

Experimental Study for Determining Electric Conductivity of Electrolyte Solutions Containing Suspended Clay Minerals

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Abstract

Ion adsorption is one of the most important characteristics of soil. There have been many studies on ion adsorption in soils which have been carried out to elucidate the adsorption mechanisms. However, few studies have been carried out to elucidate them by determining changes in electric conductivity. Determining changes in electric conductivity is a more precise method than pH determination in the adsorption mechanisms when the ionic compositions of the solution systems are known. On the other hand, the existence of charged particles disturbs the correct measurement of electric conduction in an aqueous solution. Thus accurate conductivity data for solutions containing suspended solid particles are difficult to obtain using a conventional conductivity cell and the probe of a conductivity meter.

This study deals with the development of new conductivity cells for determining electric conductivity of electrolyte solutions containing charged particles. Three types of prototype cells were developed in this study. Each of them was devised to avoid the effect of charged particles. Practical use of the above conductivity cells was also examined by determination of phosphate adsorption on clay minerals at 298.15 K. Clay minerals are one of the inorganic components in soils. Their characteristics are responsible for the chemical properties of soils. Stable conductivity data can be obtained rapidly and precisely by the three prototype cells.

This study reached the following conclusions. (i) The new procedures for determining micro changes in electric conductivity of electrolyte solutions containing suspended particles were indicated. (ii) Simultaneous determination of changes in electric conductivity and pH will become a good indicator to elucidate the mechanisms of adsorption phenomena.

Key words : changes in electric conductivity, suspension, adsorption phenomena, clay minerals, conductivity cell

1. Introduction

Information on soil clay minerals is very important for the conservation of the soil environment and for the management of agricultural systems. The characteristics of soil clay minerals can be described as follows. (i) They have large specific surface area because

all of them are very small in size (less than $2\ \mu\text{m}$ in diameter). (ii) They have surface charge due to isomorphic substitution. (iii) They are very labile and act as the solid phase that exhibits surface reactivity in soil (Saigusa, 1989).

The composition of clay minerals is responsible for the characteristics of soils. For exam-

ple, supplement of plant nutrients, mobilities of heavy metal ions and/or agricultural chemicals, consistency of soils depend on clay minerals. These characteristics of soils are also concerned with ion exchange and adsorption phenomena. There are many studies on inorganic and organic solute adsorption in soils. For example, the triple layer model offers a quantitative model of inorganic ion adsorption by soil minerals (Yates *et al.*, 1974; Davis *et al.*, 1978). However, the adsorption mechanisms of ionic species on soils have not yet been completely elucidated. Moreover, there have been few attempts to elucidate the adsorption mechanisms by determining changes in electric conductivity.

Changes in electric conductivity are a more precise way than changes in pH to analyze adsorption phenomena when the ionic compositions of the solution systems are known. For example, structural differences in the layer type of clay minerals were clearly reflected in the trend of the changes in electric conductivity. On the other hand, this phenomenon cannot be evaluated by means of changes in pH because of differences in ion sensitivity between electric conductivity and pH.

To determine the electric conductivity of electrolyte solutions containing suspended particles of clay minerals, a new procedure for examining adsorption phenomena should be studied. However, there are some prerequisites for determining electric conductivity accurately in the electrolyte solutions as follows (e.g., Robinson and Stokes, 1965).

- (1) Accurate temperature control. If an accuracy of 0.01% is sought, the temperature should be controlled ± 0.005 K or better throughout the measurements.
- (2) Avoidance of polarization at the electrodes.
- (3) Accuracy of the apparatus used for the electrical measurements.

In addition to the above prerequisites, we have to avoid the effect of charged particles in determining the electric conductivity of a sus-

pension. Several scientists tried to determine the electric conductivity of suspensions. Gu and Yu (1991) established an identification for charged suspensions in electrolyte solution and derived a formula for the effective complex conductivity of the systems. Bashir and Goddard (1990) reported on the ionic conductivity of monodisperse, neutrally-buoyant suspensions of ion-exchange beads both AC total-ion conductivity and DC specific-ion conductivity. Sonneveld *et al.* (1992) measured the conductance of conductive ceramics, graphite and metal suspensions in aqueous KOH solutions by a four-electrode cell.

However, these studies were carried out in the suspensions which compositions were completely known and the accuracy of their experimental conditions (e.g. temperature control, accuracy of the apparatus) were not enough to elucidate the adsorption mechanisms by determining the electric conductivity. It is difficult to obtain electric conductivity accurately by using a conventional conductivity cell, because charged particles disturb the conduction in an aqueous solution.

The purpose of this study was to devise new conductivity cells which can obtain stable and precise data rapidly on the electric conductivity of suspended solutions. At the same time, we attempted to examine the behavior of ionic species at the soil-electrolyte interface by the determination of electric conductivity.

