Effect of ionic strength on adsorption of As(III) and As(V) on variable charge soils

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Abstract

The study was to investigate the adsorption behavior of arsenite (As(III)) and arsenate (As(V)) on two variable charge soils, i.e., Haplic Acrisol and Rhodic Ferralsol at different ionic strengths and pH with batch methods. Results indicated that the amount of As(III) adsorbed by these two soils increased with increasing solution pH, whereas it decreased with increasing ionic strength under the acidic condition. This suggested that As(III) was mainly adsorbed on soil positive charge sites through electrostatic attraction under the acidic condition. Moreover, intersects of As(V) adsorption–pH curves at different ionic strengths (a characteristic pH) are obtained for both soils. It was noted that above this pH, the adsorption of As(V) was increased with increasing ionic strength, whereas below it the reverse trend was true. Precisely the intersect pH was 3.6 for Haplic Acrisol and 4.5 for Rhodic Ferralsol, which was near the values of PZSE (soil point of zero salt effect) of these soils. The effects of ionic strength and pH on arsenate adsorption by these soils were interpreted by the adsorption model. The results of zeta potential suggested that the potential in adsorption plane becomes less negative with increasing ionic strength above soil PZSE and decreases with increasing ionic strength below soil PZSE. These results further supported the hypothesis of the adsorption model that the potential in the adsorption plane changes with ionic strength with an opposite trend to surface charge of the soils. Therefore, the change of the potential in the adsorption plane was mainly responsible for the change of arsenate adsorption induced by ionic strength on variable charge soils.

Key words: arsenic adsorption; ionic strength; Haplic Acrisol; Rhodic Ferralsol; zeta potential

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Introduction

Arsenic is one of the important toxic elements possessing very high toxicity towards human being, animals, and plants. Chemical processes strongly affect the fate and availability of arsenic in soils. Sorption and desorption reactions on the surfaces of soils and oxides greatly influence the mobility, toxicity, and availability of arsenic in natural environments (Violante *et al.*, 2005; Pigna *et al.*, 2006; Huang, 2008). Adsorption behavior of arsenate (As(V)) and arsenite (As(III)) on soils and Fe/Al oxides have been investigated extensively using the macroscopic and spectroscopic techniques (Livesey and Huang, 1981; Pierce and Moore, 1982; Roy *et al.*, 1986; Waychunas *et al.*, 1993; Manning and Goldberg, 1996; Fendorf *et al.*, 1997; Raven *et al.*, 1998; Arai *et al.*, 2001; Liu *et al.*, 2001; O'Reilly *et al.*, 2001; Goldberg, 2002; Violante and Pigna, 2002; Waltham and Eick, 2002; Catalano *et al.*, 2007). Jain *et al.* (1999) reported that the adsorption of As(V) on ferrihydrite caused the reduction of surface charge and net OH⁻ release. This suggested that the specific adsorp-

tion of As(V) took place on the surface of the oxides. Electrophoresis mobility (EM) measurements indicate that As(III) adsorption could not significantly change the EM values of γ-Al$_2$O$_3$ suspension in 0.1 mol/L NaNO$_3$ at pH 4.0–8.0, whereas As(V) adsorption lowered the EM values at pH 4.0–10.0 (Arai *et al.*, 2001). X-ray absorption fine structure spectroscopic studies have reported the formation of both inner-sphere bidentate binuclear and monodentate As(V) complexes on ferrihydrite and goethite, and bidentate binuclear complexes on γ-Al$_2$O$_3$ (Arai *et al.*, 2001; Fendorf *et al.*, 1997; Waychunas *et al.*, 1993). X-ray standing wave measurements show the formation of bridging bidentate surface arsenate complexes on hematite (Catalano *et al.*, 2007). However, X-ray absorption spectroscopic data indicate that both inner- and outer-sphere adsorption processes coexist for As(III) on γ-Al$_2$O$_3$ (Arai *et al.*, 2001).

