EFFECT OF NONCLASSICAL POLARIZATION OF Na^+ AND K^+ ON THE STABILITY OF SOIL COLLOIDAL PARTICLES IN SUSPENSION

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The study of soil colloids is essential because the stability of soil colloidal particles are important processes of interest to researchers in environmental fields. The strong nonclassical polarization of the adsorbed cations (Na^+ and K^+) decreased the electric field and the electrostatic repulsion between adjacent colloidal particles. The decrease of the absolute values of surface potential was greater for K^+ than for Na^+ . The lower the concentration of Na^+ and K^+ in soil colloids, the greater the electrostatic repulsion between adjacent colloidal particles. The net pressure and the electrostatic repulsion was greater for Na^+ than for K^+ at the same ion concentration. For K^+ and Na^+ concentrations higher than 50 mmol L^{-1} or 100 mmol L^{-1} , there was a net negative (or attractive) pressure between two adjacent soil particles. The increasing total average aggregation (TAA) rate of soil colloids with increasing Na^+ and K^+ concentrations exhibited two stages: the growth rates of TAA increased rapidly at first and then increased slowly and eventually almost negligibly. The critical coagulation concentrations of soil colloids in Na^+ and K^+ were 91.6 mmol L^{-1} and 47.8 mmol L^{-1} , respectively, and these were similar to the concentrations at the net negative pressure.

Keywords: Strong nonclassical polarization; surface charge properties; ion–particle interactions; stability; the critical coagulation concentration.

1. Introduction

Soil colloids are the smallest and most active component of soil, ranging from 1 nm to 1000 nm in size. Colloids in the soil are as important as cells in biology.

When soil particles are as large as pebbles or sand, in the absence of colloidal particles, then soil properties would not be so complicated. Therefore, research into soil colloids is of great importance in soil science.¹ Meanwhile, aggregation is a major soil colloidal

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process that occurs in nature. Numerous researchers^{2–7} have found that electrolyte type, concentration, pH, organic matter, and oxidation–reduction potential can affect the aggregation process. Presently,^{8,9} the Derjaguin–Landau–Verwey–Overbeek (DLVO) theory is often used to explain the relationship between van der Waals attraction and electrostatic repulsion of colloidal particles in aqueous systems. When the electrolyte concentration decreases, the electrostatic shielding is weakened and the electric double layer is thickened; consequently, van der Waals attraction is reduced and electrostatic repulsion becomes dominant, allowing colloidal particles to disperse and remain stable. When the electrolyte concentration increases, the electrostatic shielding is enhanced and the electric double layer of colloidal particles becomes thinner; thus, electrostatic repulsion is reduced and van der Waals attraction plays a dominant role, contributing to colloidal particle aggregation.

However, recent studies^{3,10,11} have found that the DLVO theory is unable to explain the effect of iso-valent ions on the stability of oppositely charged colloidal particles. Tian *et al.*³ found that Li^+ , Na^+ , K^+ , Rb^+ and Cs^+ exhibit substantially different effects on the colloidal aggregation of inorganic clay minerals. Hu *et al.*,¹² Xu *et al.*,¹³ and Li *et al.*¹⁴ found that Li^+ , Na^+ , K^+ , and Cs^+ are also significantly different in terms of their involvements in soil aggregate stability and soil erosion processes. These researchers concluded that the interactions between soil particles and macroscopic phenomena result from ion-specific effects induced by the interactions between ions and the electric field on the particle surface.

As we know, soil colloids have the potential to carry a substantial amount of charge, which could yield the strong electric field (usually 10^8 – 10^9 V m^{−1}). The adsorbed ions can be strongly polarized by such strong electric field, and this strong polarization is essentially different from the classical induction and dispersion interactions.¹⁵ Therefore, the new interactions between strong electric field and ionic quantum fluctuation was called nonclassical polarization of ions at colloid/water interface. Thus, the interactions between charged soil colloids and ions are a central issue in electrochemical studies of soil.¹⁶ Moreover, Na^+ and K^+ are commonly present in the soil solution. These two cations are substantially different in terms of their contributions to soil aggregate stability and macro processes such as soil erosion and soil moisture

movement.^{17,18} Therefore, they affect soil structure formation, heavy metal migration and conversion in the soil, ion adsorption/desorption at the soil–water interface, and eutrophication of water bodies, among other ecological processes.^{18,19}

