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Electrokinetic properties of barite nanoparticles suspensions in different electrolyte media

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Abstract In this study, electrokinetic properties of barite nanoparticles have been investigated in water. A series of systematic zeta potential measurements have been performed to determine the isoelectric point (iep) and potential-determining ions (pdi), and the effect of mono-, di-, and trivalent anions sodium salts such as NaCl, $NaNO_3$, $NaCH_3COO$, Na_2SO_4, Na_2CO_3, and Na_3PO_4 on the zeta potential of barite nanoparticles. Barite nanoparticles yields an isoelectric point at pH 7.8. The zeta potential for the barite nanoparticles has ranged from +15.5 mV at pH ~ 3 to –19.8 mV at pH ~ 9.5 at 25 ± 1 °C in water. It is proved that the valency of the ions greatly influence on the electrokinetic behavior of the suspension. Monovalent anions were found to have a weak effect on the zeta potentials. The negative zeta potentials were observed in the presence of di- and trivalent anions. Charge reversal was observed for divalent anions at 1×10^{-2} M and for trivalent anions at 1×10^{-1} M. It was considered that monovalent anions are indifferent ions and di- and trivalent anions are potential-determining ions. A schematic adsorption model which accounts for the adsorption of mono- and multivalent anions in the electrical double layer of barite nanoparticles is proposed.

Introduction

Electrokinetic properties of fine particles in an aqueous solution such as the isoelectric point (iep) and potential determining ions (pdi) play a significant role in understanding the adsorption mechanism of inorganic and organic species at the solid/solution interface. They also govern the flotation, coagulation and dispersion properties in suspension systems. In flotation, these properties are used to understand the mode of collector adsorption on minerals, selection of appropriate flotation reagents and examination of activation mechanisms [1]. In coagulation, an important step in many solid–liquid separation processes including wastewater treatment systems, it is necessary to know the zeta potential and the iep of particles [2]. In the ceramics industry and in the design of nanocomposite materials, the electrokinetic properties of the colloidal particles identify the optimal conditions of a well dispersed system [3].

Barite is dense sulfate mineral that can occur in a variety of rocks, including limestone and sandstone. It is used widely because of its high specific gravity, opaqueness to X-rays, inertness and whiteness [4, 5]. For example, Barite is one of the most important fillers used in the plastics, rubber and paint industries, and is also used in pharmaceutical formulations. In addition, barite has been incorporated into polymers to form electrical-insulating barite/epoxy composites with X-ray attenuation properties [6]. On account of the novel properties of ultrafine particles, it can be expected that barite nanoparticles will have extensive applications. However, as far as we know, there are a few reports involved with the preparation of barite nanoparticles.

In our prior work, barite nanoparticles have been successfully synthesized by a novel wet grinding technique,

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using crude micron barite as source material. The preparation of the products was low-cost, and the samples showed smaller particle diameter and more narrow size distribution [7]. Nanometer effect was observed while it was used in paints and plastics as an additive.

The principal reason for determining the zeta potential of barite nanoparticles was to obtain an indication of the magnitude of the potential at the beginning of the diffuse double layer around the particle. The electrophoretic mobility behavior versus electrolyte concentration has been extensively studied previously with clay minerals such as perlite [8], montmorillonite [9], clinoptilolite [10], kaolinite [11], sepiolite [12]. But no work related to barite nanoparticles was found till now. In this work, barite nanoparticles has been subjected to a series of measurements in order to determine its iep, pdi and the effects of mono- and multivalent anions sodium salts such as NaCl, $NaNO_3$, $NaCH_3COO$, Na_2SO_4, Na_2CO_3 and Na_3PO_4 on the zeta potential of barite nanoparticles. In addition, the pH profiles of barite nanoparticles at natural, acidic and basic conditions are presented.

Materials and methods

Materials used

A barite nanoparticles sample was prepared with a novel wet grinding method from an average particle size of 1.5 μm barite as source material [7], the sample was treated before using in the experiments as below: The suspension containing 5 g/L barite nanoparticles was mechanically stirred for 24 h, after waiting for a couple of minutes, the suspension was filtered and washed with distilled water several times. The sold sample was then dried at 110 °C for 24 h to obtain the final white powders.