2. Experimental Methods

2-1. Design for new electric conductivity cells.

Three types of conductivity cells were developed in this study. They were devised to avoid the effect of charged particles. The details of each cell are described as follows.

(a) Prototype cell-1

Figure 1 shows Prototype cell-1. This cell is developed to determine the electric conductivity of suspensions immediately after centrifugation. A centrifuge tube of polyethylene was converted into a cell. The tube was 50 ml

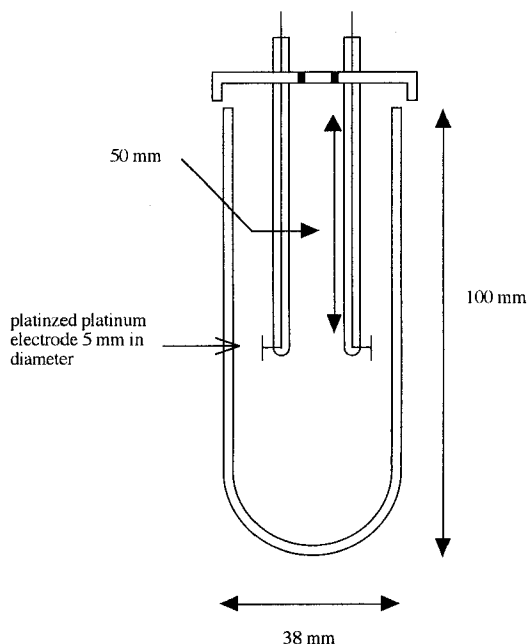


Fig. 1 Design of the Prototype cell-1.

in volume, 100 mm in height, and 38 mm in diameter. The dipping electrodes were made of platinized platinum the diameter of which was 5 mm and the depth of the electrodes was 50 mm from the edge of the tube. They were mounted in the lid of the centrifuge tube. This cell separates the supernatant from the deposition in the suspensions on centrifugation.

The adsorbent and the adsorbate were mixed in the centrifuge tube by a stirrer in the thermostated system. The tube was then centrifuged and immediately after centrifugation, the electric conductivity of the supernatant solution was determined.

(b) Prototype cell-2

Prototype cell-2 was developed by Hashitani (1978) as an apparatus for determining the solubilities of electrolytes (Figure 2). We applied the cell to separate the supernatant from the deposition in the suspensions. The cell permits the separation of the supernatant from the deposition in the suspension by means of filtering in a thermostated system. The dimensions of the cell are indicated in Figure 2.

The adsorbent and the adsorbate solution are added onto a glass filter. A vacuum and evacuation process is then repeated using a syringe. After the process, the filtrate was collected in the conductivity cell for determining the electric conductivity. The characteristics of this method include repetitions of the vacuum process to suspend the solutions and to collect the supernatant.

(c) Prototype cell-3

Prototype cell-3 is shown in Figure 3. The most striking characteristic of this cell is that determination of the electric conductivity can be carried out immediately after the filtration of the suspension. The cell of Pyrex glass is 200 mm in height and 50 mm in diameter. It consists of two separable parts. One part (A) functions for mixing the suspension and the other part (B) functions for determining electric conductivity of the supernatant. Platinized platinum electrodes whose diameter was 10 mm are mounted in (B). The details of the operation of this cell were described as follows.

The adsorbent and the adsorbate solution previously thermostated were added into (A). Filter supports of stainless steel were placed on each part of the cell. A membrane filter (pore size: $1.0\mu\text{m}$) was placed between both of the parts. Thereafter, (A) and (B) were connected tightly with rubber bands and vinyl tape.

The cell was allowed to stand for 30~720 minutes with stirring of the suspensions. After the above-mentioned time, the cell was placed upside down and suspensions were filtered by the vacuum operation from connector 1 using an aspirator. The electric conductivity of the filtrate was then determined with a conductivity bridge. All of the operations were carried out in the thermostated system.

Cell constants of the Prototype cells-1 and -3 were determined before the experiments with aqueous potassium chloride standard solutions (Robinson and Stokes, 1965).

2-2. Materials

(a) Clay Samples.

