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Water-soluble complexes of an acrylamide copolymer and ionic liquids for inhibiting shale hydration †

Cite this: *New J. Chem.*, DOI: 10.1039/x0xx00000x

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Received 00th January 2012,
Accepted 00th January 2012

DOI: 10.1039/x0xx00000x

www.rsc.org/njc

Here we report water-soluble complexes of an acrylamide copolymer and ionic liquids for inhibiting shale hydration. The copolymer, denoted as PAAT, was synthesized via copolymerization of acrylamide (AM), acrylic acid (AA) and *N,N*-diallyl-4-methylbenzenesulfonamide (TCDAP), whereas the ionic liquids used were 3-methyl imidazoliumcation-based tetrafluoroborates. The X-ray diffraction showed that compared with commonly used KCl, water-soluble complex of PAAT with 2 wt% ionic liquid 1-methyl-3-H-imidazolium tetrafluoroborate (HmimBF₄) could remarkably reduce the d-spacing of sodium montmorillonite in water from 19.24 to 13.14 Å and effectively inhibit clay swelling. It has also found that PAAT/HmimBF₄ complex with 2 wt% HmimBF₄ could retain 75% indentation hardness of shale and increase anti-swelling ratio up to 85%. ¹³C NMR study revealed that there existed interactions between PAAT and HmimBF₄. Moreover, the thermal stability of PAAT/HmimBF₄ complex is superior to PAAT, suggesting that this water-soluble complex can be used for inhibiting clay and shale hydration in high temperature oil and gas wells.

1. Introduction

With the urgent demands for the energy all over the world, the development of shale oil and gas is an attractive and challenging area which can make contributions to relieve the energy crisis.¹ The shale, which is mainly comprised of clay minerals, will hydrate when contact with water environment. The hydration and swelling of clay would directly reduce the cementation force and produce swelling force in rocks causing the loss of rock strength and indentation hardness, which could result in the collapse of shale and the failure of production. Therefore, developing the effective shale hydration inhibitor have never become as crucial as today.²

The hydration of sodium montmorillonite (MMT) has been considered the principal cause of clay hydration and swelling.³ Traditionally, inhibition of clay swelling is achieved by the use of KCl due to the weakly hydrating of K⁺,⁴ whereas the additive amount is so large coming to 3–20 wt%.⁵ Apart from that, various types of clay hydration inhibitors have been researched, such as low molecular weight polyethylene glycols (PEG),⁶ polypropylene oxides (PPO),⁷ mono and diamines,⁸ cationic amine salts,⁹ and some charged polymers.¹⁰ Unfortunately, some limitations of these chemicals like, undesirable solubility, short acting time, and temperature and/or pH sensitivity have been realized extensively.⁵

During the past decades, to reduce the additive amount of KCl and improve effectiveness of inhibition, combining of KCl with various polymers such as PEG, PPO, hydrolyzed polyacrylamide (HPAM) and other high-performance polymers, has been investigated by numerous researchers.^{6, 11, 12} It is believed that synergistic combination of components could enhance clay hydration inhibition more effectively.²

In our previous studies, a series of copolymers have been prepared to combine with KCl to inhibit clay hydration.^{13–15} In particular, the solution of AM-AA-AOAB-*O*-β-CD copolymer which was prepared

with acrylamide (AM), acrylic acid (AA), 1-allyl-3-oil acyloxyimidazole-1-ammonium bromide (AOAB), and mono-2-*O*-(allyl oxygen radicals-2-hydroxyl propyl)-β-cyclodextrin and 10 wt% KCl could reduce the *d*-spacing of MMT from 18.9 to 15.3 Å.¹⁴ However, the additive amount of KCl needs to be further reduced and more effective approaches even without use of KCl are desired. In addition, improving thermal and chemical stabilities of clay hydration inhibitors in the oil and gas well drilling with harsh conditions could be realized by introducing specific structure of copolymer.