The particle size distribution of barite nanoparticles in water was shown in Fig. 1. Mean particle size of 96 vol% barite nanoparticles is about 31.2 nm and mean particle size of 4 vol% barite nanoparticles is about 127.9 nm by peak analysis. The microstructure of the sample was investigated by transmission electron microscopy (JEM200CX Japan), as shown in Fig. 2, the barite nanoparticles are nearly elliptical and have a round shape. The average particle size is about 40 nm. The nitrogen BET surface area is about 35.69 $m^2 g^{-1}$. The average pore diameter is about 18.91 nm and the average pore volume is about 0.169 $cm^3 g^{-1}$, measured by adsorption/desorption nitrogen BET. The chemical composition of the barite nanoparticles determined by XRF is given in Table 1. All chemicals used in this study were of analytical grade.

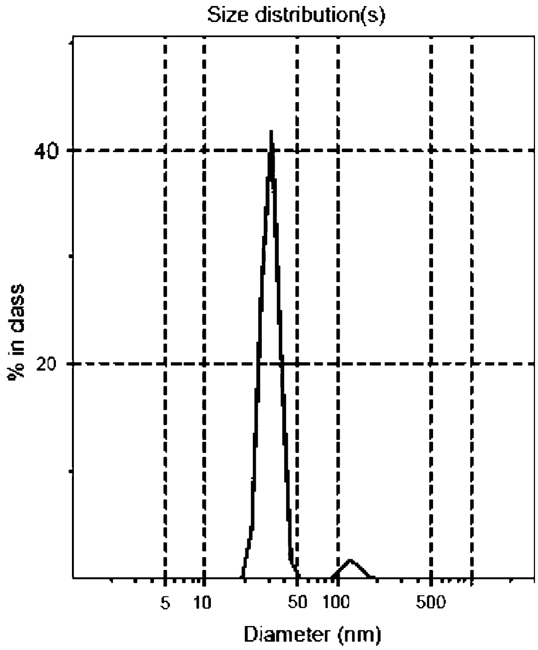

Fig. 1 Particle-size distribution of barite nanoparticles

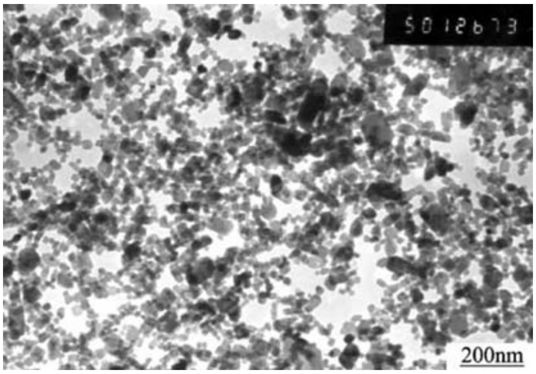

Fig. 2 TEM imagine of barite nanoparticles

Table 1 Chemical composition of barite nanoparticles

Component	Weight%
Na_2O	1.6
SO_3	29.7
Cl	0.02
SrO	1.0
Y_2O_3	0.03
ZrO_2	0.50
BaO	67.2

Zeta potential measurements

The zeta potential of barite nanoparticles was measured by a Zetasizer3000HS(Malvern) equipped with a microprocessor unit. The unit automatically calculates the electrophoretic mobility of the particles and converts it to the zeta potential using the Huckel and Smoluchowski equation. The zeta potential measurements were carried out as a function of the solid to liquid ratio, pH and sodium salts concentration of different anions valencies. In this procedure, 0.5 g of barite nanoparticles was transferred to a 250-ml polyethylene bottle to which 100 ml of an aqueous solution was added, yielding a final concentration of 5 g l^{-1}. The sample was dispersed by a thermostated shaker bath at 25 ± 1 °C, after being shaken 24 h. An aliquot taken from solution was used to measure the zeta potential. The average of 10 measurements was taken to represent the measured potential. The pH of the suspension was adjusted using dilute HCl and NaOH [8]. All solutions were prepared using distilled water.

