Influence of supersaturation on structure of sodium aluminate solutions with medium concentration: a solution X-ray diffraction study[①]

LI Jie(李　洁), CHEN Qi-yuan(陈启元), YIN Zhou-lan(尹周澜),

ZHANG Ping-min(张平民), LI Yuan-gao(李元高)

(College of Chemistry and Chemical Engineering, Central South University, Changsha 410083, China)

[Abstract] Influence of supersaturation on the structure of a series of freshly prepared supersaturated sodium aluminate solutions with medium concentration was investigated by solution X-ray diffraction. Experimental results show that the basic Al-containing species in all kinds of supersaturated solution is four-coordinated ions. Opposite to Al—O distance contracted in highly concentrated solution, a little expand of the Al—O distance from 1. 75 Å to 1. 85 Å occurs with increasing supersaturation, which is consistent with the occurrence of oligomeric aluminate species. Meanwhile, O—O distance in the first shell of H₂O—H₂O(OH) in supersaturated sodium aluminate solution is obviously longer than in hydroxide sodium solution and becomes longer and longer with increasing supersaturation. Na—O bond length is about 2. 4 Å and changes little with supersaturation. The reason for Al—O bond expanding with supersaturation and its influence on the stability of solution was discussed.

[Key words] solution X-ray diffraction; sodium aluminate solution; structural property

[CLC number] O 645; O 614. 3　　　　　　　　　　[Document code] A

1 INTRODUCTION

Though many powerful analytical techniques were performed on sodium aluminate solution[1~4], they still had some limitation. X-ray diffraction is one of the most important ways to detect solution structure directly. Some solution X-ray diffraction measurements were made as part of a much large study of alkaline aluminate solutions in Hungary in the 1970's, but no structural conclusions were draw and the data were not published in the open literature because of limitation of experimental condition and data treatment technique[5]. Recently, Radnai et al[6] had studied the highly concentrated aluminate solution and found Al—O distance contracted with increasing supersaturation. However, the property of middlingly concentrated sodium aluminate solution is obviously different from highly concentrated solution in both thermodynamic and kinetic aspects[7, 8]. The former is widely used in alumina industry production. So, it is necessary to research the structure of middlingly concentrated sodium aluminate solution further more. This paper reports the experimental results of solution X-ray diffraction on a series of middlingly concentrated sodium aluminate solution with nearly the same caustic concentration ([NaOH] ≈ 4. 8mol/ L⁻¹) and different supersaturation.

2 EXPERIMENTAL

2. 1 Solution preparation

All solutions were prepared from aluminum met-

al (99. 95% pure) and NaOH(97. 5% pure). The mass of NaOH used in any given solution preparation was the required mass of NaOH adding the extra mass needed to composite for the impurity in raw material. To prepare a solution, the correct mass of NaOH was dissolved to one-half of the total distilled water, then required mass of Al metal was added to the caustic solution slowly. As the metal dissolved completely, the liquors were filtered firstly through 3 layer of whatman paper and then through 0. 2 μm membrane. The liquor was transferred into a sealed acryl-glass container at room temperature. All the aluminate solutions were added with very little amount of sodium gluconate (99% grade) as a seed poison[6] to prevent the decomposition of supersaturated aluminate solution.

2. 2 Analysis of composition and density of liquors

Determinations of the amounts of Al(OH)₃ and NaOH was achieved by titration referring to the metallurgy industry standard analysis method YB-817-75; and densities were measured by a density meter DA-110 (Kyoto, Japan) at 25 ℃ using distilled water as density standards. Supersaturation σ is defined as[9]

$$\sigma = (R_p - R_{peq})/ R_{peq}$$
$$R_p = n(Al(OH)_3)/ n(NaOH)$$
$$R_{peq} = (n(Al(OH)_3)/ n(NaOH))_{eq}$$
$$R_{peq} = 0. 607\ 8\exp[6. 210\ 6- (2\ 486. 7-$$
$$33. 712\ 5) c(NaOH))/(273+ t)]$$

where c (NaOH) refers to the concentration of NaOH, mol/ L; t is the temperature in experiment,

℃; R_p represents molecule ratio of $Al(OH)_3$ to NaOH; R_{peq} is equilibrium molecule ratio.

Chemical compositions, supersaturation and densities of each sodium aluminate solution and the two reference liquids, pure water and 4.705 mol/L NaOH solution, are given in Table 1.

