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Activity coefficient calculation model for $NaAl(OH)_4$-$NaOH$-H_2O system①

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Abstract: Resorting to Debye-Hückel equation, the conception of the apparent dielectric constant ε' of sodium aluminate solution is introduced. By supposing that all the influences are attributed to it, ε' is successfully related to caustic ratio α_K, concentration $m_{NaOH,T}$ and temperature T. Then an activity coefficient calculation model for $NaAl(OH)_4$-$NaOH$-H_2O system from 25 ℃ to 100 ℃ is established, which can be used in much wider α_K and $m_{NaOH,T}$ ranges than those covered by the equilibrium solubility data.

Key words: Debye-Hückel equation; activity coefficient; calculation model

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1 INTRODUCTION

Concentrations of the sodium aluminate solutions in alumina industry are usually very high, and the diverges of precipitation mechanism and structure in sodium aluminate solution[1-4] also exist, which makes the study of activity coefficients extremely difficult. Therefore, though lots of work has been done on the thermodynamic properties of sodium aluminate solution[5-7] and many solubility data have been obtained, the researches of the activity coefficient are scarce. As Debye-Hückel activity coefficients calculation equation has a simple formula and definite meanings of various physical parameters, it is convenient to be used in practical calculation. Meanwhile, it is also suitable for calculating the activity coefficients of $NaAl(OH)_4$ in $NaAl(OH)_4$-$NaOH$-H_2O system at equilibrium[8].

In this paper, the idiographic issues of using Debye-Hückel model in $NaAl(OH)_4$-$NaOH$-H_2O system are analyzed, and then the resolvents to break the ranges of equilibrium solubility data and to guide the establishment of activity coefficients calculation model are brought forward.

2 PRIMARY ISSUES AND CORRESPONDING RESOLVENTS

In order to discuss conveniently, the classical Debye-Hückel model[9] is listed as follows:

$$\log \overline{\gamma}_{\pm} = -\frac{A_\gamma |Z_+ Z_-| I^{1/2}}{1 + \mathring{a} B_\gamma I^{1/2}} \tag{1}$$

where

$$A_\gamma = \frac{1.8248 \times 10^6 \rho^{1/2}}{(\varepsilon T)^{3/2}} \tag{2}$$

$$B_\gamma = \frac{50.291 \times 10^8 \rho^{1/2}}{(\varepsilon T)^{1/2}} \tag{3}$$

In Eqn.(1), I stands for the effective ionic intensity of the solution in unit of mol/kg; Z_+ and Z_- denote the charge of the cations and anions, respectively; $\mathring{a}$ refers to the ion size parameter and $\mathring{a}_{NaAl(OH)_4}$ is 3.595 Å[8]; A_γ, B_γ represent the Debye-Hückel parameters in units of $(kg/mol)^{1/2}$ and $kg^{1/2}/(mol^{1/2} \cdot cm)$, respectively; T means temperature in K; and ε, ρ stand for the dielectric constant and density (g/cm^3) of H_2O when H_2O is supposed to own a continuous phase.

Debye-Hückel model employs four basic hypotheses, which contributes the huge interaction among ions to the interaction between centric ions and ion spheres to make the model less complex. The discussion of the applicability of Debye-Hückel model in $NaAl(OH)_4$-$NaOH$-H_2O system also proves that this model is really suitable for the system. For $NaAl(OH)_4$-$NaOH$-H_2O system, the primary issues and corresponding resolvents are as follows.