The specific and non-specific adsorptions can be distinguished by evaluating the effect of ionic strength on anion partitioning (Hayes *et al.*, 1988). It was reported that the specific adsorption is unaffected by the change in ionic strength, whereas the non-specific adsorption is likely to be

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influenced greatly by the change of ionic strength because of the competitive adsorption with counteractions. It has been also reported that As(V) adsorption by γ-Al$_2$O$_3$ is almost unaffected by the change in ionic strength between pH 3.0 and pH 9.2. However, the adsorption of As(III) by this oxide is decreased with the increasing ionic strength in the pH range 4.5–9.0 (Arai *et al.*, 2001). This clearly suggests that As(III) is adsorbed through electrostatic attraction on γ-Al$_2$O$_3$ (non-specific adsorption); while As(V) is adsorbed specifically. A similar finding has also been reported for the adsorption of As(V) on goethite, in which there is almost a negligible salt effect on the adsorption of As(V) onto the surface of goethite irrespective of change in pH (Antelo *et al.*, 2005).

It has been reported that the chemical behavior of As(V) is quite similar to that of phosphate in soils (Violante and Pigna, 2002; Pigna *et al.*, 2006). Both the oxyanions are specifically adsorbed on the soil minerals, particularly on Fe/Al oxide surfaces, forming inner-sphere complexes (Pigna *et al.*, 2006). However, it has been observed that a characteristic pH usually occurs above which the adsorption of phosphate by goethite and soils increases with the increasing ionic strength and below this a reverse trend occurs (Barrow *et al.*, 1980; Bolan *et al.*, 1986). A model has developed by Bowden *et al.* (1980) to describe the adsorption mechanism of phosphate, selenite and citrate by goethite. This model was applied to explain the effects of ionic strength and pH on the adsorption of phosphate on goethite and soils (Barrow *et al.*, 1980; Bolan *et al.*, 1986). According to the model, the effect of ionic strength on the adsorption operates through its effect on electrostatic potential in the plane of adsorption, rather than through its effect on surface charge (Barrow *et al.*, 1980). However, such complex model applications are generally not subject to direct experimental confirmation because several employed fitting parameters can not be analytically measured (McBride, 1997).

Although there are reports already evaluated the effect of ionic strength on the adsorption of As(III) and As(V) onto the variable charge surfaces of Fe/Al oxides, only little information is available for such effect on the adsorption of these ions on variable charge soils. The soil with kaolinite as the predominant clay mineral and containing large amounts of iron and aluminum oxides is referred as variable charge soil (Yu, 1997). Variable charge soils carry both permanent negative charge and variable charge on their surfaces. Therefore, the surface properties of variable charge soils are different from these of pure iron and aluminum oxides which only carry variable charge on their surfaces. Thus, the objectives of this article are to investigate the effect of ionic strength on the adsorption of As(III) and As(V) using variable charge soils collected

from south of China and to probe possible mechanism involved at solid/solution interface.

1 Materials and methods

1.1 Soils

Two variable charge subsoils, Rhodic Ferralsol (located at 110°10′E, 20°20′N), and a Haplic Acrisol (located at 116°17′E, 28°23′N) were collected respectively, from Xuwen, and Jinxian, China. These soils are distributed widely in southern China, and are representative of major types of the soils in tropical and subtropical regions of China. The soil samples were dried at room temperature and ground to pass 60-mesh sieve. The clay fraction less than 2 μm in diameter was separated from the soil samples by pipette method, in which particles in the upper portion of the suspension were collected at a definite time after stirring (Pansu and Gautheyrou, 2006). The clay fraction was dried at room temperature and ground for zeta potential measurement after purification by electrodialysis under a voltage gradient of 10 V/cm between the two electrodes until the electrical conductance of the suspension did not decrease appreciably. Selected properties of these soils are shown in Table 1. The chemical properties of these soils have been studied in detail (Yu, 1997). Basically, the Haplic Acrisol is more variable in surface charge than Haplic Ferralsol, primarily due to their higher content of iron oxides. The clay minerals were determined by X-ray diffraction analysis. The clay fraction of the soils was pressured in the hole of an aluminum frame to form powder samples. Then the XRD analysis was performed using a D/max-IIIc X-ray diffractometer (Rigaku Corporation, Tokyo, Japan) with Cu K_α radiation.