On the other hand, due to the unique properties such as high ionic conductivity, thermal stability, chemical stability and recyclability, ionic liquids (ILs) are widely investigated for many applications by different research groups over the past decades as well as by our research groups.^{16, 17} Having strong hydrogen-bond-accepting anions ILs were employed for dissolution of cellulose materials.¹⁸ To prepare modified clays, ILs were allowed to intercalate into the layer structure of MMT.¹⁹ Also, ILs were used to obtain polymer gel membranes due to their high ionic conductivity.²⁰ However, little work has been reported about utilizing ILs for clay hydration inhibition.^{21, 22}

It has been demonstrated that 3-methyl imidazoliumcation-based tetrafluoroborate ILs possess devisable cations and BF₄⁻ anion being capable of forming hydrogen bond,²³ which may play an important role in clay swell inhibition. In addition, as is well known that introducing the rigid benzene ring can improve the thermal stability of the copolymer.²⁴ Therefore, a series of 3-methyl imidazoliumcation-based tetrafluoroborate ILs were utilized to inhibit the hydration and swelling of clays in the present study. Importantly, a novel copolymer with rigid benzene ring and sulfonamide structure was synthesized to improve the thermal stability of systems. The poly(acrylamide-*co*-acrylic acid-*co*-*N,N*-diallyl-4-methyl benzenesulfonamide) random copolymer, denoted as PAAT, was synthesized via copolymerization of functionalized

monomer *N,N*-diallyl-4-methyl benzenesulfonamide (TCDAP) with acrylamide (AM) and acrylic acid (AA). Water-soluble complexes of PAAT and 3-methylimidazolium-based tetrafluoroborate ILs were prepared and investigated for potential application as a new type of clay and shale hydration inhibitor.

2. Experimental section

2.1. Materials

Acrylamide (AM), acrylic acid (AA), *p*-toluenesulfonyl chloride (TsCl), diallylamine (DAP), *N*-methylimidazole (mim), tetrafluoroboric acid, sodium fluoroborate, bromoethane, allyl bromide, 1-bromobutane, 1-bromododecane, benzyl bromide, triethylamine (Et₃N), nonaphenol polyethyleneoxy (10) ether (OP-10), dichloromethane (CH₂Cl₂), chloroform (CHCl₃), acetone, ammonium persulfate ((NH₄)₂S₂O₈), sodium bisulfite (NaHSO₃), and KCl were chemically pure and supplied by Chengdu Kelong Chemical Reagent Factory, Sichuan, China. Sodium montmorillonite (MMT) and bentonite were provided by Xinjiang Xiazijie Bentonite Company, Xinjiang, China. CH₂Cl₂ was dried using anhydrous sodium sulfate, and others were used as commercial without further purification.

2.2. Synthesis of *N,N*-diallyl-4-methylbenzenesulfonamide

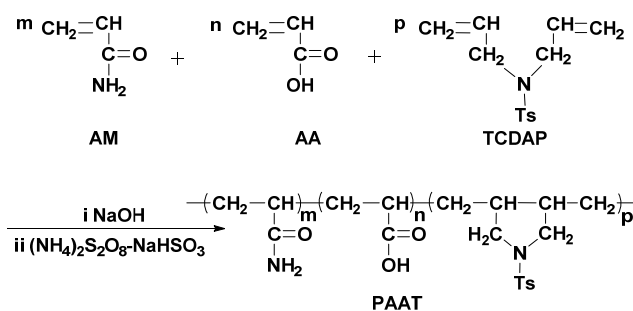
TsCl (3.81 g, 0.02 mol) and 10 mL CH₂Cl₂ were added to a 100 mL round-bottomed flask with a magnetic stir bar, DAP (2.33 g, 0.024 mol), Et₃N (4.04 g, 0.04 mol) and 5 mL CH₂Cl₂ were slowly added in the flask in a water-ice bath at 0–5 °C for 6 h. The crude product was washed with deionized water, 1:100 dilute HCl, NaOH solution and saturated NaCl in turn and dried using anhydrous sodium sulfate before it was filtered through fine fritted funnel. Finally the CH₂Cl₂ was removed under reduced pressure by a rotary evaporator. Obtained TCDAP was light yellow liquid. Yield: 90%. ¹H NMR (400 MHz, CDCl₃): 7.69–7.71 (d, 2H, ArH), 7.28–7.31 (d, 2H, ArH), 2.42 (s, 3H, Ar-CH₃), 3.79–3.81 (d, 4H, CH₂-N-SO₂-Ar-), 5.12–5.16 (m, 4H, CH₂=CH-CH₂-), 5.56–5.65 (m, 2H, CH₂=CH-CH₂) ppm. ¹³C NMR (100 MHz, CDCl₃): 21.45 ppm (Ar-CH₃), 49.34 ppm (CH₂-N-CH₂), 118.88 ppm (CH₂=CH-CH₂-), 127.16, 129.66, 137.45, 143.22 ppm (Ar-C), 132.69 ppm (CH₂=CH-CH₂) (Fig. S3, Supporting Information).

