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Transformation of monomer aluminate ions from tetrahedron to octaheron①

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Abstract: During the precipitation of gibbsite from supersaturated sodium aluminate solution, the main aluminum containing species in solution will transform from tetrahedral $[Al(OH)_4]^-$ to sixfold octahedral $[(H_2O)_2Al(OH)_4]^-$. In order to elucidate the mechanisms responsible for above transformation, the formation Gibbs free energy as well as frontier orbits of a wide range of aluminum species are studied by ab initio method at B3LYP/6-31G** level. Based on theoretical calculation results, thermodynamic possibility and coordination possibility for aluminate ion transforming from $[Al(OH)_4]^-$ to $[(H_2O)_2Al(OH)_4]^-$ are analyzed and thermodynamic permitted reaction pathways are extracted. It is found that $[Al(OH)_4]^-$ can not react directly with H_2O to carry out the variation of coordination number. Transformation of tetrahedral $[Al(OH)_4]^-$ to octahedral $[(H_2O)_2Al(OH)_4]^-$ is involved in two reaction pathways, one is realized by neutral $[Na(H_2O)_4^+ \cdot Al(OH)_4^-]$ acting mediator, the other is carried by neutral $[(H_2O)Al(OH)_3]$. Though there is a strong thermodynamic trend for the transformation of $[Al(OH)_4]^-$ to $[(H_2O)_2Al(OH)_4]^-$, the practical transformation is very slow. Thus, it can be concluded that there is a great kinetic resistance during the transformation from $[Al(OH)_4]^-$ to $[(H_2O)_2Al(OH)_4]^-$.

Key words: ab initio calculation; aluminate ion; Gibbs free energy; frontier orbital theory
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1 INTRODUCTION

The Bayer process for the production of alumina from bauxite involves a perennial gibbsite (γ-$Al(OH)_3$) precipitation step, relating to an inherently slow crystal growth from supersaturated sodium aluminate solution. According to experimental results[1, 2], the tetrahedral $[Al(OH)_4]^-$ ion is the dominant species in caustic aluminate solution while the basic growth unit of gibbsite precipitating in caustic aluminate solution is octahedral $[(H_2O)_2Al(OH)_4]^-$, the transformation of $[Al(OH)_4]^-$ into $[(H_2O)_2Al(OH)_4]^-$ is the key step in the decomposition of supersaturated sodium aluminate solution. There are many possible reaction pathways for the above transformation. However, it is very difficult to identify experimentally which one is thermodynamically permitted, and it is also very difficult to measure the thermodynamic functions of transient aluminate ions. Hence, a systematic theoretical work is important to fully understand the transformation mechanism and to further refine experimental results. The aim of this work is to investigate the thermodynamic feasibility and coordination-bond formed possibility for the transformation of monomer aluminate ion from tetrahedron to octahedron by theoretical calculation.

Clarifying the reaction pathways of tetrahedral aluminate ions transforming to octahedral ions will provide theoretical guide for enhancing the crystallization of gibbsite from supersaturated sodium aluminate solution. Gerson et al[3] investigated the transformation mechanism by a semi-empirical quantum mechanical molecular modeling method, and concluded that the polymerization among tetrahedral $[Al(OH)_4]^-$ promoted the formation of octahedral aluminate. However, their results can not interpret the influence of water and cations on the decomposition of supersaturated sodium aluminate solution, and their accuracy is uncertain. Here, by Gaussian94 ab initio method at B3LYP/6-31G** level on Sgi workstation, the Gibbs free energy $\Delta_f G_m^\ominus$ as well as frontier orbital of various kinds of ions relating to the variation of Al(Ⅲ) coordination number are obtained, and a series thermodynamically favorable reactions for the transformation of tetrahedral aluminate ion to octahedral ion are put forward.

2 METHODOLOGY

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2.1 Selection of calculation method and base set

To obtain accurate thermodynamic data, preliminary geometry optimizations are performed at Hartree-Fock level. The final results presented include corrections for electron correlation though Becke's three-parameter combination of Hartree-Fock and gradient-corrected density functional exchange combined with the nonlocal correlation functional of Lee-Yang-Parr (B3LYP)[4]. The majority of calculations were performed using the standard double-ζ 6-31G** base set which includes polarization functions for all elements[5]. Although large basis sets are desirable, there is often found to be some cancellation of errors between the incompleteness of the correlation correction and that of the basis set. As many of the species involved are anions, the addition of diffuse functions will be important, particularly for oxygen, in order to obtain accurate energetics. However, the influence of basis set on geometry is found to be smaller. Hence, in order to make the full optimization and frequency evaluation possible for all species at the same level of accuracy, those tasks have been undertaken at the double-polarization level, with a more extensive basis set being used for a single-point energy evaluation at the final configuration (B3LYP/6-311 + + G** // B3LYP/6-31G**). All calculations were performed using the program Gaussian94[6].

