

The Applicability of Debye–Hückel Model in NaAl(OH)₄–NaOH–H₂O System

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Abstract: Focusing on the most important NaAl(OH)₄–NaOH–H₂O system in the industry of alumina production, the feasibility of establishing a calculation model of activity coefficients according to Debye–Hückel theory via the equilibrium solubility data of sodium aluminate solution is discussed in this paper. Firstly, the hypotheses for applying Debye–Hückel theory into NaAl(OH)₄–NaOH–H₂O system are involved and the values of parameters are determined. Then the applicability of Debye–Hückel model in NaAl(OH)₄–NaOH–H₂O system is testified. The results indicate that Debye–Hückel model is applicable to the establishment of calculation model of activity coefficients in NaAl(OH)₄–NaOH–H₂O system and the value of $\hat{a}_{\text{NaAl(OH)}_4}$ is estimated as 0.3595 nm.

Key words: activity coefficients; Debye–Hückel theory; sodium aluminate solution; applicability

CLC No.: TF801

Document Code: A

Article ID: 1009–606X(2005)05–0525–04

1 INTRODUCTION

NaAl(OH)₄–NaOH–H₂O system plays a paramount role in the industry of alumina production, and the calculation of its activity coefficients can not only aid to perfect the theory of alumina production, but also accelerate the research and the development of new technology for reducing the production cost and energy consumption. However, the solution in alumina industry has high concentration with extremely complex structure, and the properties of the solution are easily affected by the circumstances, which makes the calculation of activity coefficients difficult. Limited researches concerning directly the calculation of activity coefficients in this system were reported in the literature^[1,2].

With the development of Pitzer theory of electrolyte solutions, some reports^[3–5] which were concerned with the Pitzer model to calculate the activity coefficients of sodium aluminate solution in simple systems appeared in recent years. These researches show that the results of Pitzer theory in calculating the activity coefficients are satisfying. But the use of Pitzer model in practical calculations is suffocating because its complex equation is involved with a number of parameters and the structure of solution is indistinct^[6]. Debye–Hückel theory brought forward in 1923 proposes a simple formula and definite meanings of various physical parameters. It is accurate when used in

electrolyte solution systems with low concentration^[7]. Due to the particularity of sodium aluminate solution, little attention has been paid to dealing with the activity coefficients of sodium aluminate solution via Debye–Hückel theory. There is still no appropriate approach to calculate activity coefficients in sodium aluminate solution.

For Debye–Hückel model is simple and there is a large number of equilibrium data, it is reasonable to establish the calculation model of activity coefficients in sodium aluminate solution based on Debye–Hückel model via equilibrium data. So it is necessary to investigate the applicability of Debye–Hückel model in calculating the activity coefficients of NaAl(OH)₄–NaOH–H₂O system.

2 HYPOTHESES AND PARAMETERS' DETERMINATION

The following extended Debye–Hückel equation reported by Helgeson et al.^[8] is taken as the basis of analysis:

$$\log \bar{\gamma}_{\pm} = - \left[A_{\gamma} |Z_+ Z_-| I^{1/2} / \left(1 + \hat{a} B_{\gamma} I^{1/2} \right) \right] + b_{\gamma} I, \quad (1)$$

where I stands for the effective ionic strength of the electrolyte solution in unit of mol/kg. Z_+ and Z_- denote the charges of the cations and the anions, respectively. \hat{a} refers to the size parameter of the electrolyte solution in unit of nm. A_{γ} and B_{γ} represent the Debye–Hückel

Received date: 2004–11–15, **Accepted date:** 2005–01–24

Foundation item: Supported by the National Natural Science Foundation of China (No.50274076) and the National Key Fundamental Research and Development Program of China (No.2005CB623702)

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parameters in units of $\text{kg}^{1/2}/\text{mol}^{1/2}$ and $\text{kg}^{1/2}/(\text{mol}^{1/2}\cdot\text{cm})$, respectively, which are defined as:

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

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

where T means temperature in K, ε and ρ are the dielectric constant and density (g/cm^3) of H_2O when H_2O is supposed to exist in a continuous phase. The values of A_γ and B_γ can be calculated by Eq.(2) and Eq.(3). Meanwhile, the values of A_γ and B_γ covering the temperature range from 0°C to 350°C can be obtained from the reference [8], being used directly.

