QUANTUM CHEMICAL STUDY OF ANIONS
IN SODIUM ALUMINATE SOLUTION[①]

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ABSTRACT

The electronic structure and the energy of various aluminate anions possibly existed in sodium aluminate solutions have been calculated by *ab initio* and DV–Xα methods of quantum chemistry. The calculation results are used to explain the experimental results of the spectroscopic study of sodium aluminate solutions. It has been found that $Al(OH)_4^-$ may be more stable than AlO_2^- in solutions. and that $[(HO)_3Al-O-Al(OH)_3]^{2-}$ may be more stable than $[(HO)_3Al \langle \overset{O}{\underset{O}{}} \rangle Al(OH)_2]^{2-}$ anions. The ultraviolet spectra of sodium aluminate solutions are also interpreted by quantum chemical method.

Key words: sodium aluminate solutions   anion   quantum chemistry

1 INTRODUCTION

Sodium aluminate solutions are important intermediate products in alumina production whose structure is concerned by the metallurgists dealing with aluminium production[1]. In recent years, we have used Raman spectra, UV spectra, IR spectra and NMR spectra to investigate the structure of sodium aluminate solutions concurrently. And quantum chemical calculation is used for the interpretation of experimental results. Some results will be described in this paper.

2 METHOD OF COMPUTATION

The electronic structure and energy of various aluminate anions are calculated by HO-NDO program of *ab initio* method. For simpler anions such as $Al(OH)_4^-$ or AlO_2^-, STO–

3G basis sets are used to optimize the equilibrated configurations by *ab initio* method. Then 3–21G basis sets are used to calculate the electronic structure and total energy of anions more accurately. For larger anions, such as dimeric anions $[(HO)_3Al-O-Al(OH)_3]^{2-}$ and $[(HO)_3Al \langle \overset{O}{\underset{O}{}} \rangle Al(OH)_2]^{2-}$, semi–empirical MNDO method is used for the optimization of geometrical configuration, then the electronic structure and the total energies of anions are calculated by *ab initio* method using STO–3G basis sets.

Since the transition state theory of Xα method offers a convenient method for excitation energy computation, we have used DV–Xα method to investigate the UV spectra of sodium aluminate solutions. The above mentioned computations are performed on a VAX 8350 computer.

3 RESULTS AND DISCUSSION

3.1 Relative Stability of AlO_2^- and $Al(OH)_4^-$ Ions

Solid sodium metal aluminate ($NaAlO_2$) and sodium aluminate solution had been considered containing AlO_2^- ions. The concept has been, however, proved to be incorrect. Solid $NaAlO_2$ has been proved containing three-dimensional network of AlO_4^- tetrahedra with sharing corners. There is also no reliable evidence to support the existence of AlO_2^- in aqueous solutions. Recently more authors tend to support the existence of $Al(OH)_4^-$ ions instead of AlO_2^- ions in aqueous solutions [2-3].

We have used ab initio method to calculate the energy difference between $AlO_2^- + 2H_2O$ and $Al(OH)_4^-$ (tetrahedral configuration). At first the configurations of H_2O and AlO_2^- are optimized by energy gradient method. The resultant configuration of H_2O is of C_{2v} symmetry, with $R(O-H) = 0.99$ Å, $\angle HOH = 100$ (°); while the resultant configuration of the AlO_2^- is of $D_{\infty h}$ symmetry, with $R(Al-O) = 1.62$ Å. The optimization of $Al(OH)_4^-$ is restricted to tetrahedral structure, i. e. with T_d symmetry, and $R(Al-O) = 1.64$ Å, $R(O-H) = 0.96$ Å. Based on optimized configuration, it has been proved that the following reaction

$$AlO_2^- + 2H_2O \longrightarrow Al(OH)_4^- + 745 \text{ kJ/mol}$$

is strong exo-energetic. Hence the $Al(OH)_4^-$ ion should be much more stable than AlO_2^- in aqueous solution. The bond order calculation has also proved that when AlO_2^- approaches two water molecules, the electron cloud transfers from one O-H bond in water molecule to Al-O bond to form Al-O-H structure, i. e., form $Al(OH)_4^-$ anion.

We have measured the NMR spectra of

sodium aluminate solutions with different concentration and caustic ratio, and found that the chemical shift varied between $70 \sim 79$ ppm. It also indicates that the coordination number of ^{27}Al is $4^{[4]}$. In addition, the substitution of deuterium for hydrogen in aluminate ions changes the Raman and IR spectra significantly. This implies that hydrogen atoms are components of aluminate anions. Therefore it is reasonable to suppose the existence of the $Al(OH)_4^-$ ions instead of AlO_2^- ions in aqueous solution.