Two varieties of clay minerals were selected

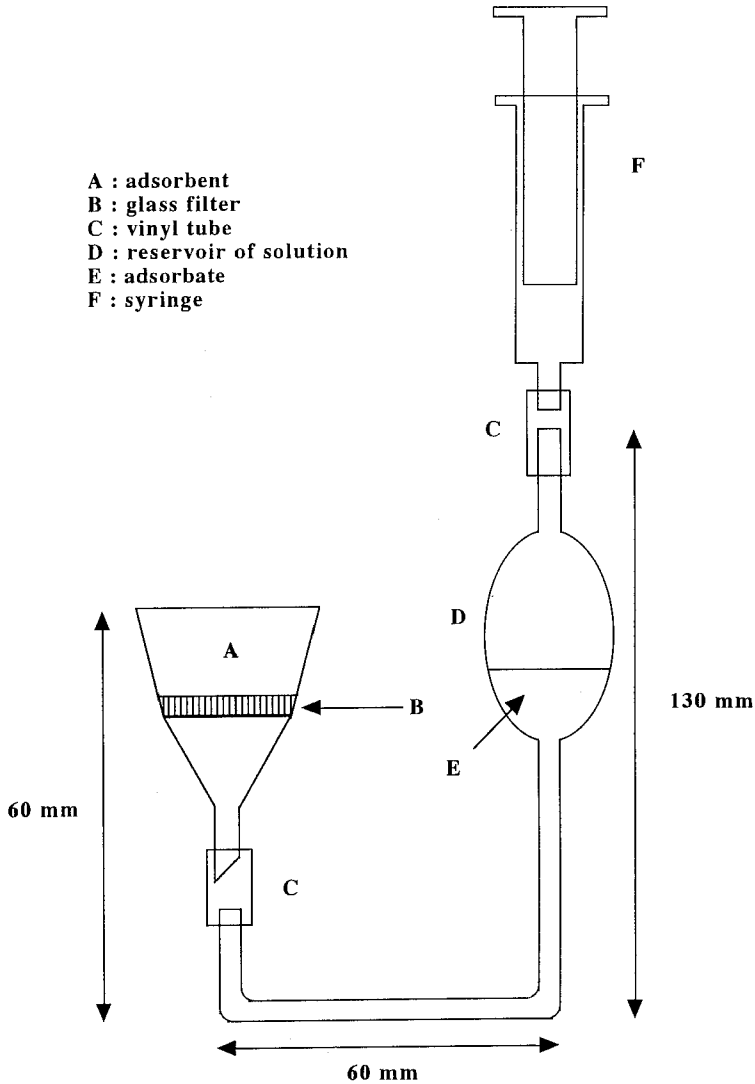


Fig. 2 Design of the Prototype cell-2.

in this study. They were tubular halloysite and protonated montmorillonite, which had been mined in Yunnan Province and Niigata Prefecture, respectively. The clay samples were washed with redistilled water before the experiments. Table 1 shows the several properties of the clay minerals used in this study. Table 2 shows the elemental analyses of the clay samples. Figure 4 and Figure 5 show the X-ray diffraction patterns of the clay samples.

(b) Reagents.

Analytical grade potassium chloride was

recrystallized from redistilled water. Potassium dihydrogenphosphate (KH_2PO_4), calcium dihydrogenphosphate ($\text{Ca}(\text{H}_2\text{PO}_4)_2$), and ammonium dihydrogenphosphate ($\text{NH}_4\text{H}_2\text{PO}_4$) were used as phosphate solutes in this study. They were used without further purification. The phosphate solutions were prepared by re-distilled water.

2-3. Determination of changes in electric conductivity.

(a) Comparison of the ability for practical use of the prototypes.