Because of limitation of the model, Debye–Hückel equation can only calculate the average activity coefficients when it is used in a mixed electrolyte solution, which means that the difference and the interaction among various anions must be neglected. Considering the feasibility and veracity, the hypotheses for applying the Debye–Hückel theory in $\text{NaAl}(\text{OH})_4$ – NaOH – H_2O system are given as follows: NaOH – $\text{NaAl}(\text{OH})_4$ solution is taken into account as a mixture of pure NaOH solution and pure $\text{NaAl}(\text{OH})_4$ solution. In other words, the interaction between OH^- and $\text{Al}(\text{OH})_4^-$ ions is neglected.

In Eq.(1), the first part in the right terms is the classical Debye–Hückel equation. The second one $b_\gamma I$ is the extended part to modify the errors of classical equation in practical use, where b_γ represents the extended-term parameter which is a function of temperature and pressure. \hat{a} is the key parameter in Debye–Hückel equation. Generally speaking, the value of \hat{a} is bigger than the sum of ion radii of crystal cell and smaller than the sum of ion radii of hydrate. It can be calculated by Debye–Hückel equation at low concentrations. But its exact value is difficult to obtain at high concentrations. The usual way to deal with it is using the sum of cation radii of hydrate and anion radii of crystal cell. For example, the value of \hat{a} for NaOH solution (0.331 nm) is the sum of Na^+ (0.191 nm) and OH^- (0.14 nm). But there is no literature about the value of \hat{a} for $\text{NaAl}(\text{OH})_4$ in sodium aluminate solution so far. It can be calculated with reference to Riedl^[9], that is, the ion-radius of $\text{Al}(\text{OH})_4^-$ is 0.0285 nm, bigger than that of OH^- . Therefore, $\hat{a}_{\text{NaAl}(\text{OH})_4} = \hat{a}_{\text{Na}^+} + \hat{a}_{\text{Al}(\text{OH})_4^-} = 0.191 + (0.14 + 0.0285) = 0.3595$ nm. The subsequent research proves the above value of $\hat{a}_{\text{NaAl}(\text{OH})_4}$ is reasonable.

3 APPLICABILITY

For the lack of activity coefficient data for comparison, the fitting model is established by regression of the equilibrium solubility data of gibbsite in NaOH solution and the values of equilibrium constants are chosen as criteria. Applicability of Debye–Hückel model is testified by comparing the values of equilibrium constants with calculated results in this study and in the references. Errors of the fitting model are accumulated in the extended-term expression.

3.1 Fitting Model via Equilibrium Data

According to the studies on the sodium aluminate and hydroxide solutions, the dominative structure of aluminate ions is likely to be tetrahedral $\text{Al}(\text{OH})_4^-$ at atmospheric pressure^[10]. In this paper, all the aluminate ions are assumed to be $\text{Al}(\text{OH})_4^-$ ions. Therefore, the dissolution of gibbsite in NaOH solution can be expressed as:



The equilibrium constant K of the above reaction can be defined as:

$$K = \frac{\alpha_{\text{NaAl}(\text{OH})_4}^2}{\alpha_{\text{NaOH}}^2} = \frac{\gamma_{\text{NaAl}(\text{OH})_4}^2 m_{\text{Na}^+} m_{\text{Al}(\text{OH})_4^-}}{\gamma_{\text{NaOH}}^2 m_{\text{Na}^+} m_{\text{OH}^-}} = \frac{\gamma_{\text{NaAl}(\text{OH})_4}^2 m_{\text{Al}(\text{OH})_4^-}}{\gamma_{\text{NaOH}}^2 m_{\text{OH}^-}}, \quad (5)$$

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

Equation (5) is further written as logarithmic form for convenient consideration:

$$\log K = \log \frac{m_{\text{Al}(\text{OH})_4^-}}{m_{\text{OH}^-}} + 2 \log \frac{\gamma_{\text{NaAl}(\text{OH})_4}}{\gamma_{\text{NaOH}}}. \quad (6)$$