Because in these regions the soils were collected from very deep layer and the whole profile is homogeneous except for the uppermost layer with a relatively higher content of organic matter, only subsoil was used in this study.

1.2 Adsorption experiments

A stock solution having 0.01 mol/L Na$_3$AsO$_3$ was prepared using reagent-grade As$_2$O$_3$ and NaOH. Then 1.0 mmol/L Na$_3$AsO$_3$ solution containing 0.01 or 0.6 mol/L NaNO$_3$ as supporting electrolyte were prepared with the stock As(III) solution. Similarly, 1.0 mmol/L KH$_2$AsO$_4$ solution containing 0.01 or 0.6 mol/L NaNO$_3$ was prepared using reagent-grade KH$_2$AsO$_4$. The required solution pH was maintained by NaOH (5.0 mol/L) or HNO$_3$ (6.0 mol/L).

Samples of 0.500 g soil in duplicates were weighed and put into centrifuge bottles. Na$_3$AsO$_3$ or KH$_2$AsO$_4$ solution (25 mL) was then added into each bottle. Suspensions

Table 1 Basic properties of the tested soil samples

Soil	Depth (cm)	OM[a] (g/kg)	pH[b]	CEC[c] (cmol/kg)	Fe$_2$O$_3$[d] (g/kg)	PZSE[e]	Dominant clay mineral
Rhodic Ferralsol	40–70	13.80	5.10	8.02	108.3	3.53	Kaolinite, gibbsite, hematite, goethite
Haplic Acrisol	80–130	4.40	4.80	8.91	51.1	4.45	Kaolinite, vermiculite, mica

[a] Organic matter, dichromate method (Pansu and Gautheyrou, 2006); [b] ratio of soil:water was 1:2.5; [c] CEC (cation exchange capacity), ammonium acetate method (Pansu and Gautheyrou, 2006); [d] DCB method (Pansu and Gautheyrou, 2006); [e] point of zero salt effect.

were shaken at a constant-temperature water bath at $25 \pm 1°C$ for 2 h. After standing for another 22 h, the solution was separated as the solid phase by centrifugation at 5000 r/min for 10 min, followed by filtration using a 0.45-µm pore membrane filter. As(V) in solution was determined by ICP-AES and As(III) was determined by constant current coulometry (Liang, 2003). The amount of As(V) or As(III) adsorbed was calculated as the difference between the total amount added and the amount remained in the bulk solution. After adsorption experiments, the pH values of equilibrium solutions were determined.

All data are reported as mean ± standard error of the replicates.

1.3 Zeta potential determination

Colloidal samples (0.025 g) of the Rhodic Ferralsol were taken into 250 mL plastic bottles (< 2 µm in diameter). Then, 200 mL of 10.0 mmol/L or 0.1 mmol/L NaNO$_3$ solutions was added into each bottle. The pH of suspension was adjusted to a range 3.0–7.0 with NaOH (5.0 mol/L) or HNO$_3$ (6.0 mol/L). Further, these suspensions were dispersed ultrasonically at a frequency of 40 kHz and a power of 300 W for 1 h at $25 \pm 1°C$. After standing for 3 d, the electrophoresis mobility was measured using JS94G+ microelectrophoresis apparatus (China) and the values of zeta potential were calculated according to the specific software (Hou et al., 2007). The suspension pH was also checked.

1.4 Soil point of zero salt effect

The potentiometric titrations were performed to investigate the soil point of zero salt effect (PZSE) (Pansu and Gautheyrou, 2006). Exactly 2.0 g of soil sample was added into a plastic beaker, then 40 mL of 0.01 mol/L NaNO$_3$ was added and suspension was agitated continuously for ca. 5 min using a bar magnet followed by measuring the suspension pH. An automatic titrimeter along with a combined electrode assembly was used to titrate the suspension with 0.1 mol/L HCl at a regulated dosage of HCl addition, i.e., 0.05 mL/2 min. The procedure was repeated with 0.1 and 1.0 mol/L NaNO$_3$ solutions as well. The adsorption of H$^+$ by the soils was calculated and intersect of H$^+$ adsorption–pH curves at different ionic strengths was reported as the soil PZSE.