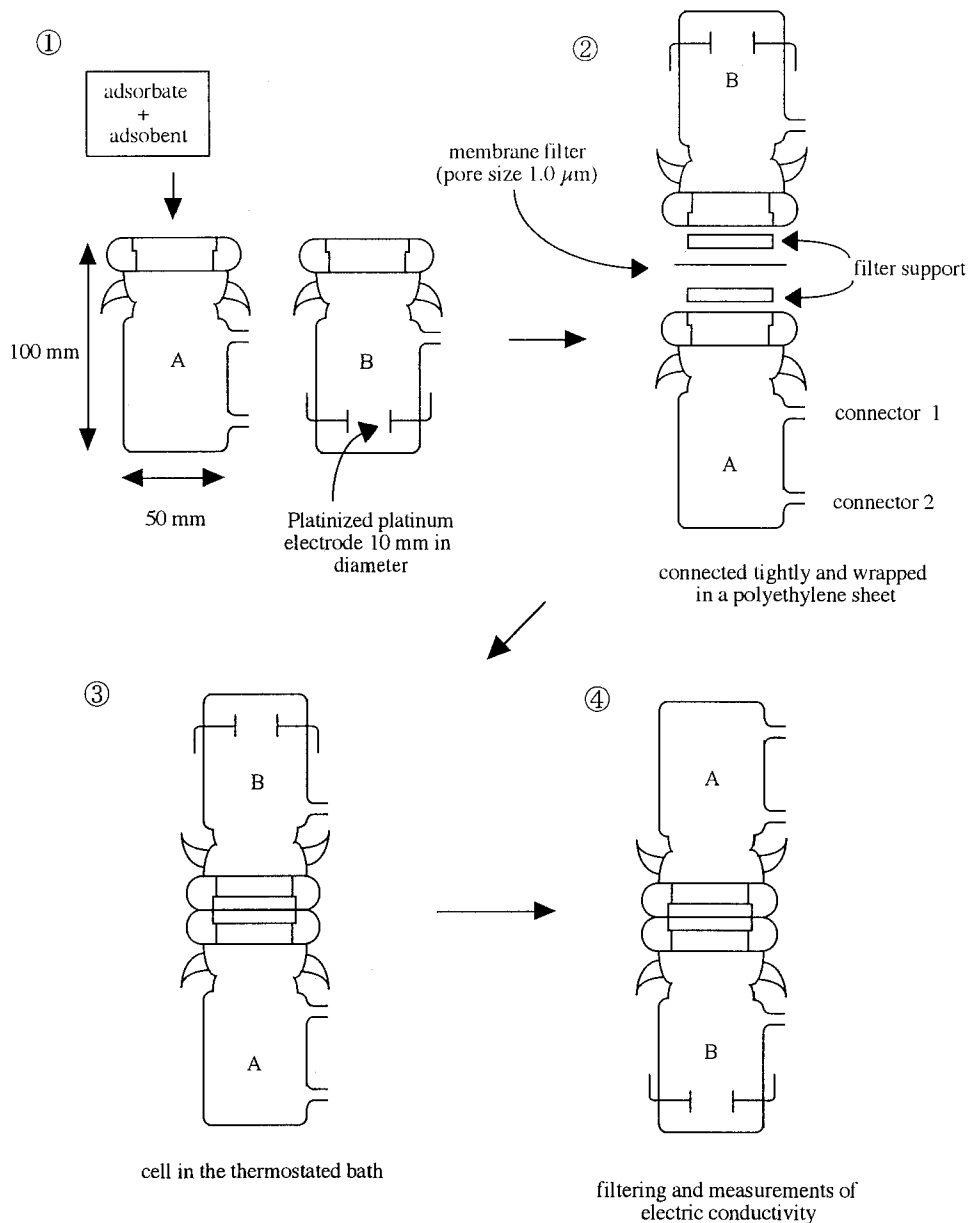


Fig. 3 Design of the Prototype cell-3.

Prototype cells-1, -2, and -3 have been determined their ability for practical use as following procedure. One gram of oven-dried clay sample was used as the adsorbent and 50.00 ml of potassium dihydrogenphosphate solutions (0.01 and 0.1 mol dm^{-3} , pH 4.50) were used as the adsorbate. The adsorbent and the adsorbate were suspended and the changes in electric

conductivity with the phosphate adsorption were determined by using the prototype cells. The operation manners of the prototypes were described in 2-1.

(b) Determinations of changes in electric conductivity and pH with phosphate adsorption on clay surface.

The adsorbates used were 0.1 mmol dm^{-3} ~

Table 1 Clay minerals used in this study

Sample name	Layer type	Moisture content (10 g kg ⁻¹)	Specific gravity (Mg m ⁻³)	Surface area (10 ³ m ² /kg) ¹⁾	pH-H ₂ O	pH-KCl	ΔpH	CEC (cmol _c kg ⁻¹) ²⁾
					a	b		
Tubular halloysite (Yunnan Prov., China)	1 : 1	7.26	2.51	87.6	5.7	3.9	1.8	6.47
H ⁺ -montmorillonite (Niigata Pref., Japan)	2 : 1	11.5	2.42	102	6.0	4.9	1.1	19.7

¹⁾ BET adsorption method (N₂ gas) was used. ²⁾ CaCl₂ was used for saturation.

Table 2 Elemental analyses of clay minerals (10 g kg⁻¹)

Sample name	H ₂ O	SiO ₂	Al ₂ O ₃	CaO	MgO	Na ₂ O	K ₂ O	(Fe ₂ O ₃)
Tubular halloysite (Yunnan Prov., China)	13.64	46.45	39.58	<0.1	0.08	0.03	0.23	1.03
H ⁺ -montmorillonite (Niigata Pref., Japan)	5.09	73.41	17.58	1.27	2.03	0.23	0.20	2.75