Purple soil is the most representative soil type in the Three Gorges Reservoir Area of Chongqing, China. A large amount of soil particles were transported into the Three Gorges Reservoir, as a result of the water impoundment. Aggregation of soil particles in the water body will affect their sedimentation and migration, significantly impacting the aquatic environment.²⁰ Therefore, it is of great importance to investigate the effect of Na^+ and K^+ particle interactions on the aggregation of purple soil. Although the nonclassical polarization of ions was included in the theoretical studies of ion–surface interactions, soil water movement, and stability of soil aggregate, its effects on the interactions between soil particles was not systematically studied. In the present study, we focused on the colloidal particles of a neutral purple soil, and the Na^+ and K^+ were used as the indicator ions. It is worth mentioning that although the concentration of Ca^{2+} and Mg^{2+} may be higher than the concentration of K^+ and Na^+ in nature soil system, the effects of nonclassical polarization of monovalent counterions on the stability of soil colloid particles in the present study, but the Coulomb effects is very strong and may cover up the effects of nonclassical polarization for the bivalent counterions, thus we selected the Na^+ and K^+ .^{20–23} The interactions between Na^+ or K^+ and purple soil particles were calculated theoretically. The critical coagulation concentration (CCC) and critical particle diameter for the aggregation of purple soil colloids were obtained by dynamic light scattering. We analyzed the effect of particle interactions on colloidal particle aggregation of the purple soil.

2. Experiment Section

2.1. Materials and sample preparation

Neutral purple soil samples were collected from an experimental farm at Southwest University (Chongqing, China) in October 2014. The samples were taken from a depth of 0–20 cm. After being air-dried, the samples were passed through a 0.25-mm sieve and stored in bottles until required for analysis. The total surface charge (16.0 cmol kg^{−1}) and specific

surface area (48.0 m² g⁻¹) of samples were measured using the combined method for determination of surface charge properties proposed by Li *et al.*²⁴ Soil pH, cation exchange capacity, organic matter content, and mineral composition were analyzed using a pH meter (soil:water ratio of 5:1), neutral ammonium acetate method, potassium dichromate oxidation–titration, and X-ray diffraction,²⁵ respectively, and each analysis was repeated three times. Soil pH was 7.11, soil organic matter content was 12.3 g kg⁻¹, and major minerals included quartz, montmorillonite, illite, and feldspar. The K⁺-soil suspensions were prepared according to the following procedure. About 30% H₂O₂ was used to oxidize organic matter. 50.0 g soil particles and 10 mL 0.1 mol L⁻¹ KOH solutions were successively added into a 500 mL beaker, and then diluted with ultrapure water until 500 mL. After 15 min of intensive sonication, the suspension was further diluted to 5 L using ultrapure water. The soil particles with the effective hydrodynamic diameter <200 nm were extracted and collected using the static sedimentation method.²⁶ As measured by the flame photometer, the concentration of K⁺ in the bulk suspension is below 0.01 mmol L⁻¹ and hence can be neglected. Then these K⁺-soil suspensions were diluted 10 times and the pH value was measured to be approximately 7.0.

2.2. Determination of soil colloidal particle aggregation

The aggregation of soil, oxides and clay minerals were determined using light scattering technique according to the work of many researchers.^{2,6,27–32} The effective diameter of soil colloidal particles as a function of time was determined to obtain the CCC and critical particle diameter, using a BI-200SM multi-angle laser light scattering system (Brookhaven, USA) with a BI-9000AT digital signal processor (Brookhaven, USA). The determination was conducted in the Chongqing Key Laboratory of Soil Multi-Scale Interfacial Processes, Southwest University, in November 2015. The NaNO₃ and KNO₃ solution were used, and the concentrations were set to 1, 10, 30, 50, 100, 300, 500, and 700 mmol L⁻¹ and 1, 5, 10, 30, 50, 100, 300, and 500 mmol L⁻¹, respectively. The effective hydrodynamic diameters of soil particles were recorded every 30 s at a scattering angle of 90°. The DLS experiments were carried out at the normal temperature (298 ± 0.5 K).