2 Results and discussion

2.1 Effect of pH and ionic strength on As(III) adsorption

The effects of pH and ionic strength on the adsorption of As(III) onto the surfaces of Rhodic Ferralsol and Haplic Acrisol were presented in Fig. 1. The amount of As(III) adsorbed by these two soils was increased with increasing pH in both 0.01 mol/L NaNO$_3$ and 0.6 mol/L NaNO$_3$ solutions. Comparatively, Rhodic Ferralsol showed a higher adsorption capacity than Haplic Acrisol for As(III). This may be ascribed to the higher content of free iron oxides in Rhodic Ferralsol than that in Haplic Acrisol as shown in Table 1. As(III) was mainly adsorbed as arsenite
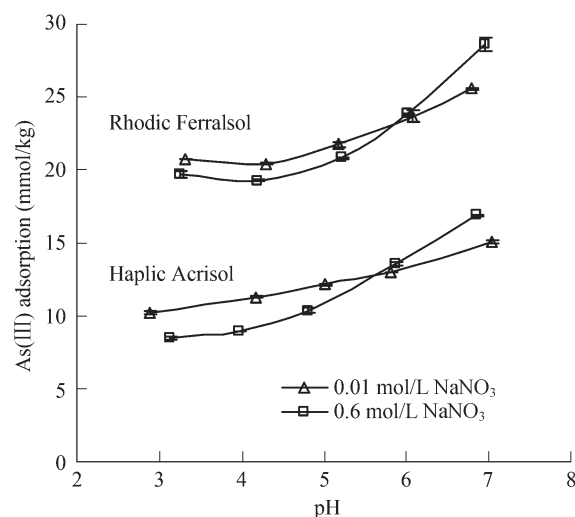

Fig. 1 Effects of pH and ionic strength on the adsorption of As(III) by two variable charge soils.

anion species on the Fe/Al oxides of variable charge soils (Pigna et al., 2006). The Rhodic Ferralsol contains a higher content of free iron oxides and possesses relatively higher adsorption capacity for As(III), and pKa_1 and pKa_2 for As(III) are 9.22 and 12.13, respectively. Therefore, under acidic condition, the predominant solution species of As(III) is H$_3$AsO$_3$ and obviously the degree of dissociation will increase with increasing solution pH. The dissociation of H$_3$AsO$_3$ at higher pH provides more arsenite anion to be adsorbed by the soils and led to increase As(III) adsorption with the gradual increase in pH. This observation is also consistent with the previous findings obtained for Fe/Al oxides systems (Manning and Goldberg, 1997; Arai et al., 2001; Goldberg, 2002).

The specific adsorption and non-specific adsorption can be easily distinguished with the change in ionic strength of the sorptive solution as it may enable to the anion partitioning (Hayes et al., 1988). The non-specific adsorption can be indicated with change in sorption process, then changing ionic strength as to observe the competitive adsorption with counteractions. It has been observed that the curves obtained for As(III) adsorption onto these two soils as a function of pH intersects each other at pH 5.6 for Haplic Acrisol and pH 6.0 for Rhodic Ferralsol (Fig. 1). It has assumed that at this intersect pH the adsorption of As(III) was independent of the ionic strength. When pH is lower than the intersect pH, As(III) adsorption was decreased with the increase in ionic strength. This indicated that the non-specfic adsorption was predominant in this pH range. However, when pH is higher than the intersect pH, As(III) adsorption increased with increasing ionic strength. This inferred that the specific adsorption occurred in this pH range. Previously, the X-ray absorption spectroscopic investigation also reported that both specific and non-specific adsorption of As(III) coexist on the surface of aluminum oxide (Arai et al., 2001). Moreover, specific adsorption behavior was obtained for As(III) onto the surface of iron oxides such as hematite, goethite, and ferrihydrite (Ona-Nguema et al., 2005). Therefore, the adsorption mechanisms for both specific and non-specific

adsorption for As(III) onto the two variable charge soils likely be involved.

