



# Wettability studies of reduced-charge montmorillonites modified by quaternary ammonium salts using capillary rise test



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## ABSTRACT

A series of montmorillonites with systematically reduced layer charge were prepared by a standard method of different fractions of  $\text{Li}^+$ -fixation in montmorillonite, which could be used to mimic an oil reservoir. Three kinds of quaternary ammonium salts (QASs) with different cationic charges and structure sizes were used singularly or in compound form to modify the reduced-charge montmorillonites (RCMs). The wettability alterations of the organo-RCMs for deionized water and cyclohexane were studied based on capillary rise method and were compared using the Lipophilic to Hydrophilic Ratio (LHR). The results indicate that RCMs singularly modified by three kinds of QASs show different wettability characteristics, whereas compound modified by QASs have a synergistic effect on the wettability. Moreover, the compound type of the QASs plays a more important role on LHR values than the mix proportion. The results of this work also indicate that it is possible to regulate the wettability of the organo-RCMs by simultaneous control of the type, the compound ratio of QASs and the layer charge characteristics, which is helpful in providing theoretical guidance for the oil production.

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## 1. Introduction

The wettability of small particles and porous materials is a very important property involved in many practical problems, especially in chemical, pharmaceutical, water treatment technologies and oil production [1–4]. There are two interfaces involved in oil recovery. One is the water/oil interface, the other is the oil/solid interface. The latter is related to the reservoir wettability [5]. Wettability of solid surface influences oil displacement efficiency a lot [6]. If the reservoir wettability is changed from mostly oil-wet to water-wet, the recovery efficiency can be improved considerably [7]. Thus the investigation on wettability of reservoir is significant for efficient oil recovery. The wettability of solid material surface is generally characterized in terms of the contact angle between solid and liquid interfaces [8]. Generally, it is difficult to determine the contact angles of clay particles by direct methods such as sessile techniques [9] and Wilhelmy plate method [10]. The capillary rise technique, however, is extensively used to measure the contact angles of small particles and porous materials, whose basic theory is Washburn's equation [11–13].

Montmorillonite is a crucial mineral with numerous favorable properties [14,15]. Since it is often present in the oil reservoir, it can be used to mimic reservoir mineral for wettability studies in practice research. Layer charge is recognized as one of the most important characteristics of 2:1 phyllosilicates, which stems from substitutions in the structure of minerals (permanent charge) and from ionizable groups on external

surfaces of the minerals (variable charge) [16]. Typically, it affects several properties of clays such as hydration of interlayer cations, swelling, cation exchange capacity and rheological properties [17–20]. The reduced-charge montmorillonites (RCMs) have often been prepared from their  $\text{Li}^+$ -forms, which is currently known as the Hofmann–Klemen effect [21]. In this approach, the composition, crystallinity, and other parameters are almost unchanged during the charge reduction. Therefore, the series of RCMs provide a unique model for probing the effect of the layer charge while keeping the other parameters constant at the same time [22].

According to reference [23], clay swelling has an adverse impact on oil recovery of water flooding and may significantly increase oil well construction costs. Minimizing clay swelling is therefore an important area attracting a large amount of interest from both academia and industry. Quaternary ammonium salt (QAS), a potential chemical flooding agent, can not only effectively reduce the extent of clay swelling, but also change the wettability of the oil reservoir [24]. In addition, QASs are commonly used for preparing organo-clay because of their versatile functionalization and cost effectiveness [25].

In the present work, organo-RCMs were synthesized by modifying the reduced-charge montmorillonites (RCMs) with three kinds of QASs, trimethyl ethyl ammonium methylsulfate (EAS), hexamethyl propyl diammonium methylsulfate (PDAS) and octamethyl diethylene triammonium methylsulfate (DETAS). They were simplified as E, P and D in the following paragraphs, respectively. The organo-RCMs were used to mimic reservoir mineral. Their wettability alterations for deionized water and cyclohexane were studied based on the capillary rise method and were compared using the Lipophilic to Hydrophilic

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Ratio (*LHR*). The objective of this paper was to find the effect that the type, the compound ratio of QASs and layer charge has on the wettability of organo-RCMs, so as to provide a theoretical guidance for oil exploration.

## 2. Capillary rise

Capillary rise in porous media has been studied for many years, since the pioneering work of Washburn in 1921 [26]. When liquid penetrates into the capillary tube, the air in the tube will be compressed and then the air pressure will increase. Given that the packed powder column is modeled as a bundle of uniform capillary tubes, the relationship of the pressure increment  $\Delta P$  of air to time  $t$  in powder bed can be expressed as follows [11]:

$$(\Delta P)^2 = \left( \frac{\beta \gamma \cos \theta}{\eta} \right) t \quad (1)$$

where  $\Delta P$  is the pressure increase of air in the porosity of packed bed,  $\beta$  is a natural parameter which is only depends on the powder bed and particle size,  $\gamma$  is the surface tension of the testing liquid,  $\eta$  is the viscosity of the penetrating liquid,  $\theta$  is the contact angle, and  $t$  is the time of liquid penetrated in powder bed. As long as the packing state and the particle size remain similar,  $\beta$  is regarded to be constant, and then the slope of measurement curve is as follows:

$$k = \frac{\beta \gamma \cos \theta}{\eta} \quad (2)$$

This slope can be experimentally determined for each type of particle packing and can be used to evaluate the wettability. However, the  $\beta$  value is rather difficult to be determined in any case, Chang et al. introduced a Lipophilic to Hydrophilic Ratio (*LHR*) concept based on the Washburn equation to compare the wetting differences of clay particles [11]. *LHR* is defined as:

$$LHR = \frac{\cos \theta_o}{\cos \theta_w} \quad (3)$$

where  $\theta_o$  and  $\theta_w$  are the contact angles of the oil phase and the water phase for one kind of powder, respectively. Combining Eq. (2) with Eq. (3), the following expression for *LHR* can be derived:

$$LHR = \frac{k_o \eta_o \beta_w}{k_w \eta_w \beta_o} \cdot \frac{\gamma_w}{\gamma_o} \quad (4)$$