3.2 Configuration and Electronic Structure of $Al(OH)_4^-$ Ions

Since some authors discussed the possibility of the existence of $Al(OH)_4^-$ ion with planar configuration (D_{4h} symmetry) in aqueous solution [5], we have used quantum chemical method to investigate the relative stability of $Al(OH)_4^-$ anions with a tetrahedral structure and with a planar structure. The results of the calculation indicate that the tetrahedral $Al(OH)_4^-$ ion is much more stable than the planar one. The total energy difference is 306 kJ/mol.

The calculated values of the atomic net charges in the optimized tetrahedral $Al(OH)_4^-$ are as follows: Al atom, $+1.35$ e; O atom, -0.44 e; H atom, $+0.071$ e. The overlap population of Al-O bond is 0.44, implying the strong covalent character of Al-O bond.

3.3 The Relative Stability of $[(HO)_3Al-O-Al(OH)_3]^{2-}$ Ion and $[(HO)_3Al \langle^O_O\rangle Al(OH)_3]^{2-}$ Ion

Existence of $[(HO)_3Al-O-Al(OH)_3]^{2-}$ and $[(HO)_3Al \langle^O_O\rangle Al(OH)_3]^{2-}$ has been preliminary discussed in references [2] and [6]. The existence of the former in solid compound

$K_2[(HO)_3Al-O-Al(OH)_3]^{2-}$ has been proved by X–ray diffraction. And the Raman or IR spectra of concentrated sodium aluminate solution indicate the existence of $[(HO)_3Al-O-Al(OH)_3]^{2-}$ ions in such solutions. But there is still no strong evidence about the existence of anion $[(HO)_3Al \langle {}^O_O \rangle Al(OH)_3]^{2-}$ in aqueous solution.

Our results of quantum chemical calculation by *ab initio* method show that

$$[(HO)_3Al-O-Al(OH)_3]^{2-} \longrightarrow$$
$$[(HO)_3Al \langle {}^O_O \rangle Al(OH)_3]^{2-} -356 \text{ KJ} / \text{mol}$$
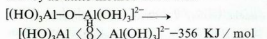
is an endo-energetic reaction. Therefore, only $[(HO)_3Al-O-Al(OH)_3]^{2-}$ ion has been proved to be existent in sodium aluminate solutions.

The optimized configuration of $[(HO)_3Al-O-Al(OH)_3]^{2-}$ ion by MNDO method has the following structural parameters: $R(O-Al) = 1.75$ Å (in terminal group), $R(O-H) = 0.97$ Å (in terminal group), $\angle AlOAl = 134$ (°) (in Al–O–Al bridge), $R(O-Al) = 1.67$ Å. The symmetry of this anion is C_s point group. The optimized configuration of $[(HO)_3Al \langle {}^O_O \rangle Al(OH)_3]^{2-}$ is shown in Fig. 1.
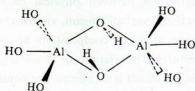
Fig. 1   The configuration of $[(HO)_3Al \langle {}^O_O \rangle Al(OH)_3]^{2-}$

The calculated structural parameters in Fig. 1 are $R(O-Al) = 1.72$ Å (in terminal), $R(O-H) = 0.97$ Å (in terminal), $\angle AlOAl = 112$

(°), $\angle HOO = 95$ (°), $R(O-Al) = 2.22$ Å (in middle part), $R(O-H) = 0.95$ Å (in middle part).

3.4 *Interpretation of the UV Spectra of Sodium Aluminate Solutions*

DV–Xα method has been used to calculate the excitation energy of various aluminate anions. The corresponding ultraviolet absorption peaks are as follows:

$Al(OH)_4^-$	2,344 Å
$Al(OH)_6^{3-}$	2,647 Å
$[(HO)_3Al-O-Al(OH)_3]^{2-}$	2,666 Å

The absorption peak of $Al(OH)_4^-$ may be overshadowed by the strong absorption of NaOH in solution. The absorption peak near 2,700 Å may be assigned to $[(HO)_3Al-O-Al(OH)_3]^{2-}$ ion, while the strong absorption band between 2,300~2,900 Å for the high α_k concentrated solution may be assigned to $Al(OH)_6^{3-}$ anion, which has been proved to be existent in sodium aluminate solutions of this kind.

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