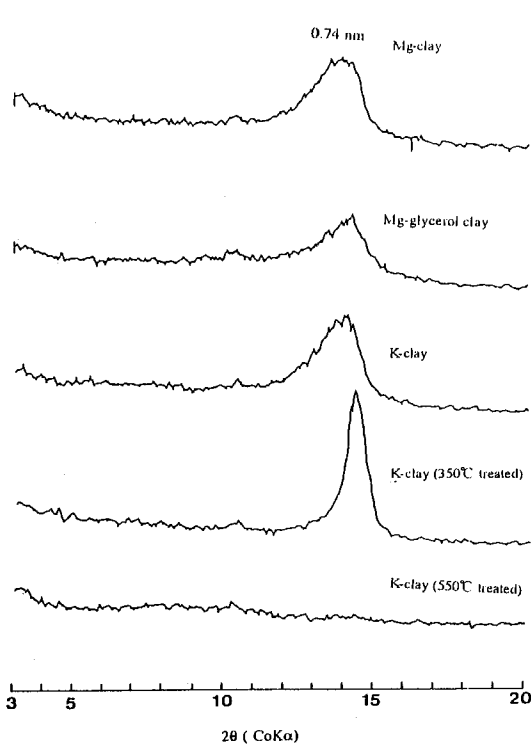


Fig. 4 X-ray diffraction patterns of tubular halloysite.

1 mmol dm⁻³ of dihydrogenphosphate ion solutions. The electrolyte solution (50.00 ml) previously thermostated was poured into the cell and wet purified nitrogen gas was bubbled in

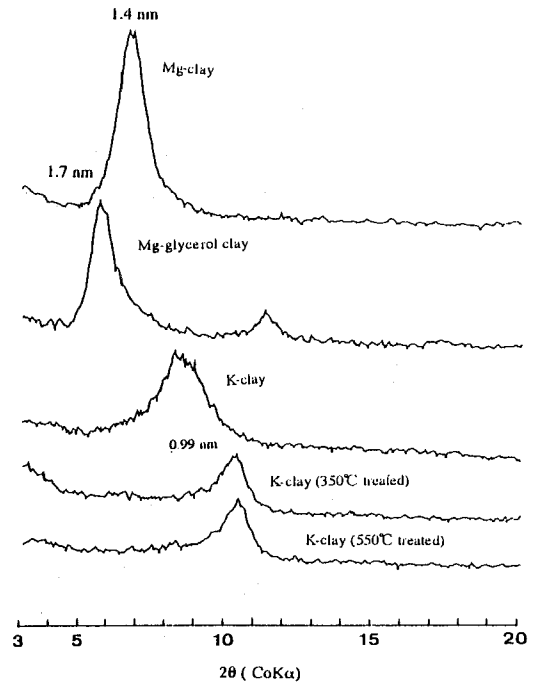


Fig. 5 X-ray diffraction patterns of H⁺-montmorillonite.

the solution for 30 minutes. Moreover, wet purified nitrogen gas had been continued to flow the upper part of the solution in the cell during the determination. Seals of the conductivity cell were gas-tight, so that a small positive pressure of nitrogen could always be

applied to completely exclude carbon dioxide from the solution. After 30 minutes of bubbling, electric conductivities of electrolyte solutions were determined as the data of initial state (reaction time of zero). Then adsorbate of clay mineral (0.1 g) was added to the solution for mixing and the adsorption was started. The cell stood for 720 minutes with stirring the suspended solution and determinations of electric conductivity of the solution had been carried out at every definite intervals (for instance 5, 10, 30, 60, and every 60 minutes).

Determinations of pH changes with phosphate adsorption on clay surfaces were carried

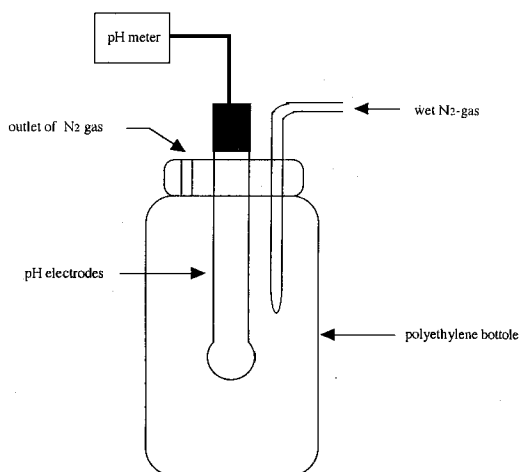


Fig. 6 The apparatus for determining changes in pH.

out by the apparatus shown in Figure 6. A determination process of pH was in the same way as that of electric conductivity.

The determinations of electric conductivity in this study were carried out by Conductivity Bridge : Type 360 B (Fuso Seisakusho LTD.) at a frequency of 1 kHz. All of the operations of the conductivity experiments were carried out in the thermostated bath (at 298.15 ± 0.0005 K). The temperature was monitored with quartz-oscillator thermometer : model 2804 A (Hewlett-Packard).

Changes in pH were determined by a digital pH meter HM-15 A (TOA Electronics LTD.). The temperature of another thermostat bath was maintained at 298.15 ± 0.001 K and the temperature was also monitored with quartz-oscillator thermometer : model 2801 A (Hewlett-Packard).