At low pH, As(III) can be adsorbed as arsenite on the positive charge sites of the soils through electrostatic attraction. NO_3^- can also be adsorbed by the soils with the same mechanism. With increasing ionic strength, the concentration of NO_3^- in soil suspension systems increased. Thus, the NO_3^- in the system competed with As(III) for adsorption sites on the soils and resulted in the decrease in the adsorption of As(III) by the soils. This is the main reason for the decrease in As(III) adsorption by the soils with the increase in ionic strength under relatively low pH condition. The enhanced adsorption mechanism for As(III) with ionic strength at higher pH will be discussed in following sections.

2.2 Effect of pH and ionic strength on As(V) adsorption

Figure 2 shows the adsorption of As(V) by the two variable charge soils. The adsorption of As(V) was decreased with increasing pH in 0.01 mol/L $NaNO_3$ system, whereas in 0.6 mol/L $NaNO_3$ system, it was almost unaffected for the similar change in pH (Fig. 2). Rhodic Ferralsol could adsorb relatively more As(V) than Haplic Acrisol, this may be also due to the higher content of free iron oxides in Rhodic Ferralsol. These pH dependent data obtained at two different ionic strengths intersect each other at pH 3.6 for the Haplic Acrisol and pH 4.5 for the Rhodic Ferralsol. The adsorption of As(V) was supported to be independent of the ionic strength at this intersect pH. The intersect pH obtained for As(V) were much lower than that for As(III) in corresponding soil systems and near the soil PZSE. PZSE is 3.6 for the Haplic Acrisol and 4.45 for the Rhodic Ferralsol (Fig. 3). Above this characteristic pH the adsorption of As(V) by the soils increased with increasing ionic strength and below which the reverse trend occurred. The changing trends of As(V) adsorption by variable charge soils with ionic strength were similar to that obtained for phosphate by goethite and soils (Barrow *et al.*, 1980; Bolan *et al.*, 1986). A model was developed earlier (Bowden *et al.*, 1980) to explain

the adsorption mechanisms in terms of pH effect. It was used to explain the adsorption behavior of goethite for the phosphate, selenite, and citrate ions. Similarly, theoretical model was also used to interpret the mechanism involved in the adsorption of phosphate on soils and goethite as a function of ionic strength (Barrow *et al.*, 1980; Bolan *et al.*, 1986). Because the increase in phosphate adsorption by soils and goethite induced by the increase in ionic strength can not be interpreted based on the colloidal chemical principles.

Extended X-ray absorption fine structure spectroscopy (EXAFS) indicated that As(V) was mainly adsorbed through the formation of inner-sphere complexes on the surfaces of Fe/Al oxides and variable charge soils (Waychunas *et al.*, 1993; Fendorf *et al.*, 1997; Arai *et al.*, 2001; Luo *et al.*, 2006; Catalano *et al.*, 2007). However, the results obtained by EXAFS studies were unable to explain the relationship between As(V) adsorption and ionic strength. It is known that the chemical behavior of As(V) is similar to that of phosphate in soils (Violante and Pigna, 2002; Pigna *et al.*, 2006). Both of these oxyanions are specifically adsorbed on soil minerals, mainly on Fe/Al oxides, forming inner-sphere complexes (Pigna *et al.*, 2006). Therefore, the model developed by Bowden *et al.* (1980) was used to discuss the mechanism involved in the adsorption of As(V) by variable charge soils as a function of ionic strength in this article. According to the model, the specific adsorption of anions on variable charge soil surfaces was supposed to take place on a plane (adsorption plane) between the Stern and diffuse layers on mineral particles. The variation in the number of ions in the diffuse layer will affect the potential on the adsorption plane and thus affect the adsorption of anions (Barrow *et al.*, 1980). For example, when pH was higher than PZSE (4.45) of Rhodic Ferralsol, the soil possessed net negative variable charge, and the surface potential and the potential in the adsorption plane were negative. The surface charge of soil particles became more negative with the increase of ionic strength as shown in Fig. 3. Under this condition, the counter-ion in diffuse layer is cation (Na^+) and the number of cations in unit area increased with the decrease in distance to soil particle surface and an increase in electrolyte concentration. Therefore, the number of cations in the adsorption plane also increased with the increase in ionic strength, which made the potential at the adsorption plane less negative and thus increased the adsorption of As(V) by the soil. Therefore, the increase of As(V) adsorption by the soil with the increasing concentration of $NaNO_3$ (Fig. 2) was attributed to the change of the potential in the adsorption plane induced by the change of ionic strength. This mechanism can also be used to interpret the effect of ionic strength on As(III) adsorption at higher pH as shown in Fig. 1. At higher pH, As(III) was adsorbed by variable charge soils as anion species. The less negative potential in the adsorption plane induced by the increase in ionic strength caused the increase in the adsorption of As(III) by these two soil samples.

