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POTENTIOMETRIC TITRATION CURVES OF ALUMINIUM SALT SOLUTIONS AND ITS SPECIES CONVERSION IN THE HYDROLYSIS-POLYMERIZATION COURSE

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ABSTRACT. A new concept of critical point is expounded by analysing the potentiometric titration curves of aluminium salt solutions under the moderate slow rate of base injection. The critical point is defined as the characteristic spot of the Al^{3+} salt solutions potentiometric titration curve, which is related to the experiment conditions. In addition, the changes of critical points reflect the influence of experiment conditions on the course of the hydrolysis-polymerization and the conversion of hydroxyl polynuclear aluminum species. According to the OH/Al mole ratio, the Al species can be divided into four regions quantitatively by three characteristic points on the titration curves: Part I, Al^{3+}/Al_a region, consist chiefly of Al^{3+} and mononuclear Al; Part II, the small/middle polynuclear Al region, including Al_2-Al_{12}; Part III, the large-size polynuclear aluminum region, consistent with predominantly Al_{13}-Al_{54} and a little sol/gel $Al(OH)_3$; Part IV, the dissolving region of sol/gel Al_c, only $Al(OH)_3$ (aq or am) and $Al(OH)_4^-$ species, which set up a base to study on the hydrolysis-polymerization of Al^{3+}. At the same time, significant effects of total aluminum concentration, temperature, halide ion, silicate radical, and organic acid radical on the titration curves and its critical points were observed. Given the three critical points which demarcating the aluminum forms, we carry out a through investigation into the fundamental regulations of these factors' influence, and offer a fresh train of thought to study the hydrolysis-polymerization of Al^{3+} in soil solutions.

KEY WORDS: Potentiometric titration, Hydroxyl polynuclear aluminum species, Hydrolysis-polymerization, Critical point, Factors affecting titration curves

INTRODUCTION

At the present time, the environmental acidification and a great deal of using polynuclear Al coagulant are believed to be due to the increasing concentration of hydroxyl aluminum in natural waters and drinking water. As an intermediate product of the hydrolysis of Al solutions, the hydroxyl polynuclear Al species is even more toxic than Al^{3+} and mononuclear Al [1-3]. However, many people are still short of a definite recognition of the hydroxyl polynuclear complexes and their formation mechanisms, the morphological structures, the physicochemical properties and the reaction mechanisms in their applied courses [4-11], which is mainly on account of the complication in the hydrolysis-polymerization reaction of Al^{3+} and its formed species, meanwhile, due to the numerous influential factors on the conversion of the Al species and the complicated composition of the products [12], including concentration, temperature, complex ion, mole ratio of OH^- to Al^{3+} (namely OH/Al, termed as n) and aging period [13]. The potentiometric titration is a basic method of exploring the conversion of Al species in the hydrolysis-polymerization. Since a long period of time, as a result of deficiency in quantitative description about the potentiometric titration curves, and the dissimilar experiment conditions, it aroused a lot of controversy and it is difficult to compare each other. By analysing the simplest titration (pH vs n) curves as a first point, the study reported here focuses on the conversion trends of the species in the hydrolysis-polymerization of Al^{3+}, and attempts to investigate the effects of various factors on the titration pH vs n curves, as well as discussing the influences of above factors in the hydrolysis-polymerization course of aluminum salt solutions.

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EXPERIMENTAL

Reagents and apparatus

0.5 M $AlCl_3$ and 1 M NaOH stock solution were prepared with corresponding reagents dissolving in double-deionised water which had been thoroughly purged with high purity N_2. The operating solutions were both diluted from their stock solutions, and their concentration should be equal as far as possible. In addition, all the standard solution should be freshly prepared, and the chemicals used in all experiments were in analytical reagent grade. Both the experimental water and the preparation water were all the double-distilled water in CO_2-free. Withal, all the solutions were stored in acid-soaked polyethylene containers. In order to avoid activity coefficient variations, a continuous ionic medium of KCl was used as the background electrolyte. The ZD-2 type digital automatic titrator (Shanghai) accompanied with ultra thermostat, JB-1A style electromagnetic stirrer, and a combination glass-calomel electrode were used to inject NaOH titrant and record pH value automatically. The electrode has been rectified according to Irving [11].