2.3. Synthesis of PAAT

TCDAP, OP-10 and deionized water were added in a 250 mL three-neck flask with a magnetic stir bar. After AM and AA were dissolved in deionized water and the solution pH was adjusted to a certain value by 1.0 mol/L NaOH solution, they were added into the flask. After 15 min under N₂ atmosphere, ammonium persulfate and sodium hydrogen sulfite (molar ratio 1:1) were added in the flask at a certain temperature for 8 h. The reaction product was washed by ethanol and dried to obtain a white granular PAAT. The synthesis route was shown in Scheme 1.

2.4. Synthesis of PAAT/ILs complexes

3-Methylimidazolium-based tetrafluoroborate ILs were prepared according to previous reported methods.^{23, 25} The structure of the obtained 3-methylimidazolium-based tetrafluoroborate ILs is shown in Fig. 1. PAAT solution was mixed with all kinds of the prepared 3-methylimidazolium-based tetrafluoroborate ILs under N₂ atmosphere at 50 °C for 4 h, respectively. The PAAT/ILs were obtained after cooling to ambient temperature.



Scheme 1. Synthesis route of PAAT.

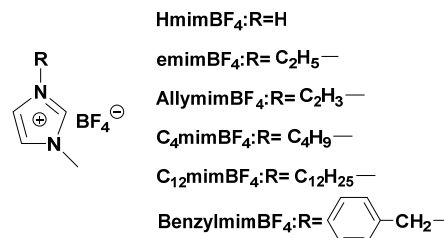


Fig. 1 Structure of 3-methylimidazolium-based tetrafluoroborate ILs.

2.5. Characterization

The apparent viscosities of copolymer solutions were measured with a Brook field DV-III + Pro viscometer (Brook field, USA). FT-IR spectra were measured with KBr pellets using WQF-520 Fourier transform infrared spectrometer in the optical range 400–4000 cm⁻¹ by the averaging of 32 scans. (Beijing Rayleigh Analytical Instrument Corporation, China). ¹H NMR and ¹³C NMR spectra were recorded by a Bruker AV III -400 NMR spectrometer (Bruker, Switzerland) in D₂O and CDCl₃. The intrinsic viscosity of copolymer was measured by Ubbelohde viscometer (Shanghai Sikeda Scientific Instruments Incorporation, China) at (30 ± 0.1) °C.

2.6. X-ray diffractometry (XRD)

The hybrid MMT mixtures were prepared by adding 0.5 g MMT to 1 g samples (KCl, ILs, PAAT and PAAT/ILs complexes solution, respectively) under the different concentration. The hybrid mixtures suspensions were kept wet for 2 h. A part of hybrid MMT mixtures were tested by XRD directly, and others were dried to constant weight at 40 °C in vacuum and then were tested by XRD. The *d*-spacing of MMT was investigated by small-angle XRD diffractometry (X'Pert PRO MPD (PANalytical B. V., Netherlands) with a Cu K α radiation target at 40 mA and 40 kV and a scan rate of 1 deg/min, step size of 0.05 degree, with the scattering angle (2 θ) ranged from 2 to 8 degree.

2.7. Anti-swelling ratio test

The bentonite which was mainly comprised of Na-MMT was used due to its remarkable hydration in water. Firstly 0.5 g bentonite was soaked in 10 mL sample solution for 2 h at room temperature. After that, the bentonite phase and the solution phase were separated by a YuHua model TG-16 supercentrifuge (YuHua Company, China) under 1500 r/min for 15 min. Then the anti-swelling ratio of bentonite was calculate according to the following equation.

$$B = \frac{V_2 - V_1}{V_2 - V_0} \times 100\% \quad (1)$$

Where B is the anti-swelling ratio, %; V_2 are the volume of swollen bentonite in distilled water, mL; V_0 are the volume of swollen

bentonite in kerosene, mL; V_f are the volume of swollen bentonite in the sample solution, mL.