When pH was lower than the PZSE (4.45) of the Rhodic Ferralsol, the soil possessed a net positive variable
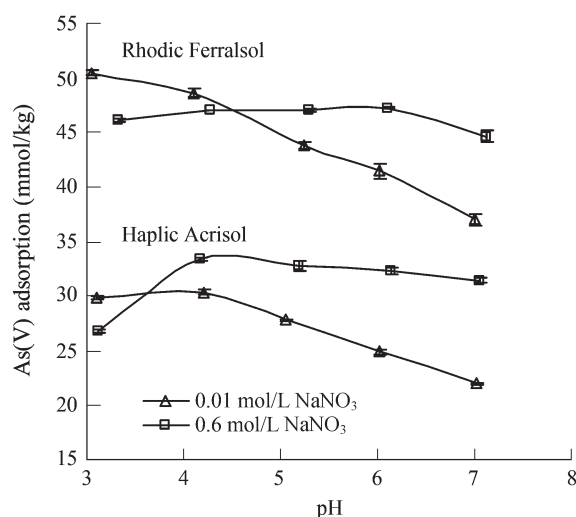

Fig. 2 Effects of pH and ionic strength on the adsorption of As(V) by two variable charge soils.

— · — 1.0 mol/L NaNO₃   —— 0.1 mol/L NaNO₃   ----- 0.01 mol/L NaNO₃
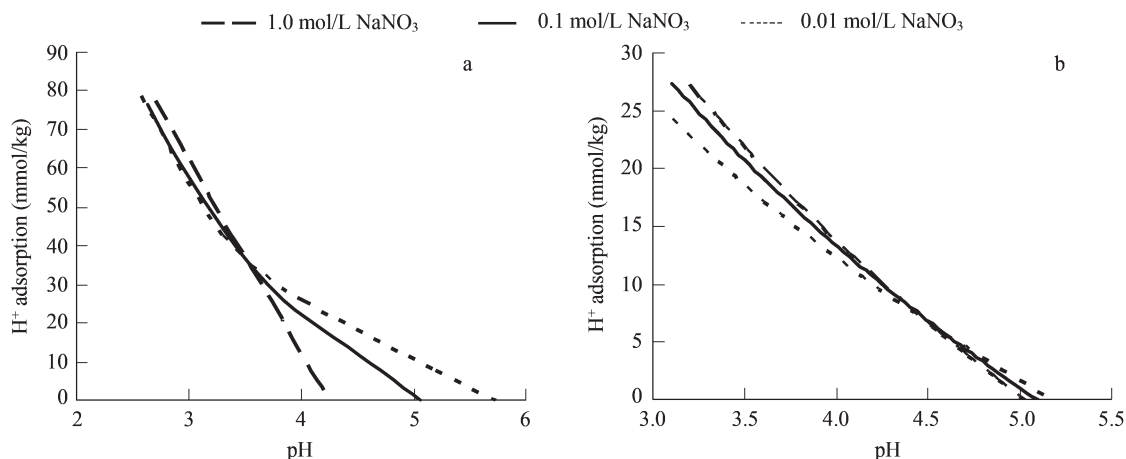

Fig. 3   Point of zero salt effect (PZSE) for Haplic Acrisol (a) and Rhodic Ferralsol (b) determined by acid-base titration.