3. Results and Discussion

3.1. Surface charge properties of the purple soil colloids in Na⁺ and K⁺ systems

Surface potentials of neutral purple soil colloids in the Na⁺ and K⁺ systems at different electrolyte concentrations were calculated using the expression of surface potential proposed by Li *et al.*³³:

$$\varphi_0 = \frac{2RT}{Z_i F} \ln \left(\frac{2a_i^0}{\sigma \kappa} \right), \quad (1)$$

where the a_i^0 is the activity of ion i species in bulk solution (mol L⁻¹), F is the Faraday constant (C mol⁻¹), R is the gas constant (J mol⁻¹ K⁻¹), T is the absolute temperature (K), σ is the surface charge density of soil colloid (mol dm⁻²), $\kappa^{-1} = \sqrt{\varepsilon RT / (8\pi F^2 I)}$ is the thickness of diffuse layer, ε is the dielectric constant of water (C² J⁻¹ dm⁻¹), I is the ion strength in bulk solution (mol L⁻¹).

The surface potentials of the purple soil were consistent in the Na⁺ and K⁺ systems at the same electrolyte concentrations as the nonclassical polarization had not been considered (Table 1). From Eq. (1), only the Coulomb effects were considered, at the same electrolyte concentrations, surface potential is equal in different species ions with same valence.

According to the electric double layer theory,^{22,34} we calculated the surface electric field strength and ion distribution in the electric double layer of soil colloidal particles.

$$E(x) = -\text{sgn}(\varphi) \times \sqrt{\frac{8\pi RT}{\varepsilon} \sum_i (a_i^0 \exp^{-Z_i F \varphi(x) / RT} - 1)}. \quad (2)$$

As shown in Fig. 1, the surface electric field strength of soil colloidal particle could reach 10⁸ V m⁻¹ and it was enhanced with decreasing electrolyte concentration. In addition, at different ion concentrations (10⁻⁵, 10⁻³, 10⁻², 10⁻¹, and 1.0 mol L⁻¹, all within the ion concentration range of soil colloidal aggregation) and at different locations of the electric double layer (5.0, 4.8, 4.4, 3.1, and 1.6 nm distance to particle surface), 98.5%, 97.2%, 94.1%, 89.0%, and 60.4% of ions were distributed in a strong electric field (>10⁷ V m⁻¹), respectively. These ions would undergo strong nonclassical polarization in such a strong electric field.

Fig. 1. Electric field strength and ion profile in diffuse layer of a soil particle.

Therefore, the nonclassical polarization of ions has to be included in the surface potential^{12,15}:

$$\varphi_0 = \frac{2RT}{\beta_i Z_i F} \ln \left(\frac{2a_i^0}{\sigma \kappa} \right), \quad (3)$$

where $\beta_i = 1 + \tilde{p}_i \kappa / Z_i F$, it is the effective charge coefficient of ion i species, $\tilde{p}_i$ is the dipole moment of ion i species results from the nonclassical polarization.

Liu *et al.*¹⁵ found that in an electrostatic field of $>10^7 \text{ V m}^{-1}$, cations experience strong nonclassical polarization in the electric double layer. This enhances the Coulomb force of ions in the electric double layer and thereby reduces the surface electric field of the particle. Liu *et al.*¹⁵ further adopted the effective charge coefficient (β) to characterize nonclassical polarization. They found that $\beta_{\text{Na}}/\beta_{\text{Li}} = 1.11$, $\beta_{\text{K}}/\beta_{\text{Li}} = 1.699$, namely $\beta_{\text{K}}/\beta_{\text{Na}} = 1.52$. Thus, taking into consideration particle surface potentials in different ion systems after nonclassical polarization, Z can be substituted with βZ . The true particle surface potentials after ion-particle interactions were obtained and are shown in Table 2. As Tables 1 and 2 show, following the interactions between the ions and strong electric field on the surface of soil particles, the absolute value of particle surface potentials generally decreased and the extent of decrease was far greater in the K^+ system than in the Na^+ system. This indicates that the difference in electrostatic repulsion between the two ion systems at the same concentrations resulted from nonclassical polarization of ions, other than the difference in hydrated ionic radius according to traditional theory.

Table 1. Surface potentials of the purple soil for Na^+ and K^+ at different electrolyte concentrations (the effect of nonclassical polarization had not been considered).