2.8. Temperature resistance test

The effect of temperature on apparent viscosity of sample solutions were tested by using a Haake RS 600 rotational rheometer (Haake, Germany) at steady shear rate of 170 s^{-1} to simulate injection rate in the range of $30\text{--}130 \text{ }^\circ\text{C}$.

2.9. Indentation hardness measurement

Indentation hardness of cores of the shale was researched by soaking the cores in solutions of the different samples at $80 \text{ }^\circ\text{C}$ for 24 h, and the core strength data of the shale were measured with RTR-1000 rapid triaxial rock testing system (GCTS, USA) in comparison to deionized water and KCl. The indentation hardness (IH) values, an indication of the mechanical property of the shale, were determined according to the following equation:

$$\text{IH} = \frac{F_M \times 10^3}{A} \times 100\% \quad (2)$$

where the indentation hardness (IH) value is the indication of the mechanical property of the shale, MPa, F_M is the maximum load before the rock is broken, kN, and A is the contact area, mm^2 . Here A is 4.446 mm^2 .

3. Results and discussion

3.1. Synthesis of PAAT

The effect of synthesis conditions on copolymerization of AM, AA and TCDAP were investigated, and the intrinsic viscosity and the viscosity-average molecular weight were measured. The results were listed in Table 1 (for the details, see Table S1-S2 and Fig. S1 in Supporting Information). The structure of PAAT was characterized by FT-IR and ^1H NMR spectroscopy and the results are presented in Fig. 2. The stretching vibration peaks of $-\text{NH}-$ and $\text{C}=\text{O}$ bond in the amide groups appeared at 3435.64 cm^{-1} and 1675.85 cm^{-1} , respectively. The peaks at 1173.49 cm^{-1} and 1049.28 cm^{-1} correspond to the stretching vibration of $-\text{SO}_2-$, suggesting the successful copolymerization of TCDAP monomer. The distinct peak around 1.54 ppm and $2.03\text{--}2.15 \text{ ppm}$ can be assigned to the $-\text{CH}_2-$ and $-\text{CH}-$ in polymeric chain, respectively. The peak at 3.74 ppm is due to the proton of $-\text{CH}_2-\text{N}-\text{CH}_2-$. The chemical shift value at 2.49 ppm is attributable to $-\text{CH}_3$ protons of $-\text{Ar}-\text{CH}_3$ in TCDAP, while the peaks at 7.42 ppm and 7.71 ppm , denoted as d and e in Fig. 2(b) respectively, are attributable to the protons of the benzene rings. These results verify the successful preparation of the copolymer PAAT.

Table 1 The optimum synthesis conditions and characteristics of PAAT

Sample	Apparent viscosity ^a (mPa·s)	Intrinsic viscosity ^b (mL/g)	Molecular weight ^b
PAAT	352.6	1372.00	6.70×10^6

^a The concentration of copolymer was 1 wt%. ^b The intrinsic viscosity and viscosity-average molecular weight was determined according to references. 26-28

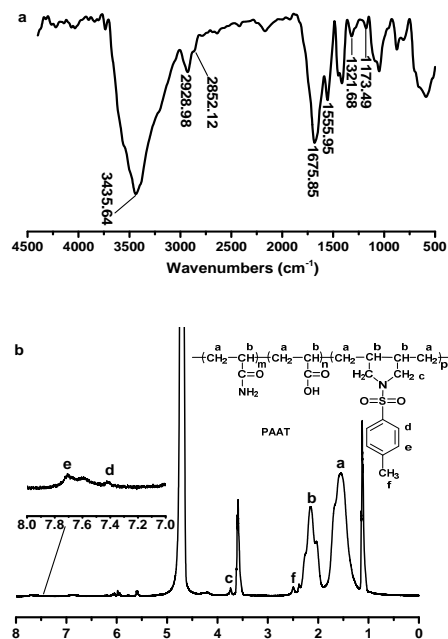


Fig. 2 (a) FT-IR spectra of PAAT; (b) ^1H NMR spectra of PAAT.