By the above calculation method, we obtained the theoretical standard Gibbs free energy of formation of $[Al(OH)_4]^-$ and Al^{3+} (in water medium) to be − 1 312.75 kJ/mol and − 492.27kJ/mol, respectively; while the experimental value is − 1305.29 ± 1.00 kJ/mol and − 488.69 ±1.60 kJ/mol separately[7]. The consistency between theoretical and experimental results prove that the calculation method in our research is reasonable.

2.2 Influence of environment on electronic structural properties of aluminate ions

An important aspect of this work is the consideration of environment in which aluminum species exist. Many of the anions are likely to be unstable in gas phase but may possibly be formed in solution. In practical Bayer liquors, there are insufficient water molecular to satisfy the hydration needs of the aluminate ions in solution. Embedding in a dielectric continuum would be inappropriate in this case as the dominant interaction is the Coulomb potential action between cations and anions, rather than solvate. Because of the high concentration of charged species, it is more reasonable to regard the supersaturated sodium aluminate solution as an amorphous "lattice". To obtain accurate Gibbs free energy of formation, each ion on average would be expected to experience the influence of an equal charge but of opposite sign to maintain electroneutrality. The presence of the counteractions around each ion is represented by a series of point-charges distributed over the surface of a sphere, centred on the center of mass, with equal partial charges so that the total charge balances that of the anion. The radius of the point-charge sphere is determined as follows[8]. First, the maximum diameter of the anion is calculated on the basis of Van der Waals radii for the constituent atoms, and this is divided into two to obtain an effective radius for the species. A number of alternative approaches for obtaining a radius were examined on the basis of properties of the underlying quantum mechanical calculations. The same approach was used to determine the diameter of a water molecule, while the ionic radius was used for a sodium cation. From the appropriate sum of the radii, the radius of the point-charge sphere can be calculated for any give number of hydration shells. For example, if two solvent shells separate the cation-anion pair then the radius is set equal to the sum of the sodium and anion radii, plus twice the diameter of a water molecule. To examine the effect of the degree of hydration, the Coulomb stabilization was calculated for the cases where there is no water of solvation or one, two and three shells of water[1]. Those four cases correspond to radii of 1.21 Ù, 5.28 Ù, 9.11 Ù and 12.95 Ù, respectively, plus the radius of the species itself. Results of geometry optimizations in different point-charge potential fields showed that the Al-O bond length in 1-shell-H_2O potential field is consistent well with experimental results[1, 9] (Fig. 1). Thus, 1-shell-H_2O potential fields reflect the cation-anion interaction in general Bayer liquors. Following discussion are based on the theoretical results in 1-shell-H_2O potential fields.

3 RESULTS AND DISCUSSION

3.1 Thermodynamic trend for transformation of aluminate ions from tetrahedron to octahedron

During the theoretical calculation, it is found that $[Al(OH)_5]^{2-}$ and $[Al(OH)_6]^{3-}$ cannot exist stably in 1-shell-H_2O potential fields, $[(H_2O)Al(OH)_4]^-$ is the most stable pentahedra aluminate ion while $[(H_2O)_2Al(OH)_4]^-$ is the most stable sixfold octahedral aluminate ions from the point of view of total energy and solvation stability energy of them.

There are many potential reaction pathways for the transformation from tetrahedral $[Al(OH)_4]^-$ to octahedral $[(H_2O)_2Al(OH)_4]^-$, and their theoretical free energy variation are listed in Fig. 2.

