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Zeta potential of limestone in a large range of salinity

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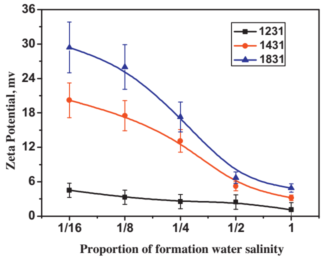
HIGHLIGHTS

- Zeta potential (ζ) of limestone in a large range of salinity is studied.
- Adsorption of oil polar fractions is favorable to the increase of the ζ.
- High salinity decreases the effect of other influencing factor on the ζ.
- Increasing salinity is beneficial to the adsorption of surfactant onto limestone.
- Salinity is the determining factor on the ζ in the high-salinity water.

GRAPHICAL ABSTRACT

Zeta potential of TP powder adsorbed surfactants in different proportions of formation water.



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ABSTRACT

Experimental investigations have been conducted to elucidate the variation of the zeta potential (ζ) of limestone in a large range of salinity. The effects of the type and concentration of inorganic salts, the pH, and the adsorption of the oil polar fractions, naphthenic acid and cationic surfactant on the ζ have been investigated in the paper. The results show that the ζ rises toward the positive with the increase of the concentration of inorganic salt, but the increase rate gets very low in the high-concentration brine. The mineral composition of the limestone has also some influence on the ζ. The high pH value results in the large ζ, and the adsorption of oil polar fractions and naphthenic acid is beneficial to the increase of the ζ. However, increasing the salinity reduces the effect of the pH, oil polar fractions and naphthenic acid on the ζ, and the ζ is nearly not affected by the above influencing factor in the formation water (total salinity: 223,802.8 mg/L). Among the three surfactants of dodecyl trimethyl ammonium chloride, tetradecyl trimethyl ammonium chloride and octadecyl trimethyl ammonium chloride, the adsorption of octadecyl trimethyl ammonium chloride onto the rock surface is more efficient to increase the ζ, and the more adsorption leads to the higher ζ in the surfactant solutions with the same salinity. The adsorption quantity of octadecyl trimethyl ammonium chloride onto the limestone is the largest when the surfactant concentration is the same, and the high salinity promotes the adsorption of the surfactant onto the limestone. Nevertheless, the ζ decreases rather than rising due to the simultaneous increase of the salinity and surfactant adsorption. The above results indicate that the salinity is the dominant influencing factor on the ζ of the limestone in various conditions, which can be used as theoretical guidance for improved oil recovery in the carbonate reservoir with different salt contents.

1. Introduction

Solid particles can create surface charges in saline solutions. The proper reaction mechanisms existing at the colloid surfaces are as follows [1]: (1) differential loss of ions from the crystal lattice

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Table 1
The properties of formation brine from the oil reservoir.

Ion type	$Na^+ + K^+$	Mg^{2+}	Ca^{2+}	Cl^-	HCO_3^-	Total salinity
Ion content (mg/L)	73,298.4	1518.8	11,272.5	137,529.5	183.6	223,802.8

because of the rupture of ionic or covalent bonds; (2) adsorption of charged species from the surrounding solution; (3) ionization of chemical groups on the surface. The above charged species result in the generation of the electrical-double-layer. Interfacial phenomena at rock/water interfaces are mainly affected by the electrical-double-layer forces, and several studies have demonstrated that the electrical-double-layer is closely associated with improved oil recovery [2–5]. The electrical-double-layer thickness, which is affected by the pH, ionic strength, and surfactant, relates to the wettability, and the wettability contributes significantly to EOR performance. Therefore, it is necessary to understand the electrokinetics of the limestone particles in the saline solutions.