3.2. Effect of different PAAT/ILs on *d*-spacing of Na-MMT

The swelling inhibition of different PAAT/ILs complexes was investigated by comparing the *d*-spacing of MMT compared with water/ILs (see Table S3 and Fig. S2, Supporting Information). It was found in our previous works that polymer solutions slightly affected the *d*-spacing of Na-MMT with the increasing concentration.²⁹ The *d*-spacing data of MMT in PAAT/ILs are summarized in Table S3. The results indicated that compared with water/KCl and water/ILs, the PAAT/ILs exhibited significant capacity of anti-swelling, for instance, with the smaller *d*-spacing 13.16 \AA by PAAT/HmimBF₄ complex. Besides, PAAT/ILs with short chain substituent (HmimBF₄, emimBF₄ and AllymimBF₄) exhibited excellent clay inhibition of MMT. The *d*-spacing of MMT enlarged with the increasing alkyl substituent of PAAT/ILs. BenzylmimBF₄ or C_nmimBF₄ ($n > 6$) is essentially insoluble in water.^{30,31}

3.3. Effect of PAAT/HmimBF₄ complex on *d*-spacing of Na-MMT

The effect of PAAT/HmimBF₄ complex with varying concentration of HmimBF₄ on the *d*-spacing of MMT was further investigated. The results are shown in Fig. 3 and 4. The *d*-spacing of MMT was obtained to be about 18.60 \AA by HmimBF₄ and PAAT/HmimBF₄ complex with 1 wt% HmimBF₄, and the *d*-spacing of MMT drastically decreased to about 13.20 \AA with 2 wt% HmimBF₄. The abrupt decrease in *d*-spacing may occur only under a critical concentration of ILs.³² The *d*-spacing of wet MMT has no obvious changes with the concentration of HmimBF₄ from 2 to 5 wt%. The *d*-spacing of corresponding re-dried MMT is higher than that of untreated MMT (*d* spacing = 12 \AA). The results suggest that HmimBF₄ have intercalated in the MMT interlayer replacing Na⁺ in the original interlayer of MMT. The intercalation of the ILs confirms the different *d*-spacing of

MMT in different samples as indicated in Table S3 due to the size effect and arrangement of ILs.¹⁹

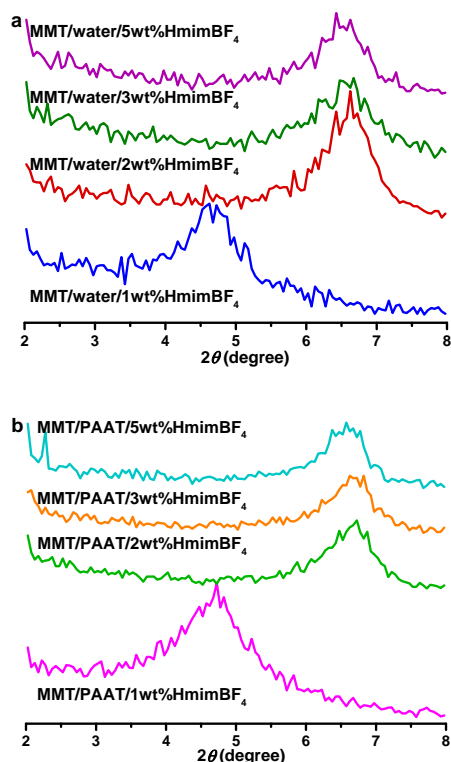


Fig. 3 XRD patterns of MMT in (a) water/HmimBF₄ with varying concentration of HmimBF₄, (b) PAAT/HmimBF₄ complex with varying concentration of HmimBF₄.