From the point of view of thermodynamic theory, a possible reaction could become practical if only it had undergone free energy decreasing process. This means the free energy variation of the

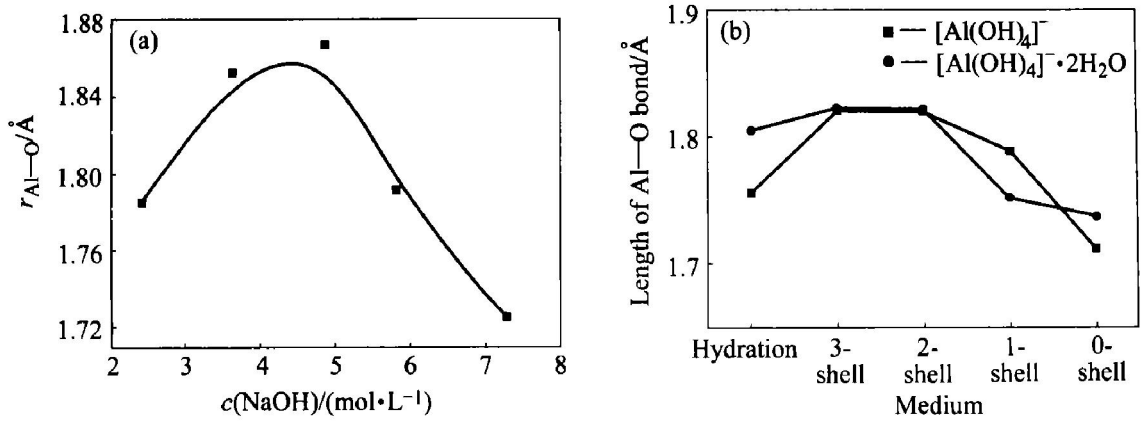

Fig. 1 Bond length of Al-O obtained by different methods
(a) —Experimental results of solution X-ray diffraction analysis; (b) —Theoretical results of ab initio calculation

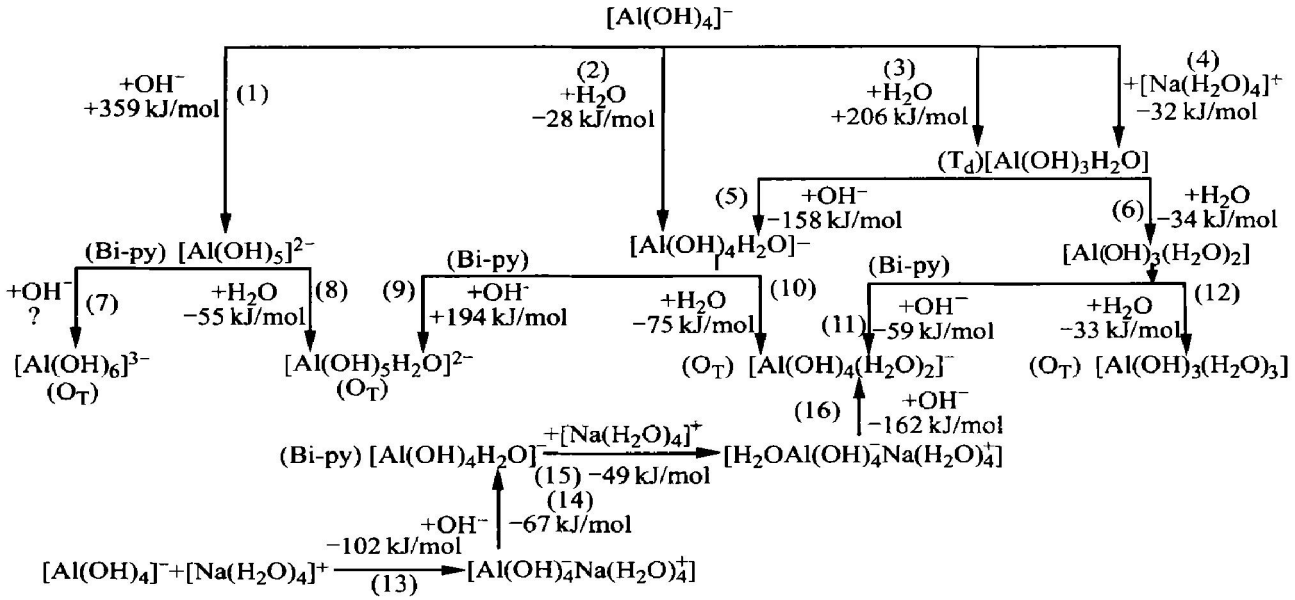

Fig. 2 Possible reaction pathways and free energy variation $\Delta_r G_m$ for transformation from monomer tetrahedral $[Al(OH)_4]^-$ to octahedral $[(H_2O)_2Al(OH)_4]^-$