1) In Debye-Hückel model, the key parameter to determine the values of activity coefficients is ionic intensity I. Supposing the aluminate ions ex-

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isted in $NaAl(OH)_4$-$NaOH$-H_2O system are only $Al(OH)_4^-$, there is only one kind of cations. When total caustic concentration $m_{NaOH,T}$ (mol/kg) is known, the ionic intensity of the whole solution is decided. But obviously, the activity coefficients are various at different caustic ratios α_K (Na_2O/Al_2O_3, molar ratio) even $m_{NaOH,T}$ is certain. So the problem of the influence of α_K on activity coefficients can not be settled only with the parameter I. In Debye-Hückel model, ε is another key parameter to determine the interaction among ions. Because the water is supposed to own a continuous phase in the case of dilute solution, the original definition of ε is the dielectric constant of water. In this paper, the conception of the apparent dielectric constant $\acute{\varepsilon}$ of sodium aluminate solution is introduced and all the influences are attributed to $\acute{\varepsilon}$. According to this, the ultimate calculation model, which provides the calculation method of the dielectric constant $\acute{\varepsilon}$ relating to α_K, $m_{NaOH,T}$ (mol/kg), T(K), is given.

2) The data used in this model are equilibrium solubility data, which causes the applicable regions of α_K and concentration limited. Resorting to the comparison of the activity data with other references, the possible correlative laws can be explored and the activity data can be extended to a broader range of α_K, $m_{NaOH,T}$ (mol/kg). Then the calculation of activity coefficients of $NaAl(OH)_4$-$NaOH$-H_2O system in non-equilibrium conditions could be sought for.

3 ESTABLISHMENT OF CALCULATION MODEL

3.1 Relationship between $\gamma_{NaAl(OH)_4}$ and α_K, $m_{NaOH,T}$, T at equilibrium

According to a large amount of studies on the sodium aluminate solution, the most possible structure of aluminate ions in sodium aluminate solution is tetrahedral $Al(OH)_4^-$ [10, 11]. In this paper, supposing all the aluminate ions are $Al(OH)_4^-$, the dissolution of gibbsite in NaOH solution can be defined as

$$Al(OH)_3 + NaOH \rightleftharpoons NaAl(OH)_4 \tag{4}$$

The equilibrium constant K of Eqn.(4) can be expressed as

$$K = \frac{a^2_{NaAl(OH)_4}}{a^2_{NaOH}} = \frac{\gamma^2_{NaAl(OH)_4} m_{Na^+} m_{Al(OH)_4^-}}{\gamma^2_{NaOH} m_{Na^+} m_{OH^-}} = \frac{\gamma^2_{NaAl(OH)_4} m_{Al(OH)_4^-}}{\gamma^2_{NaOH} m_{OH^-}} \tag{5}$$

where $a_{NaAl(OH)_4}$, a_{NaOH}, $\gamma_{NaAl(OH)_4}$, γ_{NaOH} represent the activities and the activity coefficients of the subscripted species. m_{Na^+}, $m_{Al(OH)_4^-}$, m_{OH^-} refer to the stoichiometric molar concentrations of the subscripted species in unit of mol/kg, respectively.

From Eqn.(5),

$$\gamma_{NaAl(OH)_4} = (K m_{OH^-} / m_{Al(OH)_4^-})^{1/2} \gamma_{NaOH} \tag{6}$$

In order to know the influence of α_K, $m_{NaOH,T}$ (mol/kg) and $T(K)$ on the activity coefficients in sodium aluminate solution, we ought to know the values of K and γ_{NaOH} in Eqn.(6), as well as the corresponding relationship of m_{OH^-}, $m_{Al(OH)_4^-}$ and α_K, $m_{NaOH,T}$ (mol/kg).

The values of K can be obtained by the following empirical equation reported by Wesolowski[12]:

$$\log K = -96.5506 + 2374.88/T + 16.07899 \ln T - 0.0139828 T \tag{7}$$

For γ_{NaOH}, the researches of activity coefficients of NaOH solutions have been presented completely[7, 12] at present and the satisfied results can be achieved either by extended Debye-Hückel equation or by Pitzer equation. In this paper, the values of γ_{NaOH} are calculated by Pitzer equation and parameters[13]:

$$\ln \gamma_{NaOH} = -A_\phi[m^{1/2}/(1+bm^{1/2}) + (2/b) \cdot \ln(1+bm^{1/2})] + 2m\beta^{(0)}_{NaOH} + (2\beta^{(1)}_{NaOH}/\alpha^2)[1-(1+\alpha m^{1/2} - \alpha^2 m/2) \cdot \exp(-\alpha m^{1/2})] + 3m^2 C^{\phi}_{NaOH}/2 \tag{8}$$