Na^+		K^+	
Concentrations ($\text{m mol} \cdot \text{L}^{-1}$)	Surface potential (V)	Concentrations ($\text{m mol} \cdot \text{L}^{-1}$)	Surface potential (V)
1	-0.265	1	-0.265
10	-0.207	5	-0.223
30	-0.179	10	-0.207
50	-0.169	30	-0.179
100	-0.150	50	-0.169
300	-0.124	100	-0.150
500	-0.113	300	-0.124
700	-0.105	500	-0.113

Table 2. Surface potentials of the purple soil for Na^+ and K^+ at different electrolyte concentrations (considering the effect of nonclassical polarization).

Na^+		K^+	
Concentrations ($\text{m mol} \cdot \text{L}^{-1}$)	Surface potential (V)	Concentrations ($\text{m mol} \cdot \text{L}^{-1}$)	Surface potential (V)
1	-0.238	1	-0.155
10	-0.184	5	-0.131
30	-0.159	10	-0.120
50	-0.147	30	-0.096
100	-0.131	50	-0.085
300	-0.106	100	-0.069
500	-0.094	300	-0.061
700	-0.086	500	-0.056

3.2. Comparative analysis of nonclassical polarization interactions between Na^+ or K^+ and soil colloidal particles

Li and Hu *et al.*^{21,22} showed that the ion-particle interactions include electrostatic repulsion, van der Waals attraction, and hydration repulsion. These forces can be calculated using Eqs. (4)–(7).

The electrostatic repulsive pressure that arises from the repulsive force can be calculated using Eq. (4)^{22,35,36}:

$$P_E(d) = \frac{2}{101} RT c_0 \left\{ \cosh \left[\frac{Z_i F \varphi(d/2)}{RT} \right] - 1 \right\}, \quad (4)$$

where $P_E(d)$ (atm) is the electrostatic repulsive pressure; d (dm) is the distance between two adjacent particles; c_0 is the concentration of counterion in bulk solution (mol L⁻¹), and $\varphi(d/2)$ (V) is the potential at the middle of the overlapping position of the electric double layers of the two adjacent particles, which can be calculated by the following equation^{22,35,36}:

$$\frac{\pi}{2} \left[1 + \left(\frac{1}{2} \right)^2 e^{\frac{2Z_i F \varphi(d/2)}{RT}} + \left(\frac{3}{8} \right)^2 e^{\frac{4Z_i F \varphi(d/2)}{RT}} \right] - \arcsin e^{\frac{Z_i F \varphi(0) - Z_i F \varphi(d/2)}{2RT}} = \frac{1}{4} d \kappa \kappa e^{-\frac{Z_i F \varphi(d/2)}{2RT}}, \quad (5)$$

where κ (1/dm) is the Debye-Hückel parameter, which for 1:1 type electrolytes, $\kappa = (8\pi F^2 I / \epsilon RT)^{1/2}$; and I is the ionic strength (mol L⁻¹).

The long-range van der Waals attractive pressure originating from the van der Waals force can be estimated using Eq. 6 as follows^{22,36}:

$$P_{vdw}(d) = -\frac{A}{0.6\pi} (10d)^{-3} \quad (6)$$

where $P_{vdw}(d)$ (atm) is the van der Waals pressure; A (J) is the Hamaker constant, and for soil and clay, a value of 12×10^{-20} J can be used for the Hamaker constant in a vacuum, while a value of 7.8×10^{-20} J may be used for the Hamaker constant in the aqueous solution.^{22,36}

Leng³⁴ estimated the surface hydration force of mica. Therefore, by fitting Leng's molecular simulation data, Li *et al.*²² obtained the hydration repulsive pressure as a function of the distance, as follows:

$$P_h(d) = 3.33 \times 10^4 e^{-5.76 \times 10^9 d}, \quad (7)$$

where $P_h(d)$ (atm) is the surface hydration pressure.

The net forces of electrostatic repulsion, van der Waals attraction, and hydration repulsion between colloidal particles of the purple soil in the Na⁺ and K⁺ systems at different concentrations are shown in Fig. 2.

Figure 2 shows that with decreasing electrolyte concentration, electrostatic repulsion between the purple soil colloidal particles increased in both ion systems. At the same electrolyte concentrations, electrostatic repulsion and net force were much higher in the Na⁺ system than in the K⁺ system. This also shows that at the same ion concentrations, Na⁺ was greater than K⁺ for colloidal stability. However, in the Na⁺ system with an electrolyte concentration of

Fig. 2. Distributions of the net pressure of electrostatic repulsive, surface hydration repulsive, and van der Waals attractive forces between two adjacent soil colloidal particles surfaces under different electrolyte concentrations of Na⁺ and K⁺.