The potentiometric titration experiment

In the experiment, 25 mL $AlCl_3$ standard solution was transferred into the double-decked insulated tumbler, which was added with a cover and a hole. Through the hole, alkali dropped into the Al salt solution with a Teflon capillary tube which is submerged in 30 cm of the solution under violently agitated, and the injecting rate was 0.8 $mL.min^{-1}$. The mole ratio of OH/Al increased 0.125 every time with injecting NaOH standard solution slowly until the number of n = 4. From beginning to end, nitrogen was continually bubbled through the solution to remove inorganic carbon. The temperature of the experiment is controlled at (25 ± 0.5) ^{o}C.

RESULTS AND DISCUSSION

The fraction and distribution of hydroxyl polynuclear Al species, and the analysis of potentiometric titration pH vs n curves with respect to hydrolysis-polymerization of Al^{3+}– four regions/ three characteristic points

So far, for the studies on potentiometric titration of Al salt solution, people mainly focused on the relationship between the n and the species of polynuclear Al, as well as the conjecture about the polynuclear Al species, while the invitable connection between the changes of critical characteristic points of the curves and the conversion of Al species was neglected. Referring to potentiometric titration experimental method, we found that there are 3 characteristic points which are noted as A (n_A, pH_A), B (n_B, pH_B) and C (n_C, pH_C), respectively (Figure 1) on the base titration curve when titrating Al solutions with base under the medium rate of injecting base. These characteristic points are obtained from mathematical fitting on titration curve, due to the curve according with Boltzmann distribution. In which, the critical point is the crossing point of two neighbouring tangent lines passing through inflection point on it, while the inflection point is where the second derivative's value is zero on titration curve equation.

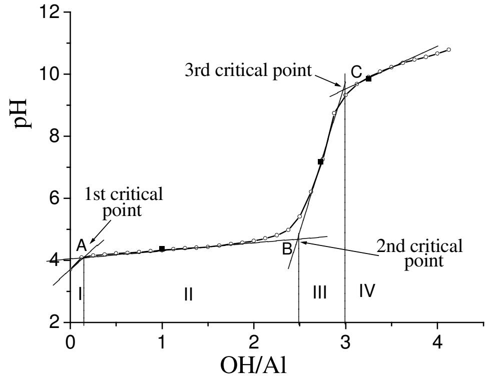


Figure 1. The base titration curve (pH vs OH/Al or n) and the differentiation of polynuclear Al species under the moderate rate of injecting base (four regions/three critical characteristic points). ($AlCl_3$ = 0.005 M; NaOH = 0.01 M; Ionic strength I = 0.02 M).

These three critical points (A, B, C) express different meanings, respectively: At the first critical point A (n = 0.2), a lot of mononuclear Al begin to convert into small/middle polynuclear Al (oligomer). At the second critical point B (n = 2.5), it is very likely that the small/middle polynuclear Al begin to form large polynuclear Al. At the third critical point C (n = 3.0), the amorphous gel or sediment have appeared. In another word, the OH/Al vs pH curve can be divided into four regions quantitatively by these three critical points (Figure 1). In the meantime, detailed exposition about the analysis of titration pH vs n curves and the critical points can be found in the disquisition [14].

It is established that the fraction of hydroxyl aluminum be in accord with some earlier work [15-17]. Generally speaking, the critical point is the characteristic point of the titration curve related to Al salt solution in the hydrolysis-polymerization course, which is related to experiment conditions. The change of critical point reflects the enormous effect of the different experiment conditions on the hydrolysis-polymerization course of Al salt solution and the conversion with respect to the species of hydroxyl polynuclear aluminum.