In sodium aluminate solution, we have

$$\alpha_K = \frac{m_{NaAl(OH)_4} + m_{NaOH}}{m_{NaAl(OH)_4}} \tag{9}$$

$$m_{NaOH,T} = m_{NaAl(OH)_4} + m_{NaOH} \tag{10}$$

In order to discuss the relationship between the activity coefficients of sodium aluminate solution and temperature, caustic ratio α_K, total caustic concentration $m_{NaOH,T}$, the corresponding function can be obtained from Eqn.(6) and solubility data[12, 14]:

$$\gamma_{NaAl(OH)_4} = p_1 + p_2 \cdot m_{NaOH,T} + p_3 \cdot m^2_{NaOH,T} + p_4 \cdot \alpha_K + p_5 \cdot \alpha_K^2 + p_6 \cdot \ln(m_{NaOH,T}) + p_7 \cdot \ln\alpha_K \tag{11}$$

The corresponding parameters of Eqn.(11) at different temperatures can be referred to Ref.[8].

3.2 Extension of $\gamma_{NaAl(OH)_4}$ laws

Theoretically, the values of $\gamma_{NaAl(OH)_4}$ under equilibrium condition can be calculated by Eqn.(11). The calculation results also show that Eqn.(11) fits well with those of references in the range of $m_{NaOH,T}$ and α_K covered by the solubility data, while there are some deviations beyond the range. That is to say, Eqn.(11) can only be used in the temperature, α_K, $m_{NaOH,T}$ ranges of the solubility data. Among the equilibrium solubility data, the high temperature refers only to low α_K and vice versa, which means that it is difficult to calculate activity coefficients by Eqn.(11) under wide α_K range in which the alumina production requires. Therefore, the extension principle of $\gamma_{NaAl(OH)_4}$ must be investigated in order to extrapolate the adaptability range.

There is no systematic research on the activity coefficients of this system, and the data are scarce. Only the data of $\gamma_{NaAl(OH)_4}$ at 40 ℃ dealing with Pizer equation are comparatively systematic[15], so we take them for comparison. Meanwhile, considering the solubility data adopted in this paper, there are only two points of temperature: 100 ℃ ($m_{NaOH,T}=0.5-11$ mol/kg, $\alpha_K=1.8-2.4$) and 70 ℃($m_{NaOH,T}=0.01-11$ mol/kg, $\alpha_K=1.8-4.5$), which have a wider range of $m_{NaOH,T}$ and their α_K values are similar to those of Ref.[15]. So the data calculated by Eqn.(11) in 100 ℃, $\alpha_K=1.5$ and 70 ℃, $\alpha_K=3$ are compared with the data[12] calculated by Pizer model at 40 ℃ and corresponding values of α_K. The results are shown in Fig. 1.