3. Results and Discussion

(a) Comparison of the abilities for practical use of the prototypes.

The results of the determinations were shown in Figure 7 and Figure 8. All of the prototypes showed a good performance for the practical use respectively. There were no significant differences in the results of conductivity data among the three prototypes. Each of the prototypes has their characteristic points as follows.

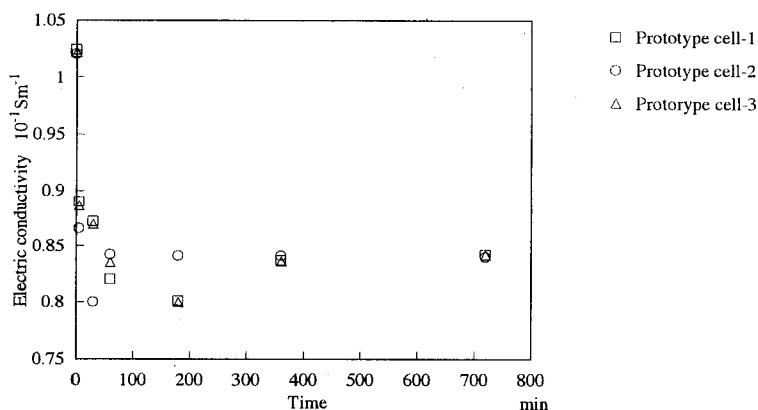


Fig. 7 Changes in electric conductivity with phosphate adsorption on tubular halloysite ($0.01 \text{ mol dm}^{-3} \text{ KH}_2\text{PO}_4$).

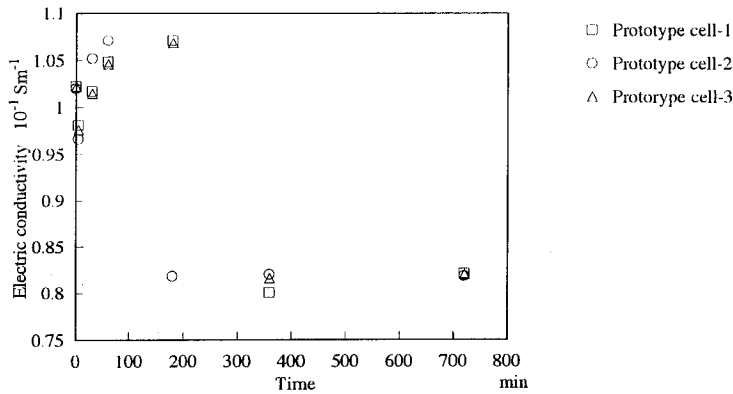


Fig. 8 Changes in electric conductivity with phosphate adsorption on H⁺-montmorillonite (0.01 mol dm⁻³ KH₂PO₄).

Table 3 Comparison of the features of the prototypes developed in this study

	Separation method of the suspended particles from solution	Possibility to maintain a temperature during determination	Optimum concentrations of electrolyte solutions
Prototype cell-1	centrifugation	possible, except the centrifugation process	$\times 10^{-4} \sim 10^{-3}$ mol·dm ⁻³
Prototype cell-2	filtration	possible, except the collection of the supernatant	depend on functions of the conductivity cell
Prototype cell-3	filtration	possible, all of operations	$\times 10^{-2} \sim 10^{-1}$ mol·dm ⁻³

With Prototype cell-1, we were able to obtain stable conductivity data rapidly when the concentrations of electrolyte solutions were low. This cell was also suitable for determining the electric conductivity of suspensions when the concentrations of clay were small.

The most striking features of the determinations by Prototype cell-2 were their rapidity to attain the adsorption equilibrium. They were required to attain the adsorption equilibria for 180~360 minutes when the determinations were carried out by Prototype cell-1 or Prototype cell-3 (Figure 7 and Figure 8). In the same condition, Prototype cell-2 was required for 60~180 minutes to attain the adsorption equilibria. The time to attain the adsorption equilibrium is owing to the repetitions of the vacuum and evacuation processes to mix the suspension. This is more efficient process for establishing an adsorption equilibrium in a short time compared with a stirring process.

Prototype cell-3 were able to obtain stable data of electric conductivity rapidly when the concentrations of the electrolyte solutions were high. This cell was the most convenient to operate for continuous determinations of electric conductivity.

The optimum concentration of the electrolyte solution for determining electric conductivity was defined by the diameter size and the interval of the electrodes. Table 3 shows the comparison of the features of the prototypes developed in this study.

(b) Determinations of changes in electric conductivity and pH with phosphate adsorption on clay surface.