>0.1 mol L⁻¹, net attraction appeared at a distance of 4–5 nm between the particles. Theoretically, when the Na⁺ concentration exceeded 0.1 mol L⁻¹ in solution, colloidal particles would aggregate. In the K⁺ system with an electrolyte concentration of >0.05 mol L⁻¹, net attraction appeared at a distance of 3–4 nm between particles. That is, when the K⁺ concentration exceeded 0.05 mol L⁻¹ in solution, the colloidal particles would aggregate. From the net force analysis of the two ion systems, we obtained the critical concentrations for colloidal particle aggregation of the purple soil of 0.1 mol L⁻¹ and 0.05 mol L⁻¹ in the Na⁺ and K⁺ systems, respectively.

The used purple soil in the present study contained some 2:1 clay minerals (e.g. illite), the K⁺ can be stably fix in siloxane cavity. The ion-surface interactions and interactions between particles were mainly determined by the exchange adsorption counterions, thus the potassium fixation was treated as a whole with the colloid particle and not considered.

3.3. Comparative analysis of the stability of soil colloidal particles in the Na^+ and K^+ systems

Using dynamic light scattering, we measured the average effective hydraulic diameter of colloidal particle aggregates of the purple soil as a function of time in the Na^+ and K^+ systems at different electrolyte concentrations (Fig. 3).

Figure 3 shows that in both ion systems, the diameter of colloidal particle aggregates increased with increasing electrolyte concentration. A linear growth of aggregate diameter was observed at lower concentrations ($\text{Na}^+ < 10 \text{ mmol L}^{-1}$, $\text{K}^+ < 30 \text{ mmol L}^{-1}$), while a power function growth was shown at higher electrolyte concentrations. In the Na^+ system, when the ion concentration increased from 1 mmol L^{-1} to 700 mmol L^{-1} , the aggregate diameter increased from 220 nm to 2030 nm . The aggregate diameter increased by almost nine times in the range of Na^+ concentration between 1 mmol L^{-1} and

100 mmol L^{-1} , while it remained nearly unchanged in the range of Na^+ concentration between 100 mmol L^{-1} and 700 mmol L^{-1} . As revealed by the variation analysis of aggregate diameter, the critical concentration in the Na^+ system was 100 mmol L^{-1} . In the K^+ system, when the ion concentration increased from 1 mmol L^{-1} to 500 mmol L^{-1} , the aggregate diameter increased from 220 nm to 2350 nm . The aggregate diameter increased by almost 10 times in the range of K^+ concentration between 1 mmol L^{-1} and 50 mmol L^{-1} , while it remained nearly unchanged in the range of K^+ concentration between 50 mmol L^{-1} and 500 mmol L^{-1} . The variation analysis of aggregate diameter revealed that the critical concentration in the K^+ system was 50 mmol L^{-1} . These values were consistent with the critical concentrations for net attraction between colloidal particles of the purple soil in the two ion systems, as described in Sec. 3.2.

Based on the study of Jia *et al.*²⁷ the aggregation kinetics of soil particles in electrolyte solutions can be described by the aggregation rate [TAA rate, $\tilde{v}_T(f_0)$]. The TAA rate was expressed as,

$$\tilde{v}_T(f_0) = \frac{1}{t_0} \int_0^{t_0} \tilde{v}(t, f_0) dt$$

$$dt = \frac{1}{t_0} \int_0^{t_0} \left[\frac{1}{t} \int_0^t v(t, f_0) dt \right] dt, \quad (8)$$

where $\tilde{v}_T(f_0)$ (nm min^{-1}) is the TAA rate from $t = 0$ to a given time $t = t_0$ ($t_0 > 0$), and the upper limit of t_0 can be the ending time of the aggregation process; f_0 (mmol L^{-1}) is the electrolyte concentration. For the poly-disperse colloidal particles, $v(t, f_0)$ (nm min^{-1}) is the growth rate of the effective diameter for the aggregates in the DLS measurements, whereas $\tilde{v}_T(f_0)$ represents the growth rate from $t = 0$ to an arbitrary time t ($t > 0$). The total average aggregation rate (TAA) can be calculated from the diameter of the colloidal particle aggregates as a function of time. The TAA can then be used to obtain the CCC of colloidal particles. This method was used in the present study to analyze the relationship between the TAA of the purple soil colloidal particles and the electrolyte concentration in the Na^+ and K^+ systems. We found that the TAA of the purple soil colloidal particles showed two trends at different electrolyte concentration in both the Na^+ and K^+ systems (Fig. 4). The TAA initially showed linear