reaction should be negative. According theoretical calculation results (Fig. 2), $[Al(OH)_4]^-$ cannot react directly with OH^- to form sixfold octahedral aluminate ion (Fig. 2: reaction(1), (7), (8)) because $\Delta_r G_m$ has a great positive value. It is also thermodynamically limited for $[Al(OH)_4]^-$ reacts directly with H_2O to form six-fold octahedral aluminate ion (Fig. 2: reaction(2), (3), (9)) because the value of $\Delta_r G_m$ is very minor. Considering the limitation of $\Delta_r G_m$, the transformation of tetrahedral $[Al(OH)_4]^-$ to octahedral $[(H_2O)_2Al(OH)_4]^-$ may be involved in two reaction pathways, one is realized by neutral $[(H_2O)Al(OH)_3]$ (Fig. 2: reaction(4), (5), (6), (11), (12)) acting as intermediate, the other by neutral $[Na(H_2O)_4^+ \cdot Al(OH)_4^-]$ (Fig. 2: reaction (13), (14), (15), (16)).

3.2 Possibility of coordination-bond increase in transformation of aluminate ion from tetrahedron to octahedron

The transformation from tetrahedral $[Al(OH)_4]^-$ to octahedral aluminate ions is a procedure of the coordination number increase of Al(III). Thereby, the transformation reactions must be not only thermodynamically permitted but also coordinate-bond formation allowed. Here, the coordinate-bond formation possibility is investigated in the light of Frontier Orbital Theory[10].

According to Frontier Orbital Theory, in coordinate reaction, the symmetrical characteristic and energy level of the frontier orbits of the metallic-atom containing species should match well with that of chelating-atom containing species. This means that the highest occupied molecular orbit (HOMO) of Al(III) containing species should match well with the lowest unoccupied molecular orbit (LUMO) of chelating-atom in chelator (such as OH^- or H_2O) in

both aspects of symmetrical character and energy level. When energy level of the HOMO and the LUMO is similar and their symmetry is matched, a coordinate bond between metallic ion and chelating-atom will form.

The frontier Orbits of all species involving in above two kinds reaction pathways (Fig. 2, reaction (4), (5), (6), (11), (12), (13), (14), (15), (16)) are illustrated in Fig. 3.

According to theoretical calculation results, the energy level of HOMO (E_{HOMO}) of H_2O or OH^- is − 12.46 eV and − 0.877 8 eV respectively, while energy level of LUMO (E_{LUMO}) of $[Al(OH)_4]^-$ is 7.06 eV (as shown in Fig. 3). Therefore, during the coordinate reaction, it is difficult for electrons to migrate from HOMO of H_2O or OH^- to LUMO of $[Al(OH)_4]^-$. Additionally, symmetrical characteristic in Fig. 3 shows that HOMO of H_2O or OH^- is mainly composed of 2p atomic orbits of oxygen, which displays mirror antisymmetry, while LUMO of $[Al(OH)_4]^-$ is associated by $3d_{x^2-y^2}$ and $3d_{z^2}$, which presents spherical symmetry (Fig. 3). So, during the coordinate reaction, LUMO of $[Al(OH)_4]^-$ cannot carry out the largest effective overlap with HOMO of H_2O or OH^-, new Al-O coordinate bond cannot be formed effectively. In brief, Al(Ⅲ) in $[Al(OH)_4]^-$ cannot run coordinate reaction directly with H_2O or OH^- based on the symmetrical characteristic and energy level of their frontier orbits.

In contrast to the fact that there is no favorable chelators in solution to coordinate with monomer $[Al(OH)_4]^-$, general chelators in caustic aluminate solution present well coordinate trend with neutral Al-containing species, such as $[(H_2O)Al(OH)_3]$ and $[Na(H_2O)_4^+ \cdot Al(OH)_4^-]$. Molecular H_2O in $[(H_2O)Al(OH)_3]$ or $[Na(H_2O)_4^+ \cdot Al(OH)_4^-]$ has altered the feature of frontier orbits of Al-containing species obviously (Fig. 3).