Figure 9~Figure 12 show the results of changes in electric conductivity and pH with phosphate adsorption on clay surface. The data of electric conductivity were obtained by Prototype cell-1. Prototype cell-1 and Prototype cell-3 were used for these experiments.

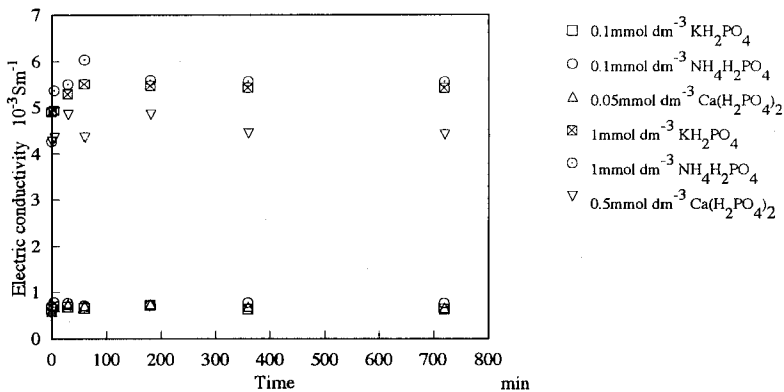


Fig. 9 Changes in electric conductivity with phosphate adsorption on tubular halloysite.

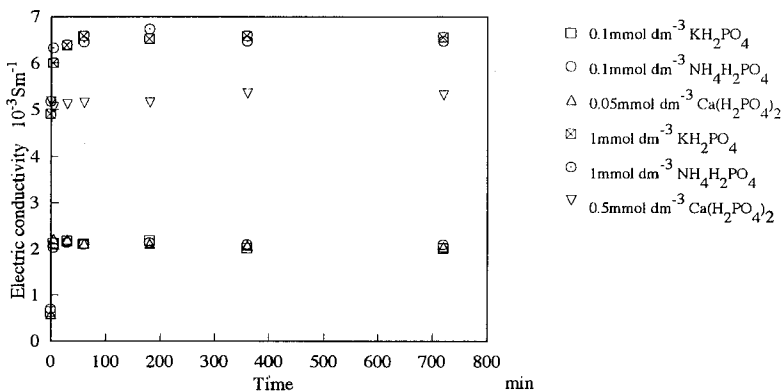


Fig. 10 Changes in electric conductivity with phosphate adsorption on H⁺-montmorillonite.

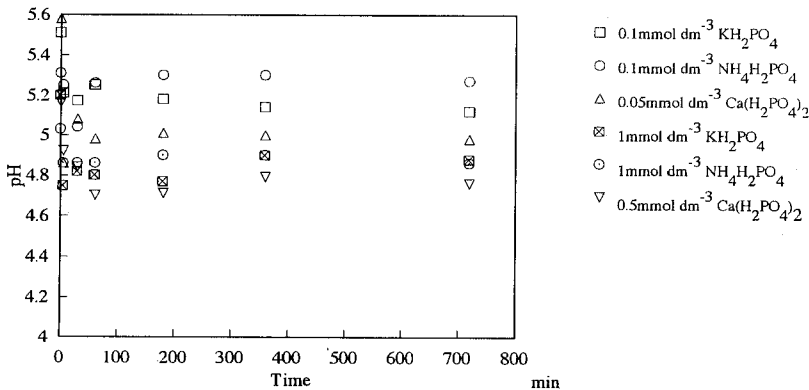


Fig. 11 Changes in pH with phosphate adsorption on tubular halloysite.

The obtained data by both cells were in agreement with ranges in the experimental error. However, Prototype cell-1 could obtain stable conductivity data more rapidly than Prototype

cell-3, because the former did not need filtration.

The obtained results are as follows. The values of electric conductivity increased with

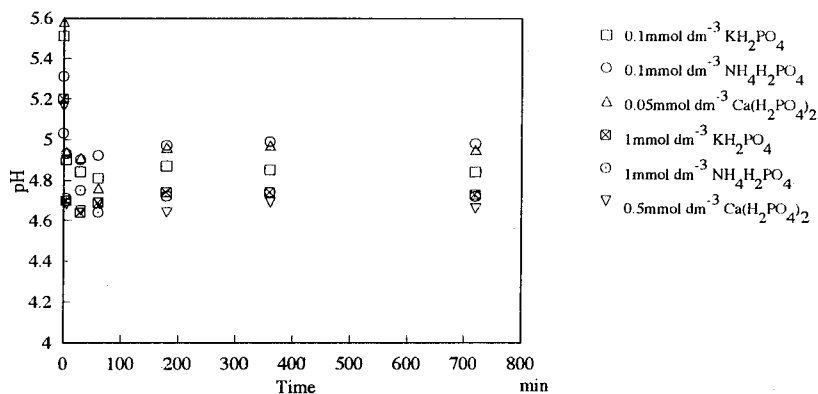


Fig. 12 Changes in pH with phosphate adsorption on H^+ -montmorillonite.

phosphate adsorption in the initial 5~10 minutes. Then the graph showed a gradual curve and reached to a plateau after 360~720 minutes. The values of pH showed a pronounced decrease at the beginning of the reaction. Then the pH began to increase and reached to a plateau at lower value than the initial pH. Changes in electric conductivity and pH were depended on following conditions, (i) layer types of clay minerals, (ii) concentrations of phosphate solutions, and (iii) counter ions of phosphate.