Effects of various factors on the potentiometric titration pH vs n curves and on the hydrolysis-polymerization species of Al salt solution

It has been shown that there is a multiplicity of factors affecting the hydrolysis-polymerization course of Al salt solution and the conversion of Al species. The shape of the potentiometric titration pH vs n curves and the change of its critical point are obviously different in the dissimilar experiment conditions and extraneous factors. The shape of the pH vs n curves and the changing tendency of the critical point reflect the conversion course of polynuclear Al species. In a later part, we will quantitatively illustrate the effects of various factors on the hydrolysis-polymerization course of Al salt solution and on the conversion regulations of Al species along with the change of the critical point, the concentrations of Al, the temperature, the halide ion, the silicate radical and the organic acid radical, etc.

Effects of the total concentration of Al(III)

Figure 2 shows the titration curves at four different concentrations of $AlCl_3$ solution. During these experiments, we found that the solutions became turbid when the concentration of Al is higher than 0.05 M and the value of n is about 2.6. However, in 0.5 M $AlCl_3$ solution, white turbidity appears immediately as soon as the base is added because of partial oversaturation, and the amount of white flocculent precipitate increased with the n value. The formation of the precipitate accords with the solubility product rule of $Al(OH)_3$ ($K_{sp} = 10^{-34.5}$ at 25 °C). With the increase of the total Al(III) concentration, the degree of hydrolysis of Al^{3+} decreases, while the pH value of the solution fall sharply due to the increasing of the total amount of hydrolysed Al. Furthermore, the change of pH value will cause the alteration of the critical point on pH vs n curve and affect the size and the content of polynuclear Al species directly. It is concluded from the Figure 2 that:

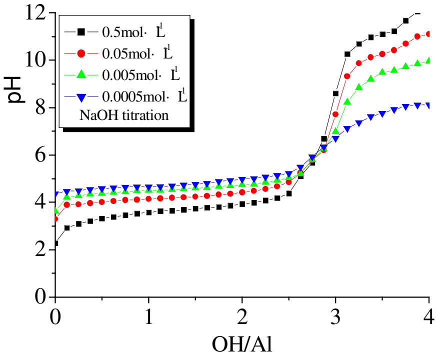


Figure 2. Effects of total Al(III) concentration (0.5-0.0005 M) on the titration curves and critical points.

1) By comparison with the tiny influence of the concentration of Al on the transfer of n_A and n_C, the second critical point n_B is greatly disturbed (see Table 1). The range of the n_B value in which polynuclear Al formed extended with the concentration increasing, and consequently made the corresponding curve in region III comparatively steep. All the above indicates that the higher the concentration, the narrower the range of OH/Al mol ratio in which high polymer comes out, whereas the broader range of OH/Al mol ratio in which low polynuclear Al species occur. It is established that the added OH^- is mainly used to form polynuclear Al when the concentration of Al^{3+} is comparatively low, which makes the pH vs n curve very flat. It is indicated that the lower the concentration within a certain range, the more helpful for the hydrolysis-polymerization of Al^{3+}.

2) In view of the pH value's change on the titration curve in longitudinal direction, the higher the concentration of Al, the lower the pH in region II, on the contrary, the higher the pH in region III and region IV. It's clear that it is helpful for the hydrolysis-polymerization of Al and the formation of oligomeric Al species in the lower n value, and less helpful for the hydrolysis-polymerization of Al in the high n value, which causes the formation of sol/gel Al_c.

3) The shapes of titration curves are slightly altered in the different concentrations of Al. We can see that there is a crossing point close to about n = 2.7 among the four curves of different concentrations of Al^{3+}, which indicates that a relatively stable polynuclear Al species is formed in this spot, and the stable polymer may be a soluble polynuclear Al species, such as $Al_{13}(OH)_{34}^{5+}$ (n = 2.62), $Al_{13}(OH)_{35}^{4+}$ (n = 2.69) or $Al_{13}(OH)_{36}^{3+}$ (n = 2.77), etc.

Table 1. Changes of critical points demarcating Al form under the different Al^{3+} concentration.

