modified bentonite with different concentrations with wet samples. (a) G0; (b) G1; (c) G2; (d) G3; (e) G4; (f) G5.

Fig. 9. Variation of interlayer spacing with concentration of PAMAM dendrimers for wet samples.

Table 2 and Table 3 illustrate the interlayer spacing of PAMAM dendrimers modified bentonite at content of 2.8 g under different pH values. There was no apparent change of interlayer spacing for G0, G1, G2, G3 and G4 with dry sample, whereas for G5, the interlayer spacing was 1.36nm at natural pH value, while a more expanded phase (1.88 nm) was observed when the pH value was adjusted to 9.0. The decrease of pH value improved the protonation of peripheral primary amine groups, which facilitate the intercalation. From table 3, it was obviously noted that the interlayer spacing was lower at pH value of 9.0 than that of natural pH conditions. This could also be correlated to, that the decrease of pH value enhances the protonation of terminated amine groups, which can be anchored on the adjacent layers with multi-adsorption and bond the sheets tighter, generating a lower interlayer spacing. A similar phenomenon was also reported by Chou et al. (2004). Furthermore, a conclusion could be drawn that, reducing pH value of the aqueous solution leads to improved inhibitive capacity of PAMAM dendrimers.

Table 2 Interlayer spacing of PAMAM dendrimer modified bentonite at different pH values

with dry sample (2.8 g).

Sample	pH value	Natural pH		pH =9.0	
		2Theta(°)	Interlayer spacing (nm)	2Theta(°)	Interlayer spacing (nm)
G0		6.6298	1.33	6.4500	1.37
G1		6.5882	1.34	6.4690	1.37
G2		4.9134	1.80	4.9804	1.77
		6.4676	1.37	6.4385	1.37
G3		4.9141	1.80	4.8923	1.81
		6.5051	1.36	6.3234	1.40
G4		5.0605	1.75	-	-
		6.5412	1.35	6.4002	1.38
G5		-	-	4.7105	1.88
		6.4880	1.36	6.3481	1.39

Table 3 Interlayer spacing of PAMAM dendrimer modified bentonite at different pH values

with wet sample (2.8 g).

Sample	pH value	Natural pH		pH =9.0	
		2Theta(°)	Interlayer spacing (nm)	2Theta(°)	Interlayer spacing (nm)
G0		5.2652	1.68	6.1979	1.43
G1		4.8784	1.81	5.1527	1.72
G2		4.4125	2.00	5.0236	1.77
G3		4.3854	2.01	4.5832	1.93
G4		4.4534	1.98	4.5870	1.93
G5		4.3675	2.02	5.5327	1.60

3.3. Inhibitive mechanism analysis

A possible model illustrating the interaction between PAMAM dendrimers and clay is presented in Fig. 10. At lower concentration, PAMAM dendrimers intercalated into the clay lattice with monolayer arrangement, whereas at higher concentration bilayer orientation was formed. The multi-adsorption between terminal amine groups and negative sites of clay

surface could bind the adjacent lattices together, expelling out the interlayer water molecules, corresponding to an effective inhibitive performance, as confirmed by the former inhibitive evaluation results. A proper decrease of pH value prompted the degree of protonation, which intensified the interaction between PAMAM dendrimers and clay, and lead to the further reduction of interlayer spacing, namely reflecting to the improvement of inhibition. The charge density played a vital role of inhibitive performance. For G0, whose charge density was higher than that of other generations, exhibited superior performance to other generations.

Fig. 10. The interaction between PAMAM dendrimers and bentonite.

4. Conclusions

The inhibitive properties of PAMAM dendrimers were further studied in this paper. PAMAM dendrimers ranging from G0 to G5 exhibited effective performance in inhibiting shale hydration and dispersion. G0 and G5 were superior to PEA, while G1, G2, G3 and G4 performed better than KCl. For the candidate PAMAM dendrimers, when intercalated into the clay interlayer in aqueous solution, monolayer arrangement is formed at lower concentration,

and bilayer orientation is formed at higher concentration. The multi-terminal amine groups can effectively bind the adjacent layers together with electrostatic attraction and hydrogen bonding, which expels the water molecules out of the interlayer and contributes to the suppression of clay dispersion. The inhibitive performance of PAMAM dendrimers is associated with pH value of aqueous medium. Reducing the pH value of aqueous solution intensifies the interaction between the polymers and clay, and induces the decrease of hydrated interlayer spacing when the dendrimers were intercalated into the galleries, corresponding to an enhancement of the inhibitive properties of PAMAM dendrimers. Understanding the pH dependence of PAMAM dendrimer inhibitive properties is of vital importance for field application. PAMAM dendrimers can be considered as potential candidates for inhibiting shale hydration and dispersion.

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