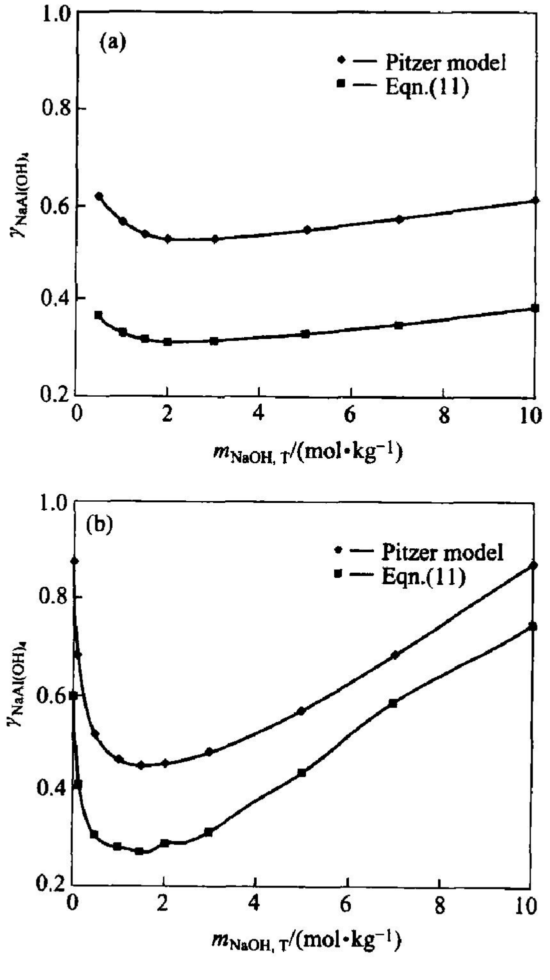

Fig. 1 Comparison of $\gamma_{NaAl(OH)_4}$ calculated by Pitzer model[12] and by Eqn.(11)
(a) —100 ℃, $\alpha_K=1.5$; (b) —70 ℃, $\alpha_K=3.0$

Fig. 1 shows that the change of $\gamma_{NaAl(OH)_4}$ with $m_{NaOH,T}$ is almost with the same trend and range when α_K is identical, which is so called the parallel law. The calculation results also show that in the range of $m_{NaOH,T}$ and α_K at any other temperature covered by solubility data, the similar parallel law is also maintained. Furthermore, the values of $\gamma_{NaAl(OH)_4}$ reduce 0.04 per 10 ℃ with temperature increasing at the same $m_{NaOH,T}$ and α_K. In order to calculate the activity coefficients of the solution beyond the equilibrium solubility data, we ought to calculate the activity coefficients at other temperatures with the same α_K and concentration by Eqn.(11), and then utilize the law to get corresponding activity coefficients.

Combining the range of solubility data, the applicable range of the laws mentioned above is: $T=298-373$ K, $m_{NaOH,T}=0.1-10$ mol/kg, $\alpha_K=1.2-15$, which can meet the practical needs of alumina production.

3.3 Calculation model of $\gamma_{NaAl(OH)_4}$

According to the above discussion, the activity coefficients of broader sodium aluminate solution range can be calculated. But the above calculation has no definite physical meanings and is difficult to be testified. What's more, the process is complicated and is hard to be taken into practical use. Therefore, supposing $NaAl(OH)_4$ owns a continuous phase, the conception of the apparent dielectric constant ε' of sodium aluminate solution is introduced and all the influence is attributed to ε'. Then the extended $\gamma_{NaAl(OH)_4}$ data are used to Debye-Hückel model to calculate the corresponding values of ε'. Accordingly, the activity coefficients can be calculated by a comparable simple formula with definite physical meanings so far as the values of ε' are ascertained.

Using Eqn.(11) and parallel law to calculate the activity coefficients of sodium aluminate solution of different temperatures, $m_{NaOH,T}$, α_K, and then using Eqns.(1)−(3) to calculate corresponding values of ε', the empirical fitting equation and corresponding parameters (listed in Table 1) of ε' related to $m_{NaOH,T}$, α_K at different temperatures can be obtained:

$$\begin{aligned}\varepsilon' = {} & p_1 + p_2 \cdot m_{NaOH,T} + p_3 \cdot m_{NaOH,T}^2 + \\ & p_4 \cdot \alpha_K + p_5 \cdot \alpha_K^2 + p_6 \cdot m_{NaOH,T} \cdot \alpha_K + \\ & p_7 \cdot m_{NaOH,T}^2 \cdot \alpha_K + p_8 \cdot m_{NaOH,T} \cdot \alpha_K^2 + \\ & p_9 \cdot m_{NaOH,T}^2 \cdot \alpha_K^2 \end{aligned} \tag{12}$$

Investigation of ε' under different conditions can obtain the following principles:

1) The values of ε' decrease with the increase of temperature in the case of a certain $m_{NaOH,T}$ and α_K, because the temperature increase leads to molecule reduce of unit volume for the solution expansion.