Concentration of Al^{3+} (M)	First critical point		Second critical point		Third critical point		Concentration of OH^- (M)
	n_A	pH_A	n_B	pH_B	n_C	pH_C	
0.5	0.17	3.3	2.8	4.2	3.0	9.7	1
0.05	0.19	3.9	2.7	4.5	3.0	9.6	0.1
0.005	0.20	4.1	2.5	4.7	3.0	9.3	0.01
0.0005	0.24	4.4	2.5	5.1	3.1	8.1	0.001

Effects of the temperature

The temperature affects the hydrolysis-polymerization course, the speciation distribution of Al^{3+}, and the pH values of solutions [18-21]. It is observed that the initial pH values of 0.005 M $AlCl_3$ solution are 3.74, 3.69 and 3.41, respectively, at the temperatures of 25 °C, 35 °C and 55 °C.

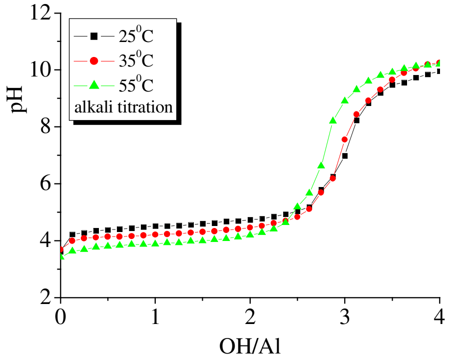


Figure 3. Effect of temperature on the titration curves ($AlCl_3$ = 0.005 M, NaOH = 0.01 M).

Figure 3 indicates that:

1) The effects of temperature on n_A, n_B and n_C are relatively slight (Table 2), which briefly indicate that the effects on the shape of titration curve and on the conversion of polynuclear Al species are comparatively small. In addition, the temperature mainly affects the conversion rate of polynuclear Al species.

Table 2. Effect of temperature on the potentiometric titration curves and its critical points ($AlCl_3$ = 0.005 M, NaOH = 0.01 M).

Temperature (°C)	First critical point		Second critical point		Third critical point	
	n_A	pH_A	n_B	pH_B	n_C	pH_C
25	0.20	4.1	2.5	4.7	3.0	9.3
35	0.19	4.0	2.6	4.5	3.1	8.6
55	0.19	3.7	2.5	4.2	3.1	9.5

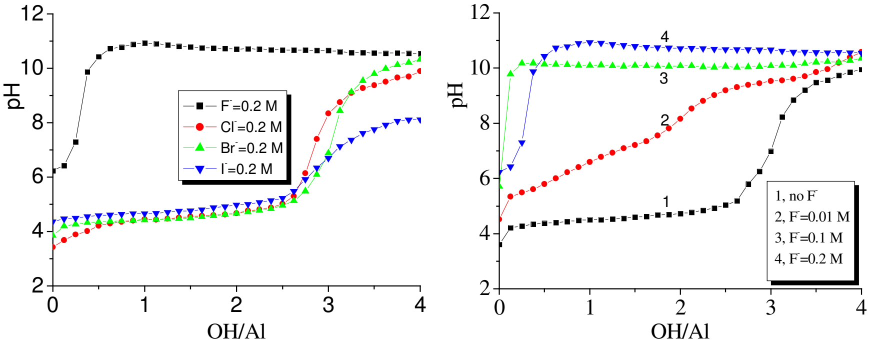
2) The higher the temperature, the lower the pH values in the former section (i.e., region II) of titration curve, which indicates that the hydrolysis degree of Al^{3+} is high in this interval [18]. That is to say, increasing the temperature takes a positive effect on the hydrolysis-polymerization of Al^{3+} and the formation of small/middle polynuclear Al species. On the contrary, the higher temperature, the higher the pH values in the latter section (region III and

region IV) of curve, and the range of Al_c comparatively extends, but the range of Al_b shrinks, which indicates that the increasing of the temperature doesn't make a contribution to the formation of large polynuclear Al species, in the opposite, it accelerates large polymeric Al species converting into sol/gel of Al_c.