According to thermodynamic analysis, neutral $[(H_2O)Al(OH)_3]$ display better thermodynamic trend to react with H_2O and OH^- (Fig. 2). However, $[(H_2O)Al(OH)_3]$ (E_{HOMO}= − 2.085 eV) would prefer to coordinate with OH^- (E_{LUMO} = − 0.877 8 eV) rather than H_2O (E_{LUMO} = − 12.46 eV) in view of the limitation of energy level (Fig. 3). Yet, their frontier orbits do not match very well in the aspect of symmetry.

According to symmetry and energy level of frontier orbital (Fig. 3) of each species listed in Table 1, Al(Ⅲ) in $[Al(OH)_4^- \cdot Na(H_2O)_4^+]$ or $[(H_2O)Al(OH)_4^- \cdot Na(H_2O)_4^+]$ has much greater bonding (re-coordination) potential than other

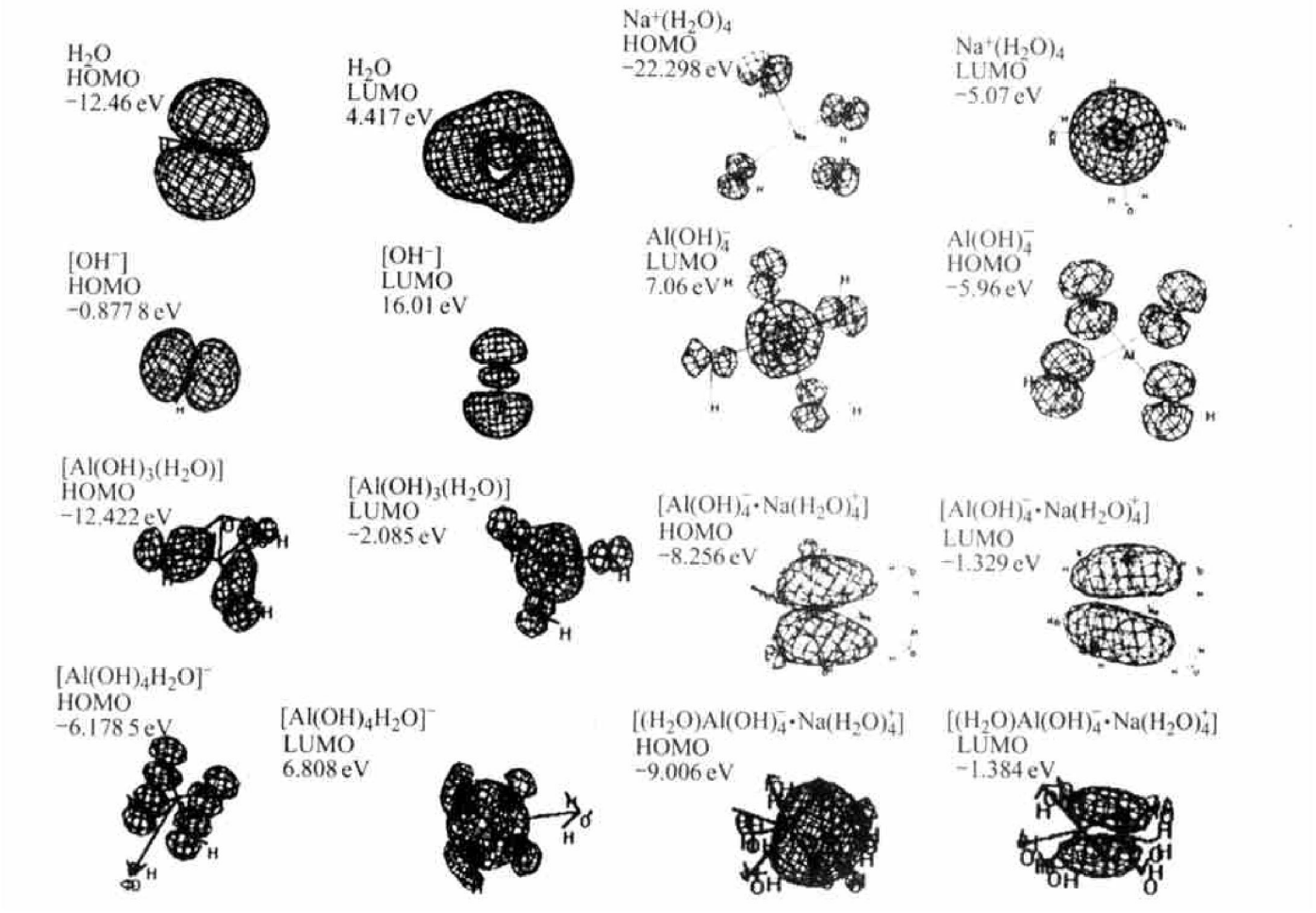

Fig. 3 Frontier orbits of reactants related to transformation of monomer aluminate ion from tetrahedron to octahedron