For a similar column packed by the same clay particles,  $\beta_o$  and  $\beta_w$  could be regarded as identical, thus Eq. (4) can be simplified as:

$$LHR = \frac{k_o \eta_o}{k_w \eta_w} \cdot \frac{\gamma_w}{\gamma_o} \quad (5)$$

where  $k_o$  and  $k_w$  are the measurement curve slopes of oil and water wetting a clay sample, respectively. Obviously the *LHR* value, which reflects the difference of wetting selectivity of a clay sample to oil and water, depends not only on the penetrating rates of oil and water, but also on the values of viscosity and surface tension of wetting liquids. This paper applies Eq. (5) to investigate the lipophilic and hydrophilic properties of a series of organo-RCMs in order to obtain some significant results about the wettability because there is so far little literature information in this aspect.

## 3. Experimental section

### 3.1. Materials

N,N-Dimethyl ethyl ammonium, N,N,N',N'-tetramethyl diamino-propane and N,N,N',N'',N''-pentamethyl diethylenetriamine were purchased from J&K Chemical Ltd. The tertiary amines reacted with dimethyl sulfate (Tianjin Guangfu Fine Chemical Research Institute, China) to obtain the corresponding quaternary ammonium salts [27]: N,N,N-Trimethyl ethyl ammonium methylsulfate (E), N,N,N,N',N',N'-hexamethyl propyl diammonium methylsulfate (P) and N,N,N,N',N'',N'',N''-octamethyl diethylene triammonium methylsulfate (D). These three kinds of QASs were confirmed by FT-IR, <sup>1</sup>H NMR and element analysis. Their chemical structures are shown in Fig. 1.

The montmorillonite (Mt) was purchased from the Zhejiang Institute of Geology and Mineral Resources, China. The purity was >97% and it was used without further purification. Its chemical composition was found to be as follows: 67.16% SiO<sub>2</sub>, 20.60% Al<sub>2</sub>O<sub>3</sub>, 4.11% MgO, 3.21% CaO, 2.20% Fe<sub>2</sub>O<sub>3</sub>, 1.47% Na<sub>2</sub>O, 0.92% K<sub>2</sub>O, 0.17% TiO<sub>2</sub> and 0.16% others. Lithium chloride (LiCl), sodium chloride (NaCl) and cyclohexane (analytic grade) were all purchased from Tianjin Guangfu Fine Chemical Research Institute, China. The deionized water was produced by reverse osmosis, passage through two stages of mixed ion exchange resin bed followed by a filtration stage of activated carbon. Apolar cyclohexane and polar deionized water corresponding to the oil phase and the water phase were used in the capillary rise test. Their characteristics are listed in Table 1.

### 3.2. Sample preparation

The reduced-charge montmorillonites (RCMs) were prepared by an ion exchange reaction with different molar contents of lithium–sodium (Li<sup>+</sup>/Na<sup>+</sup>) cations. The mixed solutions of LiCl and NaCl with a final ionic strength of 1 M and lithium fractions were 40, 50, 60, 70 and 80%, respectively [28]. The excess salts were washed out with ethanol and then the dispersions were centrifuged and spread over a silica slide. The samples were allowed to dry at 220 °C in a muffle furnace for 24 h. After cooling in the desiccator, size fractions of less than 74 μm were obtained by dry-sieving through stainless steel sieves. The materials hereinafter are referred to as Mt-40, Mt-50, Mt-60, Mt-70 and Mt-80, where the number indicates the lithium fraction used for

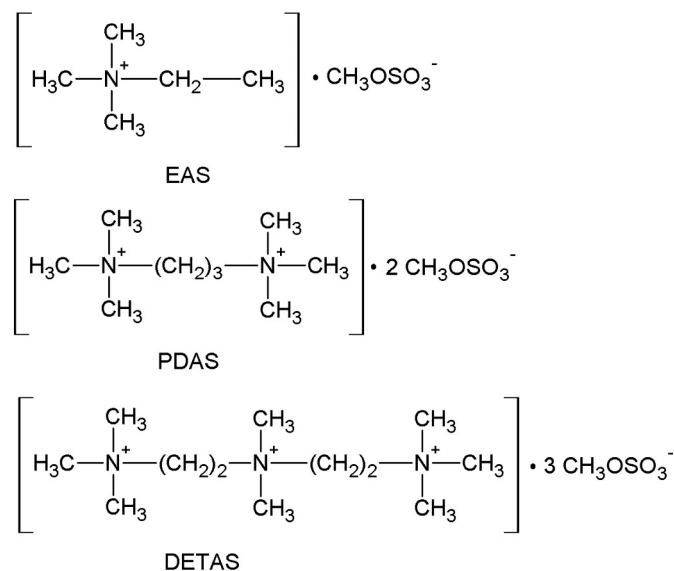


Fig. 1. Chemical structures of QASs: trimethyl ethyl ammonium methylsulfate (EAS), hexamethyl propyl diammonium methylsulfate (PDAS) and octamethyl diethylene triammonium methylsulfate (DETAS).

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