3) At higher temperature, the structural unit of metastable polynuclear Al (Al_b) is correspondingly small on account of its instability. However, even if the large polymer formed, there's a trend for it converts into oligomer or gel Al_c. These results confirm that it is very difficult for large polymer to exist stably in high temperature, yet the deprotonation accompanied with the deposition is more obvious [5].

Effects of the halide ion (F^-, Cl^-, Br^-, I^-)

The pH vs n curve shape has great discrepancy as a result of the different kinds and the varied concentration of complexing ions. Furthermore, the titration curve is no longer an inverted "S-shape" when the concentration of complexing ion exceeds a certain value. In another word, the change of the curve shape and the critical point on the curve reflect the abilities of the complexing ions to bond with Al^{3+} when they compete with OH. Figure 4 shows titration curves obtained from experiments when adding solid NaF, NaCl, NaBr, and NaI into 0.005 M $AlCl_3$ solution, respectively. It can be seen from the figure that:



(A) (B)

Figure 4. Effects of F^-, Cl^-, Br^-, I^- and the consumption of NaF on the pH vs n titration curves ($AlCl_3$ = 0.005 M, NaOH = 0.01 M).

1) The effects of Cl^-, Br^- and I^- on the three critical points are much smaller than that of F^-. Furthermore, the abilities of halide ions to affect the hydrolysis-polymerization of $AlCl_3$ solution decreases in the sequence of F^-, Cl^-, Br^-, I^- [22], which is by virtue of the differences in the structures and the properties of respective ions. From F^- to I^-, hard base transfers to soft base. According to the theory of hard and soft acids and bases (HSAB), Al^{3+} ion belongs to hard acid, and the affinity between F^- and Al^{3+} is the strongest among halide ions, so the competitive ability of F^- to OH^- in polynuclear Al molecule is the strongest, furthermore, the effect on the hydrolysis-polymerization course of Al^{3+} is also the greatest, while the responding effects of I^- is the slightest. For the position of Cl^-, Br^- and I^- which are located on the coordination external of the hydroxyl aluminum ion, the adsorption is mainly a relatively weak electrostatic effect. In addition, there is a superposition section in the midst of the titration curves of Cl^-, Br^- and I^- (see Figure 4 (A)), which indicates that the effects of Cl^-, Br^- and I^- are all comparatively slight.

However, excessive Cl^- dosage can also change the coordination environment of Al^{3+} and inhibit the further hydrolysis and polymerizing of Al^{3+}.

2) The higher the concentration of NaF, the higher the initial pH values of solutions, and the larger the changes of the curves shapes obtained. It has been observed that the three critical points shift to the left little by little until they disappear with the increasing addition of NaF, and the pH value increases gradually. When NaF concentration is enough to form AlF_6 completely, NaOH which was added later makes the pH of solution not to fluctuate after a rapid growth, and behaves as a horizontal line (see Figure 4 (B)). In this case, we can only find the first critical point. However, hydroxyl aluminum just exists as mononuclear Al species. The presence of F^- seriously obstructs the hydrolysis-polymerization course of Al salt solution [16, 22].

Effects of the silicate radical

As a weak acid, silicic acid not only lowers the pH value of the solution, but also consumes some of the OH^- that is used in the hydrolysis-polymerization of Al^{3+} in the titration course, which makes the conditions of the polymerization of Al(III) and silicic acid all change. At the same time, the polynuclear silicic acid has a certain chelation (complexation) and adsorption on Al^{3+}, which makes the interaction among the hydrolysis-polymerization products of polynuclear silicic acid and Al ion become rather complicated [23], which affects the hydrolysis-polymerization mechanism of Al^{3+}, the size, the structure, the distribution form and the transformation law of the hydrolysis-polymerization products [23, 24]. The strength of the interaction depends on the SiO_3^{2-}/Al^{3+} mole ratio. In the experiment, 0.1 M and 0.01 M Na_2SiO_3 solutions were prepared by dissolving Na_2SiO_3 in the 0.1 M NaOH solution, respectively, then using them to titrate 25 mL 0.05 M $AlCl_3$ solution, respectively, and the corresponding titration curves are shown in Figure 5.