2.3 X-ray diffraction measurements and data treatment

X-ray diffraction measurements were performed in a thermostatic room at a temperature of (25 ± 1) ℃ by an X-ray diffractometer (JEOL, Japan) using Mo K_α radiation source with a wavelength of 0.711 Ů. The observed range of scattering angles (2θ) was between $0°$ and $110°$. Times to obtain 40 000 counts were measured at each angle point. The method of measurement and the corrections for background, polarization, absorption, subtraction of the scattering pattern of the empty cell and conversion of the corrected intensities into absolute units were referred to Refs. [6, 10~12]. 75 μm thin foils of bi-oriented polypropylene were selected as the most suitable polymer windows of the cell for measurement.

The experimental structure function is defined as[6, 10]:

$$si(s) = s \left| I_{abs}^{(s)} - \sum_{j=1}^{m} x_j f_j^2(s) - \sum_{j=1}^{m} x_j I_{j,inc}(s) \right| M(s) \qquad (1)$$

where s is the scattering variable, $s = (4\pi/\lambda)\sin\theta$, λ is the wavelength of incident radiation; $I_{abs}(s)$ is the corrected intensity converted to absolute units; x_j is the mole fraction in a structural unit containing m kinds of atoms; $f_j(s)$ is the coherent scattering factor; $I_{j,inc}(s)$ is the incoherent scattering factor of a_j type scattering unit; $M(s)$ is the modification function:

$$M(s) = \frac{\exp(-0.03s^2)}{\left[\sum_{j=1}^{m} x_j f_j(s) \right]^2} \qquad (2)$$

Four types of scattering units were considered as being present in the solutions: Na^+ ions, OH^- ions, H_2O molecules and Al^{3+} ions. The parameters re-

quired to compute the scattering intensity were taken from Refs. [11~13]. The experimental pair distribution function $G(r)$ was computed from $si(s)$ by Fourier transformation according to[10]:

$$G(r) = D(r)/(4\pi r^2 \rho_0)$$
$$= 1 + \frac{1}{2\pi^2 r \rho_0} \int_{s_{min}}^{s_{max}} s^2 i(s) j_0(rs) ds \qquad (3)$$

where $D(r)$ is radial distribution functions, r is the interatomic distance, s_{min} and s_{max} are the lower and upper limits of the range of experimental data respectively, ρ_0 is the bulk number density of the X-ray "Scattering units" in 10^{24} cm^{-3} units; $j_0(rs)$ is spheric function.

$$\rho_0 = \frac{Nd}{10^{24} M_{av}} \qquad (4)$$

where d is the density of solution, g/cm^3; N is Avogdro's constant; M_{av} is average moleculer mass.

3 EXPERIMENTAL STRUCTURE FUNCTIONS

The experimental structure function $si(s)$ and pair distribution function $G(r)$ was shown in Fig. 1 and 2 respectively. In the correlation functions some peaks can clearly be distinguished. From their positions and referring to earlier results on Al^{3+}-containing and Na^+-containing solutions[14, 15], an assignment of interactions to the characteristic distance can be made.

3.1 Structure functions

One feature clearly visible in Fig. 1 is the gradual change of the shape of the double peak in the region of 2.0~3.5 Ů$^{-1}$ with chemical composition of the solutions changing from 4.637 mol/L to 1.063 mol/L^{-1}. The double peak is characteristic of water and most aqueous solutions connected to the extended hydrogen-bonded network, which change obviously with increasing dissolved salts[16]. The second peak is well-known to be sensitive to the disruption of the hydrogen bonding[17]. Experimental results showed that, the increase of aluminum concentration in the solution has a major effect on a substantial decrease of height and shift in