Results and discussion

Effect of solid concentration

The effect of solid concentration on the zeta potential of barite nanoparticles was shown in Fig. 3. The zeta potential was found to change with the solid concentration in solution. This result indicated that solid concentration in solution is a major parameter governing the surface charge generation. It is considered that the ionic species produced at the solid–liquid interface increase with increase in solid concentration and that using inadequate solids concentration can lead to erroneous conclusions in the interpretation of zeta potential measurements. Therefore, the solid-to-liquid ratio has been kept constant as 5 g l^{-1} in the subsequent zeta potentials measurements.

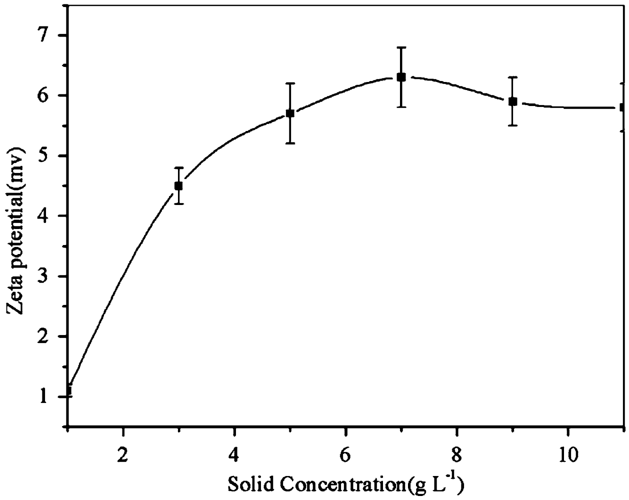

Fig. 3 Effect of solid concentration on the zeta potential of barite nanoparticles

pH profiles of barite nanoparticles

The pH profiles of barite nanoparticles in a 0.5 wt% suspension as a function of time is presented in Fig. 4 at an initial pH of natural, acidic, and basic media. Initial pH of the suspension was adjusted using dilute HCl and NaOH, the suspension was shaked for 24 h at 25 ± 1 °C. When barite nanoparticles is added to distilled water at pH 11, the suspension pH comes down and then remains almost constant upon reaching the equilibrium pH of 9.51 after 24 h. The reason for the rapid decrease in pH at first is ascribed to the rapid adsorption of OH^- ions in water onto the positively charged barite nanoparticles surface in order to provide electroneutrality. When the initial pH is adjusted to 5, the suspension pH rises to 5.66 in 24 h after barite nanoparticles addition. The rise of the suspension pH can be attributed to the adsorption of H^+ ions onto the negative sites on the barite nanoparticles surface as in broken bonds. Furthermore, when barite nanoparticles are added to distilled water at pH 7.2, suspension pH reaches 6.18 in 24 h.

The effect of pH on zeta potential and isoelectric point (iep)

The iep of a mineral represents the sum of all interactions occurring at the mineral/water interface, e.g., H^+ and OH^- adsorption, distribution of dissolved lattice ions, if present, or hydrolytic reactions of H^+ and OH^- with the dissolved lattice ions at the interface [13]. The iep also indicates that at this point (or pH) there is no charge at the surface, that is, the total positive charges are equal to the total negative charges. The heterogeneity of mineral surfaces, any detected impurities and different pretreatments such as leaching, washing, ultrasonic scrubbing and sludge