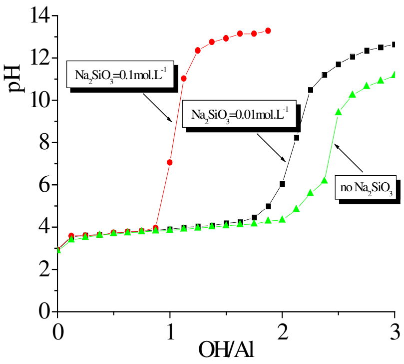


Figure 5. Effect of the soluble silicate concentration on the Al species and the titration curves ($AlCl_3$ = 0.05 M, NaOH = 0.1 M).

It can be seen from this figure that:

1) There is a great effect of SiO_3^{2-} on the second critical point n_B and the third critical point n_C, i.e., it is extremely great on the formation of polynuclear Al species Al_b and gel species Al_c [25], on the contrary, slight on the first critical point n_A (see Table 3). The higher the concentration of SiO_3^{2-}, the smaller the n_B and n_C [26], the more the intervals of region II and region III shift forward to region I. After that, it is impossible to detect polynuclear Al species when the concentration of silicic radical reaches a certain extent [27]. For the 0.1 M and 0.01 M Na_2SiO_3

solutions, the critical points n_B are 0.8 and 1.5, respectively, the mole ratios of SiO_3^{2-}/Al^{3+} are 8.0 and 1.5. From the Figure 5, it seems that SiO_3^{2-} obstructs the hydrolysis and polymerization of Al^{3+} obviously when $SiO_3^{2-}/Al^{3+} \geq 1.5$, and it obstructs the polymerization of Al^{3+} completely at the time when $SiO_3^{2-}/Al^{3+} \geq 8.0$.

2) On increasing the concentration of SiO_3^{2-}, the pH vs n curve in region III becomes steeper and steeper, and the range of OH/Al mole ratio in which the large-polynuclear Al species exists is narrower and narrower, furthermore, the pH increases rapidly simultaneous. It is likely that in the presence of a small quantity of silicic radical, the Al species in partly neutralized Al^{3+} solution are mainly in the form of small polymers however when the concentration of silicic radical reach a certain high level, it will cause the polymerization of silicic acid and the formation of higher aggregates as a result of the reaction between the polynuclear silicic acid and the product of hydrolysis-polymerization of Al^{3+} ions [28].

Table 3. Effects of the Na_2SiO_3 consumption on the critical points of the titration curves ($AlCl_3$ = 0.05 M, NaOH = 0.1 M).

Concentration of Na_2SiO_3 (M)	First critical point		Second critical point		Third critical point	
	n_A	pH_A	n_B	pH_B	n_C	pH_C
0	0.19	3.9	2.7	4.5	3.0	9.6
0.01	0.11	3.5	1.9	4.3	2.3	11.0
0.1	0.12	3.5	0.8	3.9	1.2	12.3

Effects of the organic acid radical

Similar to many inorganic anions, there is competitive coordination between soluble organic acid radical anions and OH^-. It is clear that organic acid radicals can react with aluminium and produce various organo-aluminum complex, which can obstruct or delay the hydrolytic reaction of Al^{3+} [5, 28-33], and even the polynuclear Al species can not be formed [27, 34]. In particular, the inhibition capability of the different kinds of organic acid radicals is dissimilar to the hydrolysis-polymerization course of Al^{3+}. It is principally disturbed by three aspects [22]: (1) the proportion of organic acid radicals to Al^{3+}; (2) the acidity of organic acid; (3) the stability constant of the complex produced by organic acid radicals and Al^{3+}. The effects of the concentration of $C_2O_4^{2-}$ radical on the critical point of the base titration curve for Al solution are shown in Table 4. The different concentration of sodium citrate ($Na_3C_6H_5O_7$), sodium tartrate ($Na_2C_4H_4O_6$) and sodium oxalate were added to the $AlCl_3$ solution, respectively, and then regulated its pH value to the initial pH value of $AlCl_3$ with HCl, at last, these $AlCl_3$ solutions were titrated with the base. Therefore, the titration curves obtained from this experiment which are shown in Figure 6 and Table 4, from which it can be concluded that:

1) The addition of organic acid radical decreases the concentration of Al taking part in the hydrolysis-polymerization, which causes the first region to be broadened. The further hydrolysis and polymerizing of Al^{3+} will be inhibited when the organic acid radical is in high level. In this case, only the first critical point can be found, the other critical points followed can not be distinguished.