Table 1 Chemical properties of sodium aluminate solution

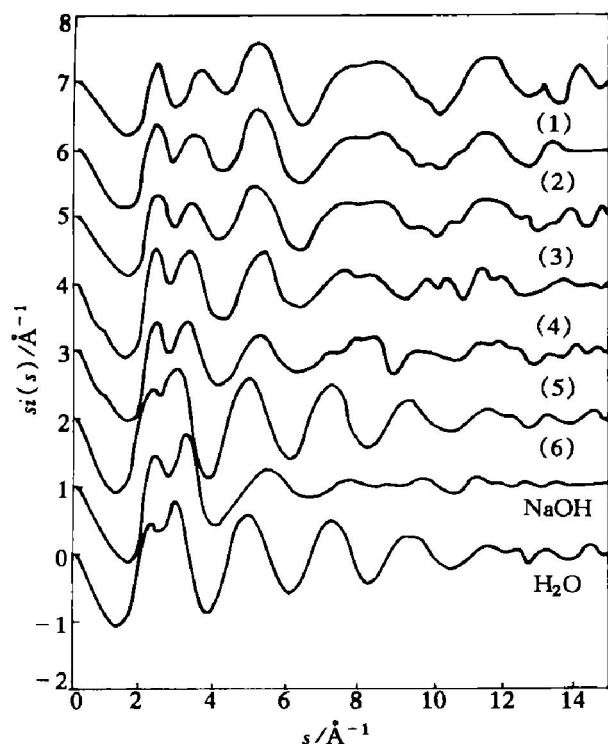| Solution	Caustic ratio	Supersaturation	$c(NaOH)/$ $(mol·L^{-1})$	$c(Al(OH)_3)/$ $(mol·L^{-1})$	$c(Na^+)/$ $(mol·L^{-1})$	$c(Al^{3+})/$ $(mol·L^{-1})$	$c(OH^-)/$ $(mol·L^{-1})$	$c(H_2O)/$ $(mol·L^{-1})$	Density/ $(g·cm^{-3})$	Number density
H_2O		0.000	0.000	0.000	0.000	0.000	0.000	55.51	1.000	0.033 4
NaOH		0.000	4.705	0.000	4.705	0.000	4.705	52.00	1.175	0.037 0
(1)	1.427	4.637	4.852	3.400	4.852	3.400	15.05	45.50	1.279	0.041 4
(2)	1.833	3.359	4.897	2.672	4.897	2.672	12.92	47.89	1.267	0.041 3
(3)	2.338	2.396	4.941	2.113	4.941	2.113	11.30	48.83	1.242	0.040 5
(4)	2.575	2.067	4.995	1.940	4.995	1.940	10.81	49.23	1.238	0.040 2
(5)	3.132	1.518	5.011	1.600	5.011	1.600	9.307	49.88	1.225	0.040 0
(6)	3.787	1.063	5.082	1.342	5.082	1.342	9.108	50.80	1.223	0.040 0

Fig. 1   Experimental X-ray structure functions

the position of the second peak and emergence of the broad fourth and fifth peaks in place of damping peaks of pure water. The results implied that the Al-containing structure units in the highly supersaturated system strongly influenced the original water structure. By contrast, in the lower supersaturated sodium aluminate solution and sodium hydroxide solution, it can be seen that double peak is little affected.

3. 2   Pair distribution functions

The structural feature of the solutions can be seen more directly from the pair distribution functions. The experimental pair distribution function $G(r)$ were computed from the structure functions according to Eqn. (3), with appropriate cutoff distance (s_{max} values) being applied. In particular, the pair distributions were back-Fouries transformed to the s-space, while zero was assigned to all $G(r)$ values up to a given r_{min}. The latter limit was determined on the assumption that no interatomic distance can occur in the liquid for all $r < r_{min}$ and, therefore, any contribution to $G(r)$ has no physical meaning. The value were set as $r_{min} = 1.5$ Ǔ for all sodium aluminate solutions, $r_{min} = 2.0$ Ǔ for sodium hydroxide solution and $r_{min} = 2.4$ Ǔ for water[6, 10]. The results of Fouries transformation of the structure functions to pair distribution functions $G(r)$ are shown in Fig. 2. Approximate value of atom pair distance from a direct reading of the pair distribution functions and coordination numbers (C_i) calculated by the integration area of the first peak in $G(r)$ function are listed in Table 2. The accuracy of atom pair distance is about ± 0.025 Ǔ for the first peak and ± 0.05 Ǔ for other peaks. The coordination number can be estimated to