(i) Layer types of clay minerals.

Protonated montmorillonite (2:1 type) showed pronounced changes in electric conductivity and pH compared to tubular halloysite (1:1 type) (Figure 9~12). Protonated montmorillonite retained interlayer cations in the layer structure. Release of the cations and the cation exchange reaction would occur at the interface.

(ii) Concentrations of phosphate solutions.

The solutions of 1 mmol dm^{-3} phosphates showed pronounced changes in electric conductivity and pH compared to 0.1 mmol dm^{-3} of phosphates (Figure 9~12). These properties depended on the concentration of the ion species in the solution.

(iii) Counter ions of phosphates.

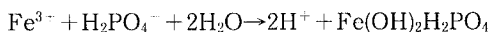
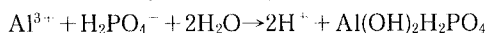
KH_2PO_4 and $\text{NH}_4\text{H}_2\text{PO}_4$ showed similar behavior of changes in electric conductivity and $\text{Ca}(\text{H}_2\text{PO}_4)_2$ showed the different behavior

(Figure 9 and Figure 10). This distinction depended on the differences of counter ions of phosphates. Namely, K^+ and NH_4^+ were not strongly hydrated in the aqueous solutions, but Ca^{2+} was hydrated in the aqueous solutions. Furthermore, K^+ and NH_4^+ were trapped into hexagonal cavity that is built into layer silicate surfaces 2:1 type clay (e.g., McBride, Murray, 1994). These differences of counter cation properties could determine the changes in electric conductivity.

Following assumptions of the mechanisms of phosphate adsorption on clay surface were concluded from the above results of (i)~(iii). At the beginning of the adsorption, exchange reaction had occurred between counter cations of solutes and other cations already adsorbed on clay surfaces, rather than anion exchange. Because the mobilities of the counter cations were more rapid than that of H_2PO_4^- . Thus H^+ release had occurred and the values of pH were decreased and the values of electric conductivity were increased. After the cation exchange, the adsorption of H_2PO_4^- had begun and released OH^- made increase the value of electric conductivity and pH.

The values of electric conductivity and pH showed tendency to gradual decrease when the adsorption reactions had attained to the equilibrium. In the acidic condition, Al^{3+} and Fe^{3+} were released from the clay minerals to the suspension. These cations formed slightly

soluble salts by following reactions.



4. Conclusions.

The following conclusions were obtained in this study.

(i) This study showed the new procedures for determining the electric conductivity of electrolyte solutions containing suspended particles. The procedures include filtration or centrifugation. Moreover, we can determine the micro changes in electric conductivity of the order of $10^{-3} \sim 10^{-6} \text{ Sm}^{-1}$.

(ii) The above results show that it is possible to analyze adsorption phenomena from changes in electric conductivity. To determine both the electric conductivity and pH at the same time is a more efficient procedure for elucidating the adsorption phenomena.

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粘土鉱物懸濁態を含む電解質水溶液の電気伝導率 測定法に関する実験

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要 約

吸着現象は、土壌の物理化学性の中で最も重要な性質のひとつである。また、電気伝導率変化は pH 変化と違い、溶液中の全イオン種の移動をリアルタイムに測定することができるという特徴がある。しかしながら、電気伝導率の精密測定は、温度条件や測定ブリッジの精度などに留意しなくてはならない。さらに、土壌溶液に含まれる懸濁態粒子がイオンの移動を妨害するため、その電気伝導率の精密測定は困難である。そのため、電気伝導率の変化から吸着現象を解析した例はほとんどない。

本研究では、懸濁態水溶液の電気伝導率変化を精密に測定するためのセルを試作し、測定法の開発を試みた。また、試作セルの実用性を確かめるため、粘土鉱物に、リン酸塩を吸着させた際の電気伝導率変化の測定を行った。

本研究により、以下の結論が得られた。(1)懸濁態を含む電解質水溶液の電気伝導率の微小変化を測定することができた。(2)電気伝導率および pH の変化を併せて測定することは、吸着現象のメカニズム解明に有効であることが示唆された。

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