2) The shapes of the titration curves can be distinguished with different dosage of organic acid salt, the higher the concentration, the greater the initial pH value of the solution, the serious aberrance in the shape of curve obtained, as well as the greater effects on the hydrolysis-polymerization course of Al^{3+}. With the increasing amount of organic acid radical, the three critical points shift to the left gradually until disappear. When the mole ratio of the organic acid radicals to Al^{3+} is 1:1, there is quite an effect on the titration curves. In the meantime, the hydrolysis-polymerization course of Al salt solution was badly obstructed by the organic acid

radicals. Observed from the changes of the titration curves, in the same mole ratio of organic acid radicals to Al^{3+}, the order according to the degree of their effects as follows: citrate > oxalate > tartrate. Furthermore, the mechanism why organic ligand could obstruct the hydrolysis-polymerization of Al^{3+} is that the complexation reaction occurs between the organic acid radicals and the polynuclear Al species which are in kinetic equilibrium that makes the hydroxyl-bridges among Al atoms of polynuclear Al be destroyed. Therefore, in the presence of organic acid, the forms of aluminum as the mononuclear Al and the oligomers can not be agglomerated [5], and the crystalloid $Al(OH)_3$ can also not be formed [22].

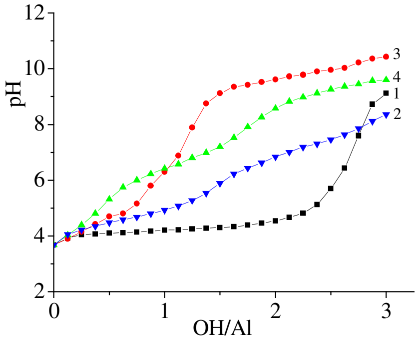


Figure 6. Effects of organic acid radical on the titration curves and their critical points. ($AlCl_3$ = 0.005 M, the mole ratio of organic acid radical: Al^{3+} = 1:1, NaOH = 0.01 M). 1, no organic acid radical; 2, sodium citrate; 3, sodium tartrate; 4, sodium oxalate.

Table 4. Effects of the $C_2O_4^{2-}$ concentration on the critical points of titration curves ($AlCl_3$ = 0.005 M, NaOH = 0.01 M).

Concentration of $C_2O_4^{2-}$ (M)	First critical point		Second critical point		Third critical point	
	n_A	pH_A	n_B	pH_B	n_C	pH_C
0.5	0.38	8.2	without	without	without	without
0.01	0.12	4.2	1.1	4.4	without	without
0.005	0.13	4.1	1.5	4.7	1.9	7.16

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REFERENCES

1. Hunter, D.; Ross, D.S. *Science* **1991**, 251, 1056.
2. Kerven, G.L.; Larsen, P.L.; Blamey, F.P.C. *Soil Sci. Soc. Am. J.* **1995**, 59, 765.
3. Comin, J.J.; Barloy, J.; Bourrie, G. *Europ. J. Agron.* **1999**, 11, 115.
4. Sposito, G. *The Environmental Chemistry of Aluminum*, 2nd ed., CRC Press: Boca Raton, Florida; **1995**; p 87.

