

INFLUENCE OF PREPARATIVE HISTORY ON STRUCTURE AND PROPERTIES OF SODIUM ALUMINATE SOLUTIONS^①

Chen, Nianyi Liu, Miaoxiu

Shanghai Institute of Metallurgy, Academia Sinica Shanghai 200056, China

Yang, Jinxiu

Chi, Likuan

Shanghai University of Science and Technology

Shandong Aluminium Factory

ABSTRACT

It has been found that samples of sodium aluminate solutions with the same composition but different preparative history may have different structure and physico-chemical properties. The structure of sodium aluminate solutions change very slowly during the storage after preparation. Sodium aluminate solutions contain several aluminium-bearing anions such as $\text{Al}(\text{OH})_4^-$, $\text{Al}(\text{OH})_5^{2-}$ and $[(\text{HO})_2\text{Al}-\text{O}-\text{Al}(\text{OH})_2]^{2-}$, etc. These anions can convert to each other but the reactions are very slow owing to the formation or breakage of covalent Al-O bond. Hence the ratio between these anions approaches equilibrium very slowly after the preparation, and the structure or properties of these solution samples before equilibrium is reached depend on their preparative histories.

Key words: sodium aluminate solutions physico-chemical properties structure preparative history

1 INTRODUCTION

Sodium aluminate solution is one of the most important intermediate products in alumina production. The structure and properties of sodium aluminate solutions with various concentration and caustic ratio have been investigated by many authors^[1,2], but the results are in contradictory. Recently, we found that the structure and properties of sodium aluminate solutions are often influenced by the preparative history of solution samples, and the results of this work will be reported in this paper.

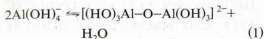
The solution samples used are prepared by dissolving high-purity aluminium into pure NaOH solutions. The solution samples prepared are stored in polyethylene bottles. Sometimes the samples are diluted or changed in composition by adding solid NaOH into solution to prepare sodium aluminate solutions with various preparative history.

2 THE INFLUENCE OF PREPARATIVE HISTORY ON THE RAMAN AND UV SPECTRA OF SODIUM ALUMINATE SOLUTIONS

It has been proved that there exists the

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following reaction in sodium aluminate solutions⁽²⁾



In the Raman spectrum of sodium aluminate solutions, the main peak at 625 cm^{-1} represents $\text{Al}(\text{OH})_4^-$ anion, and two other Raman peaks at 540 cm^{-1} and 710 cm^{-1} represent dimeric anion $[(\text{HO})_3\text{Al}-\text{O}-\text{Al}(\text{OH})_3]^{2-}$. In concentrated solutions reaction (1) shifts to rightside from dimeric anion $[(\text{HO})_3\text{Al}-\text{O}-\text{Al}(\text{OH})_3]^{2-}$. When the concentrated solution is diluted, reaction (1) shifts to leftside to make the Raman peaks at 540 cm^{-1} and 710 cm^{-1} become smaller and unobservable. Results of our experiments indicate that this is a slow reaction. For example, concentrated sodium aluminate solution containing Al_2O_3 280 g/L and Na_2O 341 g/L, after 40 d storage, is diluted sixfold (by volume) by pure water. The change of the Raman peaks at 540 cm^{-1} and 710 cm^{-1} after dilution is rather slow. Only after about 4 h they become smaller and unobservable as shown in Fig. 1. Some other experiments show that after high-purity aluminium is dissolved into concentrated sodium aluminate solutions, the Raman peaks at 540 cm^{-1} and 710 cm^{-1} gradually enlarged during storage after preparation. It means that there happens a slow process of dimeric anion formation from $\text{Al}(\text{OH})_4^-$ by reaction(1).

Besides, we have proved that there exists another reversible reaction in sodium aluminate solutions⁽³⁾



Concentrated sodium aluminate solutions with high caustic ratio containing more $\text{Al}(\text{OH})_6^{3-}$ ions exhibit an additional Raman peak near 470 cm^{-1} . By comparison with the Raman spectrum of $\text{Ca}_3[\text{Al}(\text{OH})_6]_2$ (a solid

compound containing $\text{Al}(\text{OH})_6^{3-}$ ions), it can be confirmed that the Raman peak near 470 cm^{-1} can be assigned to $\text{Al}(\text{OH})_6^{3-}$ ions. The Raman peak at 470 cm^{-1} of concentrated solutions does not disappear immediately after dilution. It means that the decomposition of $\text{Al}(\text{OH})_6^{3-}$ ions is a slow process according to the reaction $\text{Al}(\text{OH})_6^{3-} \rightleftharpoons \text{Al}(\text{OH})_4^- + 2\text{OH}^-$

We have used two different methods to prepare solution samples containing Al_2O_3 280 g/L and Na_2O 341 g/L:

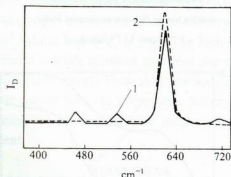


Fig. 1 The change of Raman spectra Intensity (I_D)

of sodium aluminate solution prepared by dilution

Method of preparation: concentrated solution containing Al_2O_3 280 g/L, Na_2O 341 g/L, stored for 40 d, then diluted sixfold.