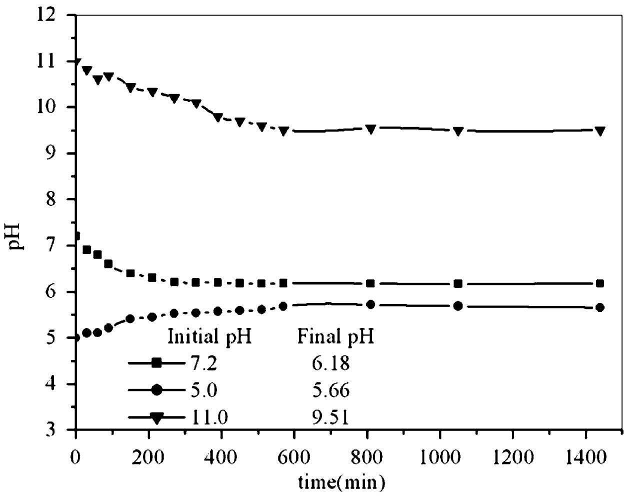

Fig. 4 pH and time (min) variation of barite nanoparticles suspension

removal are likely to be the causes of variation in the iep and zeta potential determinations [14–17].

The iep of barite nanoparticles was determined by measuring the zeta potential as a function of pH in the absence of any added electrolyte (Fig. 5). The pH of the suspension was adjusted using dilute HCl and NaOH. A net positive potential of about 6.0 mV was observed at the natural pH of 7.2 (Fig. 5). The increase of the suspension pH results in an increase in the negative charge of barite nanoparticles. This can be ascribed to the adsorption of OH^- ions onto the positive charge centers of barite nanoparticles. In addition, the reaction of OH^- with dissolved cations to form metal hydroxides may result in a decrease in the pH. The decrease of the suspension pH results in a decrease of the negative potential owing to the H^+ adsorption on the negative charge centers. At around pH 7.8, the zeta potential is about 0 mV, this shows that the barite nanoparticles surface maintains its neutral character.

The electrical charge at the barite nanoparticles surface/aqueous phase can be ascribed as below:

$$BaSO_4 + 2H^+ = Ba^{2+} + H_2SO_4, \qquad (1)$$

$$BaSO_4 + 2OH^- = SO_4^{2-} + Ba(OH)_2, \qquad (2)$$

and at iep

$$[Ba^{2+}] = [SO_4^{2-}] \qquad (3)$$

The fact of iep of barite nanoparticles indicated that the reaction responsible for the surface charge of the solid is mainly the reaction in Eq. 1 below the iep and in Eq. 2 above the iep, respectively. As seen in Fig. 5, at low pH the suspensions are positively charged, while at high pH the suspensions are negatively charged. Figure 5 shows that the iep is approximately pH 7.8. In this case, Eq. 3 is valid.