2) The values of ε' increase with the increase of α_K at a certain $m_{NaOH,T}$ and temperature, which may be explained in the way that the high α_K means the high solute concentration due to the increment of ion OH^- with smaller size and decrement of ion $Al(OH)_4^-$ with bigger size.

3) The values of ε' increase with the increase of $m_{NaOH,T}$ at a certain temperature and α_K. It is

Table 1 Parameters at different temperatures in Eqn. (12)

p	40 ℃		50 ℃		60 ℃		70 ℃	
	$m_{NaOH,T} \leqslant$ 5 mol/kg	$m_{NaOH,T} \geqslant$ 5 mol/kg	$m_{NaOH,T} \leqslant$ 5 mol/kg	$m_{NaOH,T} \geqslant$ 5 mol/kg	$m_{NaOH,T} \leqslant$ 5 mol/kg	$m_{NaOH,T} \geqslant$ 5 mol/kg	$m_{NaOH,T} \leqslant$ 5 mol/kg	$m_{NaOH,T} \geqslant$ 5 mol/kg
p_1	61.832 1	- 50.331 1	54.778 6	- 7.513 3	48.9	10.065 6	43.97	17.957 8
p_2	- 1.143 9	31.015 9	- 0.875	17.657 7	- 0.880 1	11.145 9	- 1.034 8	7.416 8
p_3	- 0.863 9	- 2.809 4	- 0.723 6	- 1.938 4	- 0.587 3	- 1.439 1	- 0.461 2	- 1.111
p_4	4.007 9	0	3.698 1	0	3.153 3	0	2.55	0
p_5	0.127 1	48.307 2	- 0.024 8	26.475 6	- 0.066 7	16.030 1	- 0.06	10.381 7
p_6	3.158 9	12.882 8	2.525 6	8.130 3	2.240 7	5.747 7	2.109 2	4.367 9
p_7	0.748 9	- 1.035 5	0.654 1	- 0.318 9	0.547 8	- 0.027 5	0.449	0.099 2
p_8	- 0.813 1	- 19.838 3	- 0.591 1	- 11.083 2	- 0.473 7	- 6.845 1	- 0.407	- 4.525 2
p_9	0.046 9	1.924 7	0.020 3	1.058 7	0.009 1	0.639 5	0.004 9	0.410 9

p	80 ℃		90 ℃		100 ℃	
	$m_{NaOH,T} \leqslant$ 5 mol/kg	$m_{NaOH,T} \geqslant$ 5 mol/kg	$m_{NaOH,T} \leqslant$ 5 mol/kg	$m_{NaOH,T} \geqslant$ 5 mol/kg	$m_{NaOH,T} \leqslant$ 5 mol/kg	$m_{NaOH,T} \geqslant$ 5 mol/kg
p_1	39.566 4	20.93	35.546 4	245.917 9	31.878 6	142.225
p_2	- 1.188 9	5.156 3	- 1.256 4	- 73.296 8	- 1.341 2	- 38.971 8
p_3	- 0.356 8	- 0.880 4	- 0.285	5.708 2	- 0.221 9	2.890 4
p_4	2.060 2	0	1.830 2	- 224.498	1.601 4	- 121.459
p_5	- 0.051 9	7.045 9	- 0.071 9	54.906 2	- 0.071 4	30.638 9
p_6	2.014 5	3.518	1.812	79.974 8	1.697 9	44.250 8
p_7	0.365 7	0.147 4	0.317 2	- 6.262 2	0.268 6	- 3.319 6
p_8	- 0.357 5	- 3.144 6	- 0.299 2	- 19.407 3	- 0.266 2	- 10.979 3
p_9	0.002 9	0.276 4	- 0.001 1	1.621 4	- 0.001 9	0.912 3