Fig. 3. The diameter of soil aggregates as a function of time under different electrolyte concentrations of Na^+ and K^+ .

growth, with slopes of 0.409 and 3.329, respectively; therefore, the TAA of aggregates in the K^+ system increased much faster than that in the Na^+ system. When the electrolyte concentrations increased to a certain level in the Na^+ and K^+ systems, the TAA of aggregates remained nearly unchanged with increasing electrolyte concentration; the TAA in the Na^+ system increased to 30.1 and the TAA in the K^+ system reached 34.2 (indicating the relationship $\text{Na}^+ > \text{K}^+$).

In addition, two linear relationships were obtained by fitting the trends of TAA at different electrolyte concentrations. The CCC values of the purple soil in the Na^+ and K^+ systems were obtained from the electrolyte concentration intersecting the two linear relationships, using the methods of Jia *et al.*²⁷ and Tian *et al.*³ Figure 4 shows that the CCC values of the purple soil in the Na^+ and K^+ systems were 91.6 mmol L^{-1} and 47.8 mmol L^{-1} (indicating the relationship $\text{Na}^+ > \text{K}^+$). These values were close to the critical concentrations for net attraction between colloidal particles of the purple soil in the two ion

systems, as described in Sec. 3.2. Additionally, the results show that in the Na^+ system, when the electrolyte concentration was lower than 91.6 mmol L^{-1} , soil colloidal particles agglomerated slowly and showed a dispersive state. However, when the electrolyte concentration was higher than 91.6 mmol L^{-1} , soil colloidal particles aggregated rapidly and showed an agglomerative state. In the K^+ system, when the electrolyte concentration was lower than 47.8 mmol L^{-1} , soil colloidal particles agglomerated slowly and showed a dispersive state. However, when the electrolyte concentration was higher than 47.8 mmol L^{-1} , soil colloidal particles aggregated rapidly and showed an agglomerative state.

4. Conclusions

In this study, we analyzed the effect of nonclassical polarization on surface charge properties of neutral purple soil colloidal particles in Na^+ and K^+ systems. The electrostatic repulsion, hydration repulsion, and van der Waals attraction between soil colloidal particles in the presence of Na^+ and K^+ ions were calculated theoretically. We then measured the aggregate diameter of the purple soil colloidal particles as a function of time. The main conclusions are as follows:

With regard to surface charge properties of the soil colloidal particles, all soil particle surface potentials decreased in the Na^+ and K^+ systems owing to the effect of nonclassical polarization. The extent of the decrease was much larger in the K^+ system than in the Na^+ system. In both ion systems, electrostatic repulsion between the soil colloidal particles increased with decreasing electrolyte concentration. At the same electrolyte concentrations, the electrostatic repulsion and net force were much larger in the Na^+ system than in the K^+ system. This also shows that at the same ion concentrations, Na^+ was greater than K^+ for colloidal stability. In the Na^+ and K^+ systems, the critical concentrations for net attraction between the soil colloidal particles were 100 mmol L^{-1} and 50 mmol L^{-1} , respectively. In both the Na^+ and K^+ systems, the TAA of the soil colloidal particles showed two trends at different electrolyte concentrations. The TAA initially showed a linear growth, with the slopes of 0.409 and 3.329, respectively. When Na^+ and K^+ concentrations increased

Fig. 4. The TAA rates for the soil aggregation as a function of the electrolyte concentration of Na^+ and K^+ .

to a certain level, the TAA of aggregates remained nearly unchanged with increasing electrolyte concentration. The CCC values of the soil colloid in the Na^+ and K^+ systems were 91.6 mmol L^{-1} and 47.8 mmol L^{-1} , equivalent to the critical concentrations for net attraction between the two ions and soil colloidal particles.

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