5. Wang, C.Y.; Bi, S.P. *ACS Symp. Ser.* American Chemical Society: Washington, DC; **2002**; 822, 246.
6. Phillips, B.L.; Lee, A.; Casey, W.H. *Geochim. Cosmochim. Acta* **2003**, 67, 2725.
7. Gürses, A.; Yalçin, M.; Dogar, C. *Water, Air, Soil Pollut.* **2003**, 146, 297.
8. Nandy, T.; Shastry, S.; Pathe, P.P.; Kaul, S.N. *Water, Air, Soil Pollut.* **2003**, 148, 15.
9. EL-Masry, M.H.; Sadek, O.; Mekhemer, W.K. *Water, Air, Soil Pollut.* **2004**, 158, 373.
10. Rustad, J.R.; Loring, J.S.; Casey, W.H. *Geochim. Cosmochim. Acta* **2004**, 68, 3011.
11. Irving, H.M.; Miles, M.G.; Pettit, L.D. *Anal. Chim. Acta* **1967**, 38, 475.
12. Wang, D.S.; Wei, S.; Yi, X. *Colloids Surf. A: Physicochem. Eng. Aspects* **2004**, 243, 1.
13. Duan, J.; Gregory, J. *Adv. Colloid Interface Sci.* **2003**, 100-102, 475.
14. Bi, S.P.; Wang, C.Y.; Cao, Q.; Zhang, C.H. *Coord. Chem. Rev.* **2004**, 248, 441.
15. Stol, R.J.; van Helden, A.K.; Bruyn, P.L. *J. Colloid Interface Sci.* **1976**, 57, 115.
16. Letterman, R.D.; Asolekar, S.R. *Wat. Res.* **1990**, 24, 931.
17. Hek, H.; Stol, R.J.; Bruyn, P.L. *J. Colloid Interface Sci.* **1978**, 64, 72.
18. Busch, M.; Seubert, A. *Anal. Chim. Acta* **1999**, 399, 223.
19. Phillips, B.L.; Casey, W.H.; Karlsson, M. *Nature* **2000**, 404, 379.
20. Phillips, B.L.; Casey, W.H.; Karlsson, M. *Environ. Sci. Technol.* **2000**, 34, 3242.
21. Wang, S.L.; Wang, M.K.; Tzou, Y.M. *Colloids Surf. A: Physicochem. Eng. Aspects* **2003**, 231, 143.
22. Hsu, P.H. *Soil Chemical Florilegium*, Science Press: Beijing; **1986**; p 19.
23. Gao, B.Y.; Yue, Q.Y.; Wang, Z.S.; Tang, H.X. *Environ. Chem.* (Chinese) **2000**, 19, 1.
24. Tang, Y.X.; Yang, K.; Wu, S.Q. *Environ. Chem.* (Chinese) **1997**, 16, 60.
25. Boisvert, J.P.; Jolicoeur, C. *Colloids Surf. A: Physicochem. Eng. Aspects* **1999**, 155, 161.
26. Browne, B.A.; Driscoll, C.T. *Environ. Sci. Technol.* **1992**, 27, 915.
27. Larsen, P.L.; Kerven, G.L.; Bell, L.C. *Effects of silica acid on the chemistry of monomeric and polymeric (Al_{13}) aluminum species in synthetic soil solutions*, 3rd International Symposium on Plant Soil interactions at Low pH, Dordrecht; **1992**; p 1.
28. Gao, B.Y.; Li, C.P. *Environ. Chem.* (Chinese) **1993,** 12, 268.
29. Krishnamurti, G.S.R.; Wang, M.K.; Huang, P.M. *Clays and Clay Miner.* **1999**, 47, 658.
30. Tombacz, E.; Filipcsei, G.; Szekeres, M. *Colloids Surf. A: Physicochem. Eng. Aspects* **1999**, 151, 233.
31. Narayanan, R.; Laine, R.M. *J. Mater. Chem.* **2000**, 10, 2097.
32. Marilyne, V.S.; Guy, B. *J. Inorg. Biochem.* **2001**, 85, 143.
33. Changui, C.; Stone, W.E.E.; Vielvoye, L. *J. Chem. Soc. Dalton Trans.* **1990,** 1990, 1723.
34. Masion, A.; Thomas, F.; Tchoubar, D. *Langmuir* **1994**, 10, 4353.