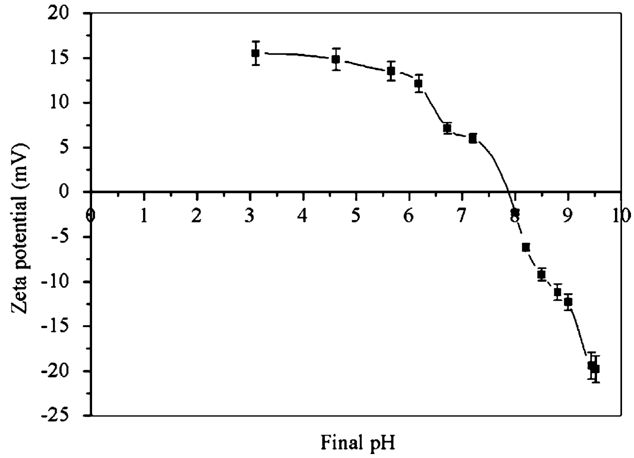

Fig. 5 Effect of pH on the zeta potential of barite nanoparticles

The effect of various electrolytes on zeta potential

The effect of monovalent anion

Figure 6 presents the changing of the zeta potential of barite nanoparticles with electrolyte concentration in the presence of NaCl, $NaNO_3$, and $NaCH_3COO$, respectively. The measurements were performed at the neutral pH of the medium and the temperature of 25 ± 1 °C. For a cation as a potential-determining ion (pdi), it should render the surface more positive with an increase in the concentration of the cation. Similarly, a potential-determining anion should make the surface more negative with an increase in its concentration. As shown in Fig. 6, the surface is, at first, more positively charged, and then the positive decreases with the concentration of electrolyte increases. By acting as indifferent electrolytes which are defined as counterions adsorbed by electrolytic attraction and thereby by compressing the double layer, they render the surface of the solid less positive [18, 19]. In simple electrolyte systems, e.g., NaCl, and $NaNO_3$, no net specific adsorption occurs and pH_{pzc} equals pH_{iep}. Other authors often refer to such systems as being "in the absence of specific adsorption" since pH_{pzc} equals pH_{iep} [20]. Evidently, these monovalent (NO_3^-, Cl^-) anions are not potential-determining ions because they are known as indifferent electrolytes [21, 22]. The monovalent anions cannot be adsorbed specifically onto barite nanoparticles, and are not capable of causing a charge reversal. The monovalent anions only accumulate as counterions in the EDL at the positively charged barite nanoparticles, due to coulombic attraction. Consequently, the monovalent anions compress the EDL and change the magnitude of the zeta potential of barite nanoparticles (see Fig. 7).

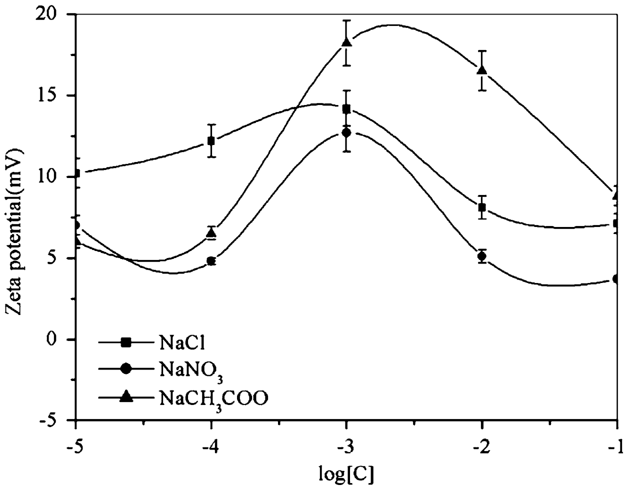

Fig. 6 Variation of the zeta potential of barite nanoparticles with monovalent anion concentrations

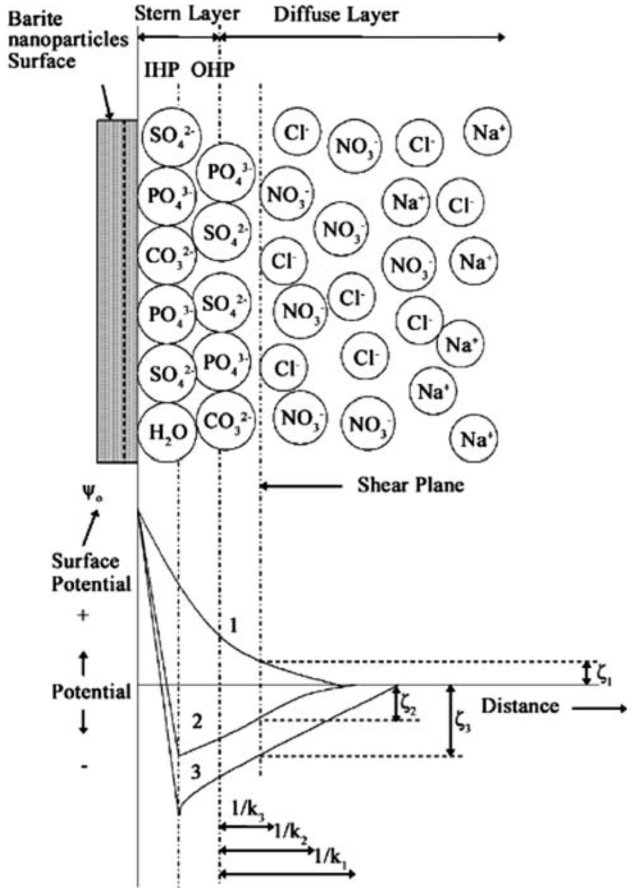

Fig. 7 Schematic illustration of the structure of the EDL of barite nanoparticles