charge, and the surface potential and the potential at the adsorption plane were positive. The counter-ion in the diffuse layer was anion (NO_3^-). Under this condition, soil surface charge (positive value) increased with the increasing ionic strength (Fig. 3). Whereas the increasing number of NO_3^- ion in the adsorption plane with increasing the ionic strength may cause the reduction of the potential at the adsorption plane and thus decreased the adsorption of As(V) by the soil. In addition, As(V) can also be adsorbed on positive charge sites of the soil under this condition through electrostatic attraction. NO_3^- in the soil suspension system also competed with As(V) for adsorption sites. Therefore, the increasing concentration of NO_3^- with the increase in ionic strength resulted in the decrease in As(V) adsorption by the soil.

The above interpretation proposed for the adsorption of As(III) or As(V) onto the surfaces of these two variable charge soil samples obtained at different ionic strengths may also be explained with the help of zeta potential measurements. The zeta potential is an electrical potential at the shear plane of the electric double layer on colloid particles. Although the exact location of the shear plane in the electric double layer cannot be ascertained, it is generally considered that it is located near the interface between the Stern layer and the diffuse layer (Yu, 1997). Therefore, the shear plane is near the adsorption plane in the model described previously. The values of zeta potential were obtained for these two soil samples at different ionic strengths and the results for the Rhodic Ferralsol were presented in Fig. 4. Figure 4 clearly indicates that the zeta potential become less negative with the increase in ionic strength when pH is above the PZSE of the soil, whereas it behaves oppositely when pH is below the PZSE of the soil. The changing trend of soil zeta potential with pH and ionic strength is opposite to that of the soil surface charge with pH and ionic strength (Fig. 3). These results are consistent with the prediction of effect of ionic strength on the potential in the adsorption plane by the model mentioned previously. The results of zeta potential values also provide the direct correlation to the hypothesis that the potential in the adsorption plane increased with increasing (become less negative) ionic strength when pH
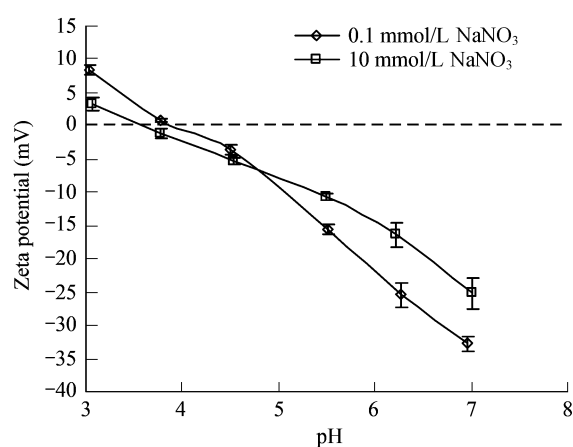

Fig. 4   Effect of ionic strength on zeta potential of Rhodic Ferralsol.

is above the PZSE of a variable charge surface and follows the reverse trend with ionic strength when pH is below the PZSE of the variable charge surface. This is perhaps the first experimental proof to support the hypothesis that the potential in the adsorption plane changes with ionic strength with an opposite trend to the soil surface charge as earlier suggested by Barrow *et al*. (1980). Figure 4 also shows that the difference of zeta potential between two ionic strengths was increased with increasing pH when pH was above the PZSE of the soils. However, it was decreased with pH when pH was below the PZSE of the soil. These changing trends of zeta potential values are also consistent with the effect extent of ionic strength on As(V) adsorption at different pH levels. Figure 2 clearly shows that the difference of As(V) adsorption between two ionic strengths increased with increasing pH when pH was above the PZSE of the soils.

Further, it was found that intersect of As(V) adsorption–pH curves at different ionic strengths for Rhodic Ferralsol was higher than that of Haplic Acrisol. This is also in consistent with the PZSE of the two soils and ascribed to a higher content of free iron oxides in Rhodic Ferralsol. Since iron and aluminum oxides show relatively higher values of PZSE in pH range 7–9, depending on their characteristics and their crystallinity. More content of iron and aluminum oxides in a soil would result in a higher PZSE of the soil along with the intersect point in As(V)

adsorption–pH curves.

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