± 0.5 at best; but may be as poor as ± 1.2 units for broader peaks. According to the results of pair distribution functions, the shape of the present curve of water is in excellent agreement with published functions[6, 15]. The main peak at 2.85 Ǔ corresponds to hydrogen-bonded first neighbor distance, and an average coordination number of oxygen is about 3.6 to 4.0 molecules. Compared to that of pure water, the pair distribution of sodium hydroxide solution exhibits a broadening of the first peak with an obviously decrease in height and significant shift of the peak position down to 2.60 Ǔ. Apparently, the change results from that the $Na^+ - H_2O$ first neighbor distance is shorter than that of $H_2O - H_2O$, with a value around 2.4 Ǔ[15]. The experimental results of water and sodium hydroxide solution are in good accordance with Ref. [12], which shows that present experimental results are reliable.
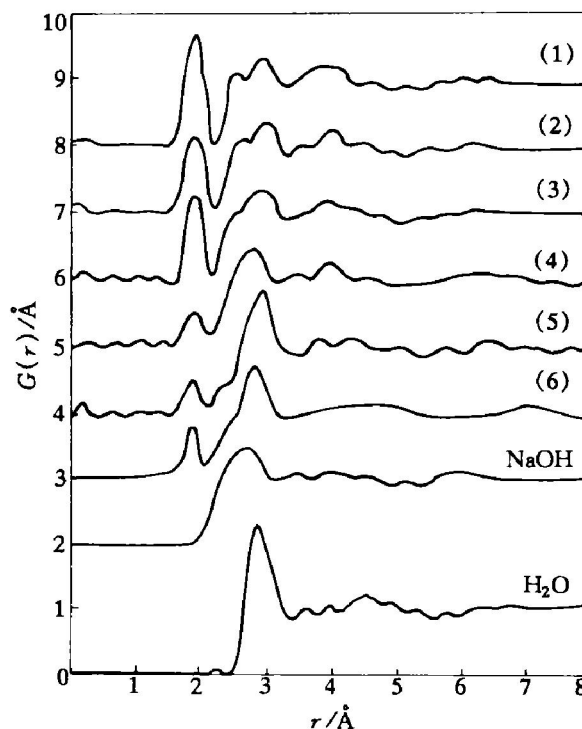

Fig. 2   Experimental X-ray pair
distribution functions

For sodium aluminate solutions, the first peak at about 1.8 Ǔ is certainly ascribable to $Al - OH(H_2O)$ interaction in the first coordination shell, because they emerged only in series aluminate solution. Based on the results listed in Table 2, each Al^{3+} ion in aluminate solution are surrounded by four oxygen ions in the first shell, which indicates that the basic structure of aluminate in solution is four-coordinated.

It is noticeable that the $Al - O$ distance broadens with increasing aluminate concentration, though it has been reported that $Al - O$ distance decrease as the concentration of the aluminate ions increase[5] in highly concentrated solution ($[NaOH] > 7.7$ mol/L, as illustrated in Fig. 3). Both kinds of aluminate solution belong to $Na_2O-Al_2O_3-H_2O$ system,

Table 2   Bond length from direct reading of pair distribution functions and coordination number calculated from integration to characteristic peaks

	Peak assignment	H₂O	NaOH (4.705mol/L)	(1)	(2)	(3)	(4)	(5)	(6)
Bond length	Al—O			1.85	1.86	1.80	1.78	1.75	1.75
	Na—O		2.35	2.35	2.40	2.38	2.35	2.35	2.40
	O—O	2.85	2.67	2.85	2.85	2.80	2.75	2.70	2.70
Coordination number	Al—O			3.9	4.1	3.7	4.2	4.2	4.4
	Na—O		4.8	5.2	5.2	4.8	4.4	4.0	3.8
	O—O*	3.9	5.6	8.6	7.2	6.5	5.8	4.9	4.0
	O—O*	4.0	7.6	9.0	7.2	6.3	5.3	4.7	4.0

O* refers to OH or H₂O

and the only difference between them is concentration. Therefore, their branding can only be resulted from the remaining amount of bulk water. If the remaining water in a solution were calculated, and it is supposed that the average coordination number of water of each ion, such as $Al(OH)_4^-$, Na^+, OH^- and molecular H_2O, to be four[6], it can be found that there is hardly enough water in highly concentrated solutions to satisfy the stoichiometric requirements of such high coordination numbers (as illustrated in Fig. 4), while there is almost just enough water in intermediate solutions to satisfy the coordination numbers. So, The supersaturated aluminate solution with medium concentration is located at the divergence of bulk water whether it is exhausted or not. It means that the free water in solution may lead

Fig. 3   Al—O distance(r_{Al-O}) vs caustic ratio($α_k$)