The effect of divalent anion

Figure 8 presents the zeta potential of barite nanoparticles in the presence of various divalent anions electrolytes, Na_2SO_4, and Na_2CO_3, the measurements were performed at the neutral pH of the medium and the temperature of 25 ± 1 °C. As the concentrations of divalent anions increase in the solution, the zeta potential of barite nanoparticles decreases (becomes less positive). Note that at low divalent ion concentrations (10^{-4} and 10^{-3} M), barite nanoparticles does not give a charge reverse. However, as the concentrations of divalent ions increase (10^{-3} M and more) it gives a charge reverse. Indeed, charge reversal requires, in addition to ion exchange, specific adsorption of counterions in EDL, namely, in the inner Helmhotz plane (IHP) of the Stern layer (see Fig. 7). While divalent anions such as SO_4^{2-}, and CO_3^{2-} reverse the sign of the surface, these anions are adsorbed specifically onto barite nanoparticles. It is also assumed that these anions may be adsorbed specifically in the IHP of the stern. Meanwhile, They have lower the surface potential by charge neutralization and compress the thickness of the EDL with a reduction in the zeta potential (see Fig. 7).

The effect of trivalent anions

Figure 9 shows the change of the zeta potential of barite nanoparticles with electrolyte concentration in the presence of trivalent anions electrolytes, Na_3PO_4, the measurements were performed at the neutral pH of the medium and the temperature of 25 ± 1 °C. As seen in figures, the surface is, at first, more positively charged, and then the positive decreases as the concentration of electrolyte increase. A sharp decrease and a charge reversal occur at 3.6×10^{-2} M, approximately. It is clear that PO_4^{3-} anion is able to reverse the surface sign of barite nanoparticles. This may be explained on the basis of the specific adsorption of PO_4^{3-} counterions in the IHP of the stern layer, as shown in

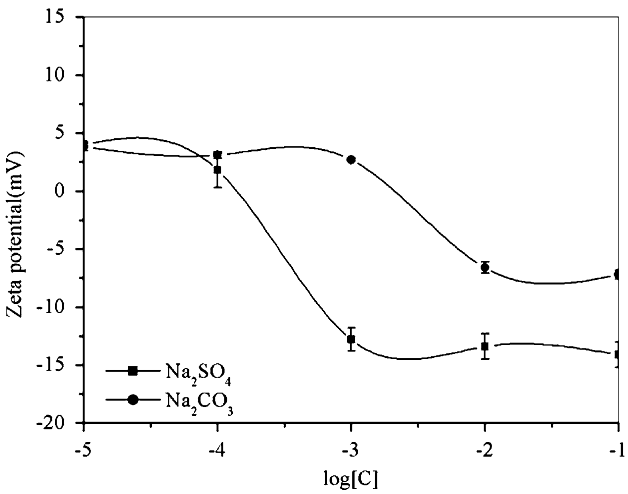

Fig. 8 Variation of the zeta potential of barite nanoparticles with divalent anion concentrations

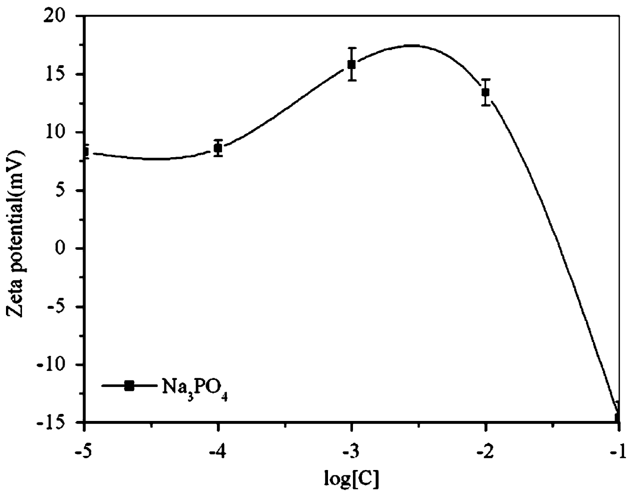

Fig. 9 Variation of the zeta potential of barite nanoparticles with trivalent anions

Fig. 7, particularly above a Na_3PO_4 concentration of 3.6×10^{-2} M.