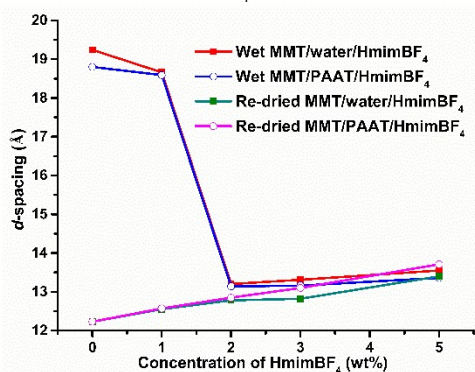


Fig. 4 The *d*-spacing of MMT in PAAT/HmimBF₄ complex with varying concentration of HmimBF₄

3.4. Anti-swelling ratios

The anti-swelling ratios of 0.3 wt% PAAT with different concentrations of HmimBF₄ ranging from 1 to 5 wt% were measured. The anti-swelling ratios of 1 to 5 wt% KCl solution and 1 to 5 wt% HmimBF₄ were also measured in comparison with PAAT/HmimBF₄ complex. The results are shown in Fig. 5. The pictures of swollen bentonite in different concentrations of KCl, HmimBF₄ and PAAT with different concentration of HmimBF₄ are also shown in Fig. 6. The anti-swelling ratio increases with the addition of KCl as well as HmimBF₄. When the concentration reaches about 3 wt% for PAAT/HmimBF₄ complex, its effect on the anti-swelling ratio is minimal. The anti-swelling ratio of KCl solution is much higher than that of the HmimBF₄ when the concentration is below 2 wt%. With

the concentration more than 3 wt%, the clay-swelling inhibition of HmimBF₄ is more effective than that of KCl under the same concentration. The anti-swelling ratio of PAAT/HmimBF₄ complex reaches a maximum, i.e. 85 % when the concentration of HmimBF₄ is 2 wt%.

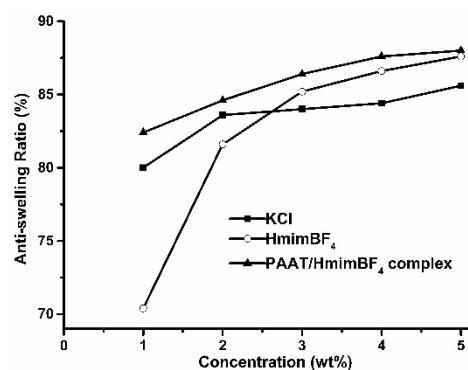


Fig. 5 The effect of concentration on anti-swelling ratio.

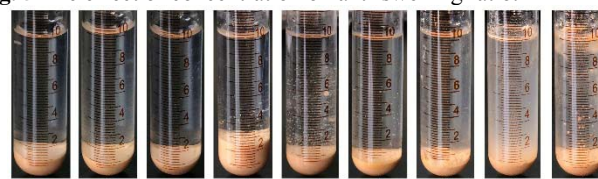


Fig. 6 Photographs of swollen bentonite in different samples (a-g: 1 wt% KCl, 2 wt% KCl, 3 wt% KCl, 1 wt% HmimBF₄, 2 wt% HmimBF₄, 3 wt% HmimBF₄, PAAT/1 wt% HmimBF₄ complex, PAAT/2 wt% HmimBF₄ complex, PAAT/3 wt% HmimBF₄ complex).

3.5. Interaction between PAAT and HmimBF₄.

Interaction between PAAT and HmimBF₄ are confirmed by ¹³C NMR method. The ¹³C NMR spectra of HmimBF₄, PAAT, and PAAT/HmimBF₄ complex are presented in Fig. 7. The chemical shift value at 183.81 ppm and 182.60 ppm can be assigned to the -COO⁻ of PAAT and PAAT/HmimBF₄ complex, respectively. Obviously, the resonance of -COO⁻ of PAAT/HmimBF₄ complex shifts to higher field compared to that of PAAT (from 183.04-183.81 ppm to 182.61-182.82 ppm), which is attributed to the electrostatic interaction. This electrostatic interaction could be the driving forces of ILs to exist in the peripheral space of the copolymer chains (Fig. 10 a). Apart from that, it is worth mentioning that hydrogen bonds might develop with oxygen atom in O=S=O or C=O groups of HmimBF₄ (Fig. 10 a).³³