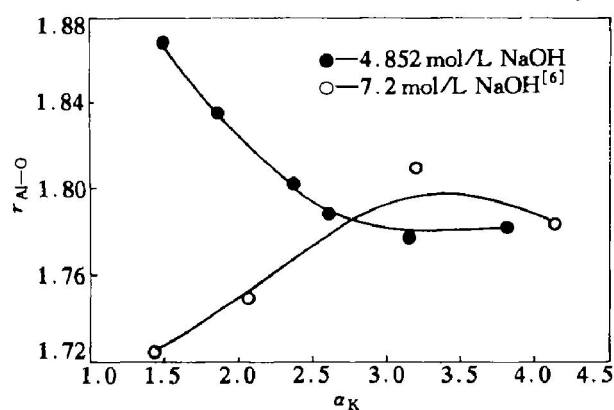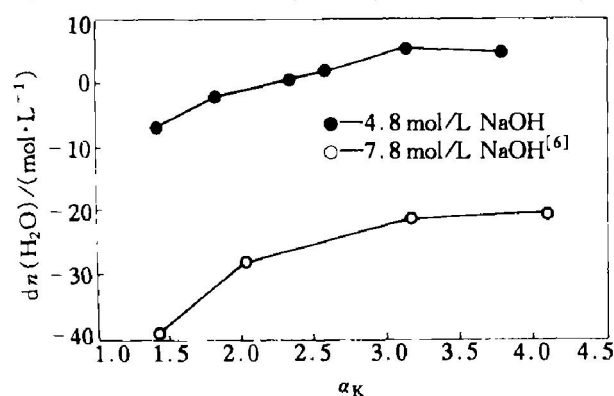**Fig. 4**   Residual water amount dn(H₂O) vs caustic ratio $α_k$

the second coordination state of aluminate ion in medium concentrated solution to be different from that in highly concentrated solution, which results in that the bond length change of Al—O in medium concentrated solution deviates from that in highly concentrated solution.

It is interesting that Na—O distance changes little in the series solution within the precision of the measurements. H_2O —$H_2O(OH)$ distance in the first coordination shell decreases with the dissolution of NaOH and $Al(OH)_3$ into water, but H_2O —H_2O (OH) distance in aluminate solution is significantly longer than that in sodium hydroxide solution and it increases with supersaturation.

Compared pair distribution functions of sodium aluminate solution with that of pure water (as shown in Fig. 2), a gradual structural rearrangement of aluminate solution can also be observed in the longer distance. A broad peak emerged in the range of 3.4~ 4.3 Ů replaces the broad maximum of pure water between 4 Ů and 5 Ů. This is obviously due to a structural rearrangement, which is readily explained by the breaking of the long range structure of bulk water and development of a more compact, shorter range local order in the high supersaturated solution because there are relative larger amount of Al(III) with high columbic field in highly supersaturated solution.

3.3   Relationship between Al—O bond length and stability of sodium aluminate solution

It is important to note that, in $AlCl_3$ and $Al(NO_3)_3$ solution, Al—O distance changes little with concentration[14]; however, there is a significant change in the series sodium aluminate solution with different relative supersaturations, which is an indication of a species change in solution. For the same series of aluminate solution, the expanding distance may be the result of the oligomerization of Al $(OH)_4^-$. It is reported that $[Al(OH)_4^- \cdot 4H_2O]$, $Al_2O(OH)_6^{2-}$, $Al_2(OH)\text{-}(OH)_6^-$, $Al_2(OH)_2(OH)_6^{2-}$ are the most possible dimer in highly supersaturated solution[18]. The results of *ab initio* (Gaussian94) theoretical calculation show that Al—O distance become

longer with the formation of dimeric aluminate. The average Al—O distance changes from 1.785 $\overset{\circ}{U}$ in [$Al(OH)_4^- \cdot 4H_2O$] to 1.85 $\overset{\circ}{U}$ in $Al_2(OH)_2(OH)_6^{2-}$. In highly supersaturated solution some dimeric aluminate species such as $Al_2O(OH)_6^{2-}$, $Al_2(OH)(OH)_6^-$, [$Al_2(OH)_2(OH)_6$]$^{2-}$ may be formed . It is reported that [$Al(OH)_4^- \cdot 4H_2O$] is the only Al-containing species in lower supersaturated solution[18], thus, in which Al—O distance is the shortest . According to quantum theoretical calculation[18], dimeric aluminates are unstable species compared to monomer aluminate. The more the dimeric aluminate, the more unstable the solutions is.