The change of zeta potential with concentration of the electrolytes $NaNO_3$, Na_2CO_3, and Na_3PO_4 is shown in Fig. 10. While $NaNO_3$ acts as an indifferent electrolyte, Na_2CO_3, and Na_3PO_4 change the electrokinetic properties of the interface. This is described differently for mono- and multivalent anions in accord with the formula of $1/k = 3/ZC^{1/2}$ in water at 25 °C [21], where $1/k$ is the thickness of the diffuse layer (Å), Z denotes the valency, and C represents the ion concentration (mol l^{-1}). This formula indicates that the valency contributes significantly to the thickness of EDL and consequently causes a reduction in the zeta potential for the same anion concentration. For example, in the presence of 1×10^{-1} M of mono- (Cl^-, NO_3^-), di- (SO_4^{2-}, CO_3^{2-}), and trivalent (PO_4^{3-}) anions the $1/k$ values of barite nanoparticles are 9.49, 4.75, and 3.16 Å, respectively. Accordingly, Fig. 7 illustrates the thickness of the double layer for mono- ($1/k_1$), di- ($1/k_2$), and trivalent ions ($1/k_3$), respectively. These values are smaller than those $1/k$ values of clay mineral suspensions of micron dimension in different electrolyte media [10, 12], because the smaller particles have larger specific area, the more electrolytes anions is adsorbed on the surface of the particles, and in turn compress the thickness of the EDL.

Curve 1, curve 2, and curve 3 shows the variation of the surface potential of barite nanoparticles with the distance depart from nanoparticles surface in the presence of mono-, di- and trivalent anions electrolytes. ζ_1 of curve 1 is positive value, and it is clear that monovalent (Cl^-, NO_3^-) anions can only compress the EDL and reduce the zeta potential. The di- (SO_4^{2-}, CO_3^{2-}) and trivalent (PO_4^{3-}) anions are able to reverse the surface sign of barite nanoparticles. So, ζ_2 and ζ_3 are negative value. This may be explained on the basis of the specific adsorption of di-, and trivalent counterions in the IHP of the stern layer.

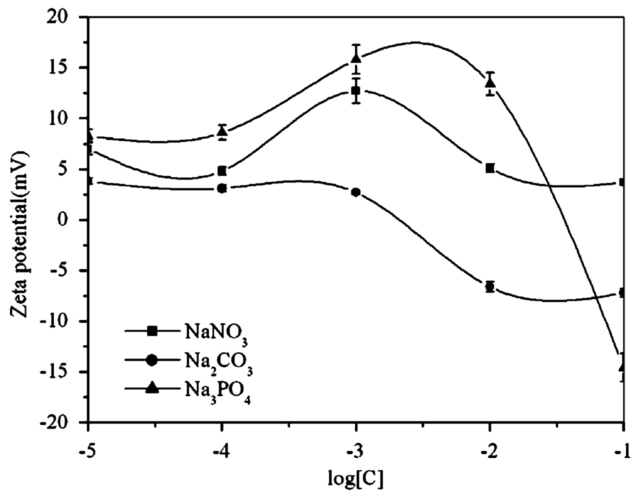

Fig. 10 Variation of the zeta potential of barite nanoparticles with mono-, di-, and trivalent anion concentrations

Conclusion

A series of zeta potential measurements have been performed to determine the isoelectric point (iep), potential-determining ions (pdi), and the effect of mono-, di-, and trivalent electrolytes on the zeta potential of barite nanoparticles. Barite nanoparticles yields an isoelectric point at pH 7.8. The zeta potential of barite nanoparticles is affected by solid concentration. However, it remains positive charged at all solid concentrations. Multivalent anions exert a greater influence on the zeta potential of barite nanoparticles than monovalent anions. Monovalent anions can only compress the EDL and reduce the zeta potential, while di- and trivalent anions are capable of even reversing the sign of the zeta potential of barite nanoparticles. A model is proposed to illustrate the accommodation of mono- and multivalent ions in the EDL.

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