Table 1 Thermodynamically favourable pathways for transformation of aluminate ion from tetrahedron to octahedron (in 1-shell-H_2O potential field)

Reaction	$\Delta_r G_m$/(kJ · mol^{-1})
(1) $[Al(OH)_4]^- + [Na(H_2O)_4]^+ \rightleftharpoons [Al(OH)_3(H_2O)]\ (T_d) + [Na^+(H_2O)_3(OH^-)]$	−32
(2) $[Al(OH)_3(H_2O)] + OH^- \rightleftharpoons [Al(OH)_4\ H_2O]^-$ (Bi-*py*)	−158
(3) $[Al(OH)_4\ H_2O]^- + H_2O \rightleftharpoons [Al(OH)_4(H_2O)_2]^-\ (O_T)$	−75
(4) $[Al(OH)_4]^- + [Na(H_2O)_4]^+ \rightleftharpoons [Al(OH)_4^- \cdot Na(H_2O)_4^+]$	−102
(5) $[Al(OH)_4^- \cdot Na(H_2O)_4^+] + OH^- \rightleftharpoons [Al(OH)_4(H_2O)]^-$ (Bi-*py*) $+[Na^+(H_2O)_3(OH^-)]$	−67
(6) $[Al(OH)_4\ H_2O]^- + [Na(H_2O)_4]^+ \rightleftharpoons [Al(OH)_4(H_2O)^- \cdot Na(H_2O)_4^+]$	−49
(7) $[Al(OH)_4(H_2O)^- \cdot Na(H_2O)_4^+] + OH^- \rightleftharpoons [Al(OH)_4(H_2O)_2]^-\ (O_T) + [Na^+(H_2O)_3(OH^-)]$	−162

Al-containing species.

$[Na(H_2O)_4]^+$ in $[Na(H_2O)_4^+ \cdot Al(OH)_4^-]$ has significantly altered not only the symmetry but also energy level of frontier orbits of Al-containing species (Fig. 3). Energy level of LUMO of $[Na(H_2O)_4^+ \cdot Al(OH)_4^-]$ and $[Na(H_2O)_4^+ \cdot (H_2O)Al(OH)_4^-]$ are all decreased by −1 eV as compared with that of $[Al(OH)_4]^-$. The component of their LUMO are mainly composed of $3d_{z^2}$ and $3p_Z$, which present mirror antisymmetry. So, LUMO of $[Na(H_2O)_4^+ \cdot Al(OH)_4^-]$ is specially favorable for overlaping with HOMO of OH^-, which will lead to electrons migrate from the HOMO to the LUMO and promote the formation of a new coordinate bond.

From the point of view of Frontier Orbital Theory, Al (III) in $[(H_2O)Al(OH)_3]$ and $[Na(H_2O)_4^+ \cdot Al(OH)_4^-]$ has strong potential to coordinate with H_2O or OH^-.

4 CONCLUSIONS

In terms of the limitation of both thermodynamics and Frontier Orbital Theory, $[Al(OH)_4]^-$ cannot react directly with chelator to realize the transformation of monomer aluminate ions from tetrahedron to octahedron. The transformation of aluminate ion from tetrahedral $[Al(OH)_4]^-$ to octahedral $[Al(OH)_4(H_2O)_2]^-$ may undertake two kinds of reaction pathways as shown in Table 1. One pathway is made up of reactions (1)—(3); the other is reactions (4)—(7). Both of reaction pathways are involved in the formation of neutral intermediate: one is tetrahedral $[Al(OH)_3H_2O]$, the other is $[Al(OH)_4^- \cdot Na(H_2O)_4^+]$. No matter which reaction pathway does the transformation process undertake, $[Na(H_2O)_4]^+$ will play an important role in promoting the formation of octahedral aluminate ions.

Considering both thermodynamic and re-coordination possibility, the second pathway (reactions (4) to (7) in Table 1) should be the dominant way in the transformation of monomer aluminate ion from tetrahedron to octahedron.

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