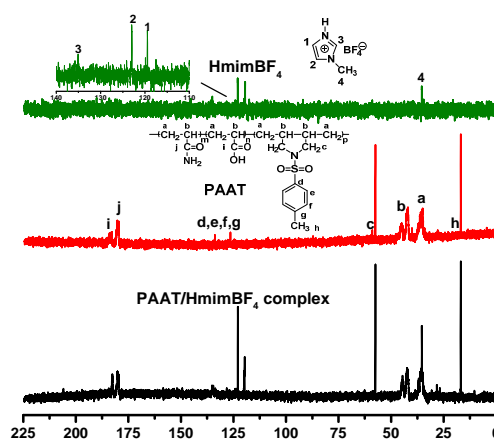


Fig. 7 ^{13}C NMR spectra of HmimBF₄, PAAT and PAAT/HmimBF₄ complex.

3.6. Temperature resistance

Fig. 8 shows the temperature resistance of 0.2 wt% PAAT and PAAT/HmimBF₄ complex solutions with copolymer concentration of 0.2 wt% and HmimBF₄ concentration of 2 wt%. The apparent viscosity of PAAT gradually reduces with the rise of temperature. Although the viscosity of solution decreases due to the addition of HmimBF₄ containing organic cation, the apparent viscosity of PAAT/HmimBF₄ complex shows an increase from 30 to 60 °C. And the viscosity of solution maintains almost same value from 60 to 110 °C which can be ascribed to the strong interaction among PAAT/HmimBF₄ complex within this temperature range. At high temperature, the apparent viscosity of PAAT and PAAT/HmimBF₄ complex solutions both greatly decreases because the further temperature increasing causes the destruction of the interaction of the polymer molecules.

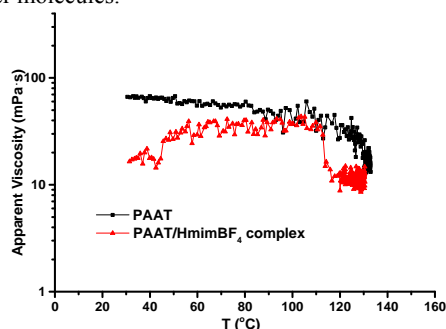


Fig. 8 Temperature resistance of apparent viscosity of PAAT and PAAT/HmimBF₄ complex.

3.7. Indentation hardness

The hydration and swelling of the clay can lead to the collapse, fracture and deformation of rock. Indentation hardness analysis is important for evaluation of the performance of clay hydration inhibitor. The components of used core mineral is 47.3% illite, 22.0% illite-montmorillonite mixed-layer, 23.0% chlorite and 7.7% kaolinite. The results of test are listed in Table 2. The indentation hardness of origin rocks was about 482.77 MPa and the indentation hardness retained in deionized water was 21% due to the strong hydration of clay. The indentation hardness retained 351.06 MPa (73%) with 2 wt% HmimBF₄, which is slightly higher than the value 348.92 MPa (72%) with 3 wt% KCl. The even higher retained indentation hardness, up to 360.23 (75%), can be obtained using PAAT/HmimBF₄ complex. In our previous work,¹⁵ the PANAAcopolymer synthesized via copolymerization of AM, AA, *N,N*-diallylbenzylamine (NAPA), and 2-(acrylamide)-2-methylpropane-1-sulfonic acid (AMPS) could retain 74% indentation hardness but it had to blend with 3 wt% KCl. In the present study, the inhibition of clay hydration of PAAT/HmimBF₄ complex is significantly enhanced compared with PAAT (62%). Fig. 9 shows photographs of core samples of the shale before and after soaking in different solutions. The original core samples after the hardness test under external stress shows brittle failure. Through the comparison for the photographs of core samples of the shale before and after soaking in different solutions, no cracks can be observed on the core samples after the cores soaked in HmimBF₄ and

PAAT/HmimBF₄ complex solutions. These results clearly demonstrate that PAAT/HmimBF₄ complex can be potentially used for shale inhibition.

Table 2 Results of indentation hardness test

Soaking samples ^a	Maximum load (kN)	Indentation hardness (MPa)
Water	0.4504	101.38
KCl	1.5513	348.92
PAAT	1.3252	298.07
HmimBF ₄	1.5608	351.06
PAAT/HmimBF ₄	1.6016	360.23

^a The concentration of KCl, HmimBF₄, copolymer was 3, 2 and 0.3 wt%, respectively.