The ζ is the potential at the shear plane of the electrical-double-layer, and it is significantly affected by the pH and ionic strength of water. In general, H^+ and OH^- are potential determining ions for rock particles, and the surface charge is pH dependent and can be either negative or positive. However, formation water causes carbonate dissolution and mineralogical changes. Ions commonly existing in the formation water, such as Na^+, Ca^{2+}, Mg^{2+}, H^+, Cl^-, HCO_3^-, and SO_4^{2-}, can form the chemical complexes due to various reasons either in the bulk aqueous phase or at the rock surface [6,7]. As a result, different research results of the carbonate particle's ζ were obtained. Some scientists reported negative charges for calcite [8,9], whereas other investigators found that calcite had positive charges [10,11]. Additionally, the ζ of the sandstone have been studied by many researchers, but the investigations on the ζ of the carbonate rock are relatively few [12–14]. More important, the previous researches on the ζ are mainly conducted in the low-salinity solution [14,15], and the effect of the high salinity on the ζ of the calcite is not clear. Therefore, the ζ of limestone in a larger range of salinity should be investigated, especially the influence of the high ionic strength on the ζ is more necessary to be clarified since more and more high-salt reservoirs have been discovered.

In the paper, the effects of the type and concentration of inorganic salts, the pH, and the adsorption of the oil polar fractions, naphthenic acid and cationic surfactant on the ζ have been investigated. The differences on the ζ of limestone particles between this study and other research work that has been published are: (1) This research was the first to investigate the ζ of different natural limestone particles in such a large range of salinity (the highest salinity is 223,802.8 mg/L); (2) The influence of Na^+, Ca^{2+} and Mg^{2+}, which are the main cations in the formation water, on the ζ were studied comparatively; (3) The influence law of the oil polar fractions and organic acid with different concentrations on the ζ was researched in this paper. In the literature, the effect of these polar fractions on the ζ was only studied qualitatively; (4) The interaction between surfactant adsorption and the ζ was investigated. Hence, the research results will not only provide a clear understanding of the electrical-double-layer force between the limestone and the formation fluids with a large range of salinity, but also help to elucidate the mechanisms of improved oil recovery in the carbonate reservoir.

2. Materials and methods

2.1. Materials

Synthetic formation water was tested simulating a field case in the oil reservoir in Xinjiang of China (Table 1). It was prepared using deionized water and then passed through 1-μm filter paper. Limestone cores were also collected from the same reservoir. A ceramic mortar and pestle were used to crush the limestone cores into fine powders (main size distribution: 3–5 μm). The powder's XRD analysis results are shown in Table 2, and the mineral compositions are obviously different. Prior to use, the limestone powders were treated by ultrasonic cleaning with ethanol and distilled water successively, and then they were heated at 80 °C for 12 h. Dodecyl trimethyl ammonium chloride (1231, ≥98%), tetradecyl trimethyl ammonium chloride (1431, ≥98%), and octadecyl trimethyl ammonium chloride (1831, ≥98%) used in this experiment were all purchased from Sinopharm, and the asphalt and naphthenic acid were produced in Karamay.

2.2. Measurements of zeta potential

Phase-analysis light-scattering (PALS) technique was applied to determine the zeta potential of limestone particles at 25 °C. The solution of solid/brine sample was prepared by adding 1 wt% of solid powder to the brine, and then the powder suspension was established by shaking it for two minutes with ultrasonic oscillator. The pH of the solution was adjusted by using either HCl or NaOH solution, and the measurements were conducted at pH = 8 unless stated. Finally the zeta potential was measured, and three runs were conducted for each sample, with the average being taken (all the ζ in the paper is the actual value instead of the absolute value).

2.3. Adsorption of the surface activesubstance onto limestone particles

The surface activesubstance in the paper refers to the oil polar fractions (resin–asphaltene), naphthenic acid and cationic surfactant. Asphalt with the total content of asphaltene and resin exceeding 40% was dissolved in *n*-hexane, and then the asphalt simulated oil with the asphalt concentration of 0 mg/g, 1 mg/g, 2 mg/g, 3 mg/g, 4 mg/g and 5 mg/g was produced, respectively. The content of asphalt in *n*-hexane could be measured with the colorimetric method, and the adsorption capacity of the asphalt onto the limestone particle was the concentration difference of asphalt in *n*-hexane before and after the adsorption process. The standard curve of asphalt absorption is showed in Fig. 1, and the linear regression

Table 2
XRD analysis results of carbonate cores.

Sample	Mineral content (%)							
	Quartz	Potash feldspar	Plagioclase	Calcite	Ankerite	Siderite	Pyrite	Clay mineral
TP	9	–	–	82	4	–	1	4
AD	1	–	–	98	–	–	–	1
AO	16	1	–	71	–	1	2	9
S86	19	2	9	47	14	–	1	8