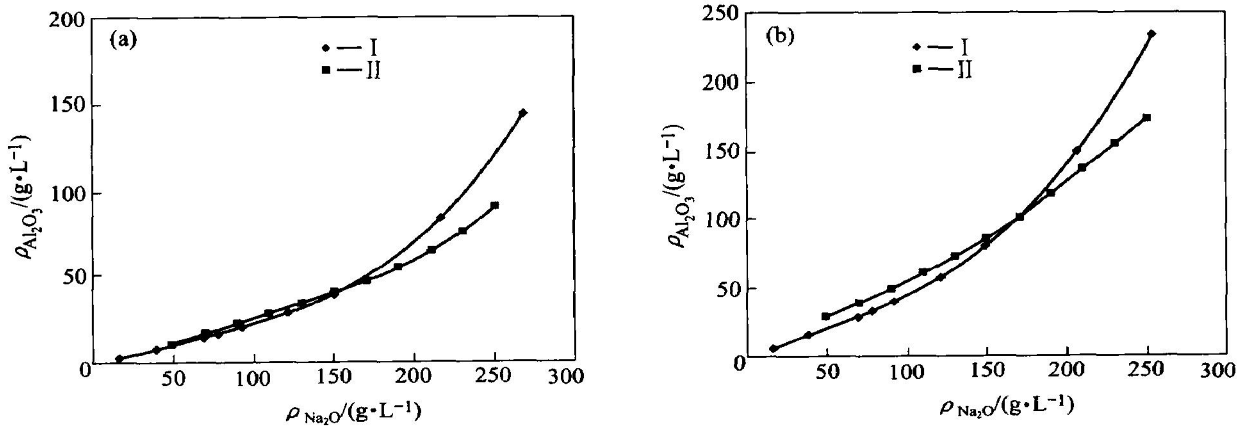

Fig. 2 Comparison of equilibrium solubility data calculated by calculation model in this study(II) and reference(I)

(a) —40 ℃; (b) —70 ℃

maybe caused by the solute concentration increases along with the $m_{NaOH,T}$.

All the principles mentioned above accord with the dielectric theories, proving the rationality of introducing $\acute{\varepsilon}$.

From the work mentioned above, combining parameters of Debye-Hückel model[7], the activity coefficients calculation model for $NaAl(OH)_4$-$NaOH$-H_2O system is obtained:

$$\log \gamma_{NaAl(OH)_4} = -\frac{\dfrac{1.824\,8\times 10^{6}\rho^{1/2}}{(\acute{\varepsilon}T)^{3/2}}m_{NaOH,T}^{1/2}}{1+3.595\times 10^{-9}\times\dfrac{50.291\times 10^{8}\rho^{1/2}}{(\acute{\varepsilon}T)^{1/2}}m_{NaOH,T}^{1/2}} \quad (13)$$

where ε' can be calculated by Eqn. (12).

4 EXAMPLES

Employing the calculation method provided above, the solubility data of Al_2O_3 in NaOH solution are obtained and compared with those reported by Russell et al[14]. Fig. 2 shows the comparison results of solubility curves at 40 ℃ and 70 ℃.

The comparison in Fig. 2 indicates that the current results derived from our method are in good agreement with those of literature. When the ionic intensity reaches 6 mol/kg, the results are also satisfactory. This strongly supports the outstanding applicability of the method to solutions with high concentration. But the calculated data are a bit less than the literature data in the system with the concentration above 6mol/kg, which may be due to the inaccuracy of the equilibrium solubility data or the tetrahedral $Al(OH)_4^-$ ions being not dominative resulted from the structure change of aluminate ions at high concentration.

5 CONCLUSIONS

1) By introducing the conception of the apparent dielectric constant ε' of sodium aluminate solution and attributing all the influences to ε', the classical Debye-Hückel equation can be resorted to calculate the activity coefficients of sodium aluminate solution with a wider range of concentration.

2) It is a feasible way to calculate the activity coefficients of solutions basing on the equilibrium solubility data, and it also offers a new idea of the calculation and measurement of activity coefficients for similar systems.

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