Inspired by the successful development of shale oil/gas exploration in North American, multiple continental oil fields in China have vigorously put forward its evaluation and exploration of shale oil. However, the outcomes of shale oil drilling in China are not well as expected. One of the important reasons is that the fluidity of shale oil is poor, resulting in the low effectiveness of production. The shale oil fluidity is, to some extent, determined by its occurrence status, which is influenced by not only the pore structure characteristics, but also the reservoir medium or surrounding rock. It means that occurrence status is closely related to the oil-water-rock interaction. Wettability is a comprehensive parameter to characterize the rock-fluid interaction, and it has important significance in understanding the characteristics and mechanism of oil-water occurrence in shale.

The previous studies have mostly focus on the wetting characterization of quartz and calcite to represent the sandstone and carbonate reservoir, respectively. It will cause error when directly applying those results to the shale that has complex mineral composition. In addition, the effect of the chemical properties of formation water on the wettability is still controversial (Berg et al., 2010). The purpose of the work is to investigate the wetting characterization of six common minerals in shale by measuring the contact angle of droplet in the mineral surface in air (sessile drop) and in water (pendant drop). The contact angles between the liquid and minerals are decreased with decreasing liquid surface tension. In our experiments, the polarity and surface tension of kerosene, NN-DMDA, 3-Dodecylthiophene increases gradually, resulting in the reducing extent of spreading.

The pendant drop method was used to measure the contact angle between kerosene, NN-DMDA, 3-Dodecylthiophene and mineral surface in aqueous phase. The contact angle is defined between the water-oil interface and the solid surface, and is measured through the high polar phase, in this case water. The contact angles of all the experiments are less than 90º indicating that the minerals are hydrophilic, and the interfacial tension between water and mineral are smaller than that between oil components and mineral. In oil-water systems, the wettability of the rock minerals can vary with the oil composition properties. The contact angles between NN-DMDA with minerals are the highest in our experiments, indicating that the NN-DMDA has the best affinity with mineral.

The adsorption of polar components of crude oils onto the mineral surface in aqueous phase is sensitive to the brine type and salinity (Anderson, 1986; Shabib et al., 2014). This work discusses the influence of brine type and salinity on the wettability of minerals with NN-DMDA. In the presence of aqueous solutions of calcium chlorides, the contact angles are less than 90º for all the minerals. The contact angles of quartz, potassium feldspar, dolomite and

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Experimental Investigations of the Mineral Wettability in Shale and its Influence Factors

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pyrite with NN-DMDA increase first and then decrease with increasing salinity (Fig. 1a), indicating that their hydrophilicity decreases first and then increases. Whereas the contact angles of calcite, and albite increase first and then to be stable or increased slightly with increasing salinity (Fig. 1b), indicating that the wettability is constant after a certain salinity. For the aqueous solutions of sodium bicarbonate, the contact angles of quartz, albite and potassium feldspar increase first and then decrease with increasing salinity (Fig. 1c). It is noted that at the salinity of 8000 and 15000 mg/L, the wettability of these minerals reverses from hydrophilic to hydrophobic. With increasing salinity, the contact angles of calcite and dolomite also increases and then decreases but with small variation, whereas the contact angle of pyrite is monotonously decreasing (Fig. 1d).

4. The mineral wettability shows different characteristics in different salinity range. Brine types and salinity can influence the stability of water film and the magnitude of interfacial tension, which mainly through the effect of multivalent metal cations on solubility of crude oil surfactant, and the pH value on the rock surface charge properties and surface active agent ionization process (Shabib et al., 2014; Alotaibi et al., 2010). Take pH effect for example, the pH value of sodium bicarbonate solution is between 8.31 and 8.89. In this aqueous, the quartz and calcite surface show negative charge and positive/less negative charge, respectively, and NN-DMDA shows positive charge through the protonation of amidogen. According to the “opposite charges attract”, NN-DMDA are more easily adsorbed onto the surface of quartz, resulting in the weaker hydrophilic of quartz than calcite, even reverse to hydrophobic.

In summary, the common non-clay minerals in shale are hydrophilic, but with a different degree of hydrophilicity. The wettability of rock minerals varies with oil components, brine type and salinity. Sodium bicarbonate solution can significantly change the wettability, even lead to the phenomenon of reversed wettability for some minerals (i.e., quartz, albite). This results would form the basis for further understanding the wetting properties of shale.

References