Additionally, H_2O—$H_2O(OH)$ distance in aluminate solution is significantly longer than that in sodium hydroxide solution (as listed in Table 2), which may imply that interaction of water in high supersaturated solution is weaker than in lower supersaturated solution and sodium caustic solution. Thus, the water in high supersaturated solution is more active than in lowly supersaturated solution[5]. Meanwhile, within the same Al_2O_3-Na_2O-H_2O system, the basic structures of solutions are similar, the expansion of Al—O and H_2O—$H_2O(OH)$ bond will result in the solution more and more unstable. So, in Al_2O_3-Na_2O-H_2O phase diagram and the procedure of decomposition, solutions with medium concentration are more unstable than diluted and highly concentrated solution, as well as it decomposes more quickly than the latter.

4   CONCLUSIONS

1) The basic structure of aluminate in caustic solution is four coordinated ions. Al—O bond length alters from 1.75 $\overset{\circ}{U}$ to 1.85 $\overset{\circ}{U}$ with the increase of supersaturation because of dimeric aluminate species formed in high supersaturated solution. Whether residual water amount in bulk solution is sufficient to the coordination of ions or not influences Al—O bond length alteration trend to supersaturation.

2) Addition of sodium aluminate makes a gradual structure rearrangement. Shorter range local order became more compact, and weak longer range order formed gradually.

3) Al—O and H_2O—$H_2O(OH)$ distance expansion with supersaturation will result in supersaturated sodium aluminate solution becoming more and more unstable .

[REFERENCES]

[1]   Chen N Y, Liu M X. Studies on the anionic species of sodium aluminate solutions[J]. Science in China, Series B, 1993, 36: 32– 38.

[2]   Moolenaar R J. The structure of the aluminate ion in solutions at high pH[J]. J Phys Chemistry, 1970, 74: 3629– 3636.

[3]   Griffiths V S, Socrates G. Raman spectra of aqueous solutions of lithium, sodium and potassium aluminates[J]. J Molecular Spectroscopy, 1968, 27: 358– 363.

[4]   Watling H. Spectroscopy of concentrated sodium aluminate solution[J]. Applied Spectroscopy, 1998, 52(2): 250– 258.

[5]   Zambo J. Structure of sodium aluminate liquiors: molecular model of the mechanism of their decomposition[J]. Light Metal, 1986, 199– 214.

[6]   Tamas R, Peter M M, Glenn T H, et al. Structure of aqueous sodium aluminate solutions: a solution X-ray diffraction study[J]. J Phy Chem A, 1998, 102: 7841 – 7850.

[7]   Terri J S, James A C, Gerson A R, et al. A static light and X-ray scattering study of supersaturated caustic aluminate liquiors[J]. Langmuir, 2000, 16: 4784– 4791.

[8]   YANG Zhong-yu. Technology of Alumina Production [M]. Beijing: Metallurgical Industry Press, 1993. 27.

[9]   Misra C. Solubility of sluminium trihydroxide (hydrargillite) in sodium hydroxide solutions[J]. Chemistry and Industry, 1970, 20: 619– 622.

[10]   Klug H P, Alexander L E. X-ray Diffraction Procedure for Polycrystalline and Amorphous Materials, 2nd [M]. New York: John Wiley & Sons Inc, 1974. 791.

[11]   FANG Chun-hui, FANG Yan. Study on solution structure by X-ray diffraction analysis —1 experiment techniques[J]. J Salt Lake Science, 1995, 3(4): 66– 71.

[12]   Magini M, Licheri G. X-ray diffraction of ions in aquesous solutions: hydration and complex formation[J]. CRC Boca Raton FL, 1988. 211.

[13]   Ibers J A, Hamilton W C. International Tables for X-ray CrystalloGraphy, Vol IV [M]. Birmingham: Kynoch Press, 1974. 99.

[14]   Heinzinger K. Computer simulation of aqueous electrolyte solution[J]. Pyhsica, 1985, 131B: 196– 216

[15]   Hitoshi O. An attempt to parameterize the structuredness of solvents[J]. J Solution Chemistry, 1992, 21 (1): 39– 47.

[16]   Postorino P, Tromp R H, Riccl M A, et al. The interatomic structure of water at supercritical temperature [J]. Nature, 1993, 366: 668– 670.

[17]   Yamanaka K, Yamaguchi T, Wakita H. Structure of water in the liquid and supercritical states by rapid X-ray diffractometry using an imaging plate detector [J]. J Chem Phys, 1994, 101(11): 9830– 9836.

[18]   LI Jie. Structural Characteristic and Decomposition Mechanism of Supersaturated Aluminate Solution[D]. Changsha: Central South University, 2001. 75.

(Edited by YANG Bing)