1—just after dilution; 2—4 h after dilution

(1) Solution sample I: it is prepared directly by dissolving high-purity aluminium into concentrated NaOH solution, and stored for 120 d.

(2) Solution sample II: it is prepared by a two step method. At first high-purity aluminium was dissolved with diluted NaOH solution and a solution with a caustic ratio of 1.48 was prepared; then stored for 45 d, and more solid NaOH were added to adjust its composition being equal to that of solution 1. Fig. 2 and Fig. 3 illustrate the Raman spectra and UV spectra of these two solution samples

respectively.

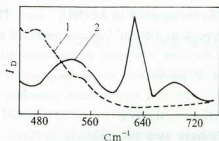


Fig. 2 The Raman spectra Intensity (I_p) of solution samples of sodium aluminate solution having different preparative history

1—sample I; 2—sample II

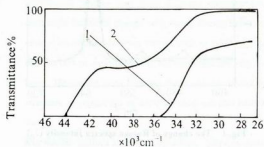


Fig. 3 The UV spectra of solution samples of sodium aluminate solution having different preparative history

1—sample I; 2—sample II

It can be seen from Fig. 2 and 3 that the solution I more $\text{Al}(\text{OH})_6^{3-}$ has a Raman spectrum peak at 470 cm^{-1} , while the solution II contained more $\text{Al}(\text{OH})_4^-$ and $[(\text{HO})_3\text{Al}(\text{OH})_3]^{2-}$ ions has Raman peaks at 540, 625 and 710 cm^{-1} . This is another example of the influence of the preparative history on the structure of sodium aluminate solutions.

Results of our experiments show that the UV spectra of concentrated sodium aluminate solutions with high caustic ratio changes slowly in storage. Their absorption increases gradually between $2,300 \text{ \AA}$ and $2,900 \text{ \AA}$. This may be the results of the formation of $\text{Al}(\text{OH})_6^{3-}$ ions.

3 THE INFLUENCE OF PREPARATIVE HISTORY ON ELECTROCONDUCTIVITY AND VISCOSITY OF SODIUM ALUMINATE SOLUTIONS

Fig. 4 illustrates the viscosity change of two samples of sodium aluminate solution containing Al_2O_3 281 g/L and Na_2O 341 g/L. Solution sample I was prepared by dissolving high-purity aluminium into NaOH solution directly; while solution sample II was prepared by dissolving high-purity aluminium into NaOH solution containing 320 g/L to make a sodium aluminate solution with lower caustic ratio, and then stored for 15 d, added more solid NaOH to prepare a solution sample having the same composition as that of sample I. It can be seen also from Fig. 4 that these two solution samples with different preparative histories, but having the same composition exhibit quite different viscosity in spite of having similar increasing tendency in storage.

The electroconductivities of these two solutions are also different, e. g. the electroconductivity of sample I stored for 17 d is 0.034 V/cm , while that of sample II is 0.038 V/cm . It can be noted that the samples having higher viscosity exhibit lower electroconductivity. The Raman spectrum of solution sample I has higher Raman peak at 540 cm^{-1} . By comparison of the Raman spectra of the above solution samples and that of the solid compounds $\text{K}_2[(\text{HO})_3\text{Al}-\text{O}-\text{Al}(\text{OH})_3]$ and $\text{B}_2[\text{Al}_2(\text{OH})_{10}]$, it can be seen that the 540 cm^{-1} peak may be assigned to anions like $[(\text{HO})_3\text{Al}-\text{O}-\text{Al}(\text{OH})_3]^{2-}$ or $[\text{Al}_2(\text{OH})_{10}]^{4-}$. It is reasonable that the higher content of such dimeric anions will make the solutions exhibit higher viscosity or lower electroconducting.

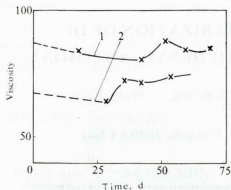


Fig. 4 The change of viscosity of two sodium aluminate solution samples with different preparative history

1—sample I; 2—sample II

The results of quantum chemical calculation indicate that the Al—O bond in aluminate anions has significant covalent character. For example, the most stable configuration of $[(HO)_3Al-O-Al(OH)_3]^{2-}$ anion has the net atomic charges as illustrated in Fig.5.

The overlap population of the Al—O bond in Al—O—Al bridge is 0.47. It means that the Al—O bond exhibits significant covalent character. Its formation or breakage needs significant activation energy, so the chemical reactions may be rather slow at room temperature.

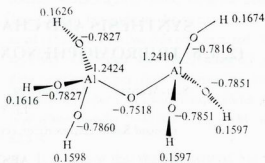


Fig. 5 The net atomic charges in dimeric anion

The mutual conversions of $Al(OH)_4^-$ and $Al(OH)_6^{3-}$ involve the mutual conversion of sp^3 orbital and sp^3d^2 orbital. The high energy level d orbitals involved may give rise to high activation energy. These slow reactions may be the reason why the preparative history influences the physico-chemical properties so evident.

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