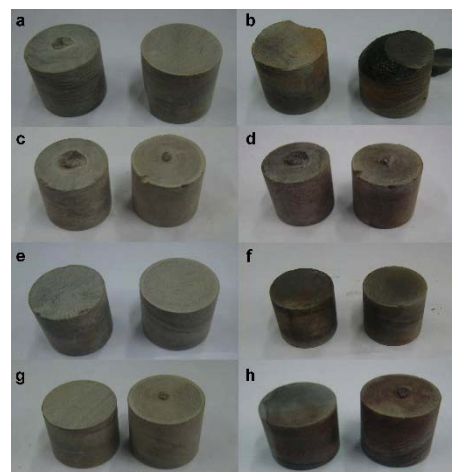


Fig. 9 Photographs of original core samples of shale before hydration: (a), (c), (e) and (g); and after soaking in different solutions: (b) water, (d) HmimBF₄, (f) PAAT, and (h) PAAT/HmimBF₄ complex.

3.8. Clay hydration and swelling inhibition mechanism

Fig. 10 depicts the possible mechanism for the clay hydration and swelling inhibition with the PAAT/HmimBF₄ complex. The enhanced clay inhibition can be attributed to the electrostatic interactions between the cations of HmimBF₄ and negative charges on the clay surfaces (Fig. 10, b). Besides it is believed that the absorbed copolymer chains of PAAT/HmimBF₄ complex can prevent further clay hydration by encapsulating the clay particles and improve the acting time and scour resistance (Fig. 10, b). Meanwhile, hydrogen bonds formed between water molecule and some groups such as O=S=O, -NH₂ groups of PAAT and/or anion BF₄⁻ of HmimBF₄ could compete with the ones between water molecule and the silica or alumina functionalities reducing the ingress of water into MMT.²

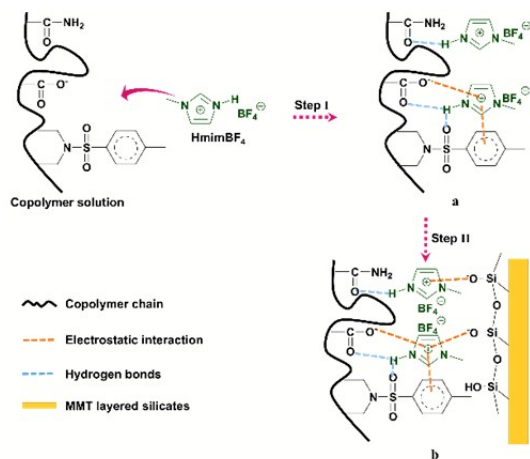


Fig. 10 Schematic representation of the clay hydration and swelling inhibition mechanism (a. interaction between copolymer and HmimBF₄, b. interaction between copolymer and HmimBF₄).

4. Conclusions

In conclusion, complexes of copolymer PAAT and ionic liquid HmimBF₄ were successfully prepared. The *d*-spacing of MMT is significantly reduced by PAAT/HmimBF₄ complex from 19.24 to 13.14 Å, and the PAAT/HmimBF₄ complex with 2 wt% HmimBF₄ can improve the indentation hardness retention of shale to 75% and increase the anti-swelling ratio up to 85%, effectively minimizing clay hydration and swelling. ¹³C NMR spectra verified the existence of electrostatic interaction and hydrogen bonds between PAAT and HmimBF₄, and the possible clay hydration and swelling inhibition mechanism has been presented. It is also shown that PAAT/HmimBF₄ complex exhibits better thermal stability than PAAT, suggesting that it can be used as potential clay and shale hydration inhibitor in high temperature oil and gas wells.

Acknowledgements

The authors gratefully acknowledge the National Natural Science Foundation of China (Nos. 51274172 and U1262209) for financial support.

Notes and references

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† Electronic Supplementary Information (ESI) available: [The effect of synthesis conditions on copolymerization and the intrinsic viscosity of PAAT; The *d*-spacing of MMT in different PAAT/ILs complexes; ¹H NMR and ¹³C NMR spectra of TCDAP and PAAT]. See DOI: 10.1039/b000000x/

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