Synthesis and property of a novel clay anti-swelling agent

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Abstract. In this work, a novel oil field clay anti-swelling agent triethylallyl ammonium bromide (TEAAB) was prepared. The effect of reaction condition on TEAAB yield was studied, and the optimal reaction conditions is reaction temperature 60 °C, reaction time 7 hours, and molar ratio of raw materials of (triethylamine: bromopropene) = 1.4. Anti-swelling results showed that TEAAB has an excellent anti-swelling performance and the anti-swelling rate is up to 98% when the dosage was 6%.

Introduction

Shale make up over 75% of the drilled formations, and over 70% of the borehole problems are related to shale instability clay [1]. Wellbore instability is one of the main problems that engineers meet during drilling, and it is an important factor to the reduction of reservoir permeability. When shale meets the working fluid outside, the water will be inevitable penetrates into the lattice structure of clay, which can cause the result that the volume of clay formation is increased, and leading to the decline of oil and gas reservoir permeability [2-4]. The degree costs for oil and gas wells drilling have continually increased over the past decades, exploration and development operations have expanded globally as the economics of exploring and producing for oil and gas have improved in drilling technology [5-6]. Thence, the reservoir protection is extraordinarily important in the exploration. Therefore, the development of novel and efficient clay anti-swelling agent become significant issue of oilfield workers [8-10].

The organic cationic and its polymer, due to the clay-stabilization ability is much more than inorganic salts and water-soluble polymer electrolyte, has served as the most developed and widest used anti-clay swelling reagent in the oil field. The clay surface will with a negative charge due to lattice substitute. A variety of clay anti-swelling agent have been implicated in the oilfield, however, the cation volume is too large to function well.

Therefore, in this work, we have designed a suitable small organic cation: triethylallyl ammonium bromide (TEAAB). The effect of reaction condition on the target yield was studied, and we have studied its anti-swelling performance.

1. Experimental

1.1. Materials
Triethylamine, allyl chloride, acetone, anhydrous ethanol, Chengdu Kelong Chemical Reagent Factory, the above reagent are all analytical grade, Sodium bentonite (Na-MMT) was purchased from Xiazi Street Bentonite Co., Ltd.

1.2. Preparation of TEAAB
Pre-heat the water bath to the required temperature, and accurate amount of triethylamine, acetone and bromopropene are added to the water bath, keep the condensation reflux at a certain temperature. Because the product is insoluble in acetone, a snow-white knot is obtained after the reaction is completed. Then, decant the acetone and dry the product in a vacuum oven to constant weight and calculate the yield.

1.3. Structure Characterization
TEAAB was firstly washed with acetone to remove the non-polarity impurities and then washed with ethanol to elute polarity impurities, after drying in the vacuum oven, FT-IR spectra were recorded via a WQF-520 Fourier transform infrared spectrometer in the wave number range of 4000-500 cm⁻¹.

1.4. Anti-swelling performance evaluation of TEAAB
Weigh 0.50g bentonite and 10ml pure water to a 10 ml centrifuge tube and centrifugated for 15 min at 1500 r/min. Then read the volume V1 of the mixture. Repeat the previous step, added 10 ml kerosene and read the volume V2 of the mixture. Then added 10 ml TEAAB and read the volume V3 of the mixture. Anti-swelling rate was calculated by the following formula (1):

$$\sigma = \frac{V_1 - V_3}{V_1 - V_2}$$

(1)

2. Results and discussion

2.1. Effect of reaction conditions on TEAAB yield

2.1.1 Reaction temperature
The smooth progress of the reaction needs to be carried out at a certain temperature, but the quaternary ammonium salt will decompose at a certain temperature. Under the conditions of reaction time for 6 hours and molar ratio of raw materials was (triethylamine: bromopropene =1: 1.2), the effect of the reaction temperature on the product yield was studied.

Figure.1 Effect of reaction temperature on TEAAB yield.
It can be seen from the results that as the reaction temperature increases, the yield of the product shows an upward trend. When the reaction temperature was 60 °C, the yield is the highest at 63.5%. As the reaction temperature was continue to increase, the yield was slightly reduced. The reason may be that the product has been decomposed at 70 °C. Therefore, the optimal reaction temperature was 60 °C.
2.1.2 Reaction time

The reaction time will greatly affect the product yield. When the reaction time is short, the reaction is not sufficient. When the reaction time is completed, it is not necessary to extend the reaction time. Under the conditions of reaction temperature at 60 °C and molar ratio of raw materials was (triethylamine: bromopropene = 1: 1.2), the effect of the reaction time on the product yield was studied.

![Figure 2. Effect of reaction temperature on TEAAB yield.](image)

It can be seen from the Figure 2 that with the increase of reaction time, the yield of the product shows an upward trend, but when the reaction time exceeds 7 hours, the continued extension of the reaction time has little effect on the yield. Therefore, the optimal reaction time for this reaction is 7 h.

2.1.3 Reaction molar ratio

Both the reaction raw materials bromopropene and triethylamine are easy to volatilize. Therefore, the effect of the raw material ratio on the product needs to be examined. Under the conditions of reaction temperature at 60 °C and reaction time was 7 h, the effect of reaction molar ratio (triethylamine: bromopropene) on the product yield was studied, and the results are shown in Figure 3.

![Figure 3. Effect of molar ratio on TEAAB yield.](image)

From the results showed in Figure 3 we can conclude that as the molar ratio of the raw materials (triethylamine: bromopropene) increased, the yield of the product shows an upward trend. When the molar ratio was 1.4, the yield of the product was 71.3%. Therefore, the optimal reaction molar ratio (triethylamine: bromopropene) was 1.4.

It can be seen from the research results that the optimal reaction conditions for TEAAB are: reaction temperature is 60 °C, reaction time is 7 hours, and molar ratio of raw materials of (triethylamine: bromopropene) is 1.4.
2.2. Anti-swelling performance evaluation

The anti-swelling performance of TEAAB with different concentrations on clay is shown in Figure 4. From left to right the concentration is 1%, 2%, 4%, 6%, 8%, and 10% and the corresponding anti-swelling rate is 94%, 95%, 95.6%, 97.2%, 98.0%, 98.0%. As the concentration increases, the anti-swelling effect has a clear upward trend. The anti-swelling performance of pure water TEAAB and kerosene is shown in Figure 5, from left to right is kerosene, 0.8 % TEAAB and pure water. It can be clearly seen that the product has a nice anti-swelling performance.

3. Conclusion

In this work, a novel oil field clay anti-swelling agent triethylallyl ammonium bromide (TEAAB) was prepared from triethylamine and bromopropylene. The effect of reaction condition on TEAAB yield was studied. We have used centrifugal method to study its anti-swelling performance, and found that it has excellent anti-swelling performance. When the dosage is 6%, its anti-swelling rate can be as high as 98%. Results showed that TEAAB will be a nice anti-swelling agent and has a good application prospect in oil and gas field.

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