Substituting Debye–Hückel extended Eq.(1) to Eq.(6), the equation is then rearranged as follows:

$$\log \frac{m_{\text{Al}(\text{OH})_4^-}}{m_{\text{OH}^-}} - 2A_\gamma I^{1/2} \left[\left(1 + \hat{a}_{\text{NaAl}(\text{OH})_4} B_\gamma I^{1/2} \right)^{-1} - \left(1 + \hat{a}_{\text{NaOH}} B_\gamma I^{1/2} \right)^{-1} \right] = \log K - (b_{\gamma, \text{NaAl}(\text{OH})_4} - b_{\gamma, \text{NaOH}}) I, \quad (7)$$

$$\text{where} \quad I = \frac{1}{2} \sum_i m_i Z_i^2. \quad (8)$$

Supposing the anions in the system are only $\text{Al}(\text{OH})_4^-$ and OH^- , according to the electronic charge

balance principle, Eq.(8) can be written as follows:

$$I = \left(m_{\text{Na}^+} + m_{\text{Al(OH)}_4^-} + m_{\text{OH}^-} \right) / 2 = m_{\text{Na}^+}. \quad (9)$$

Equation (7) as the activity coefficients calculation model is established on the basis of the chemical equilibrium expression, with all terms being divided into the left and the right parts. The terms which can be determined by the solubility data include $m_{\text{Al(OH)}_4^-}$, m_{OH^-} and I . The unknown terms on the left side of Eq.(7) to be determined are the Debye–Hückel parameters A_γ and B_γ as temperature functions, and \hat{a}_{NaOH} and $\hat{a}_{\text{NaAl(OH)}_4}$. Providing the influence of pressure is neglected, the term $\log K$ can be expressed as that being only related to temperature, so is the term $(b_{\gamma, \text{NaAl(OH)}_4} - b_{\gamma, \text{NaOH}})$. So the right terms of Eq.(7) can be expressed as a function with temperature and ionic strength. Consequently, the object equation and correlative parameters can be obtained by regression of the solubility data.

The selected solubility data cover the temperatures from 25 °C to 100 °C^[3,11]. The empirical fitting equation corresponding to Eq.(7) is obtained by linear regressing:

$$\log \frac{m_{\text{Al(OH)}_4^-}}{m_{\text{OH}^-}} - 2A_\gamma I^{1/2} \left[\left(1 + a_{\text{NaAl(OH)}_4} B_\gamma I^{1/2} \right)^{-1} - \left(1 + a_{\text{NaOH}} B_\gamma I^{1/2} \right)^{-1} \right] = p_1 + p_2/T + p_3 \ln T + p_4(T) - [p_5 + p_6/T + p_7 \ln T + p_8(T) + p_9(T^2)]I, \quad (10)$$

where T denotes temperature in K.

The values of adjustable parameters in Eq.(10) are listed in Table 1.

Table 1 The values of parameters in Eq.(10)

p_1	p_2	p_3	p_4	p_5
-1 345.1	39 776	229.0316	-0.3163	-12 060
p_6	p_7	p_8	p_9	
255 500	2 264.8	6.6850	0.0033	

3.2 Discussion of the Applicability

3.2.1 Calculation of equilibrium constant

The empirical equilibrium constant expression of gibbsite in NaOH solution over the range from 25 °C to 100 °C is given as follows according to Eq.(10) and the values of parameters in Table 1:

$$\log K = -1 345.1 + 39 776/T + 229.0316 \ln T - 0.3163T. \quad (11)$$

The values of $\log K$ obtained from Eq.(11) are listed in Table 2.

There are many reports concerning solubility data of gibbsite in NaOH solution. Among all the previous reports, the work of Wesolowski^[3] using the Pitzer model has been testified as the best^[2,12]. So the results of Wesolowski are chosen as comparison criterion in this study, which are also listed in Table 2.

Table 2 Comparison of $\log K$ values for gibbsite dissolution based on the Eq.(11)

T (°C)	This study	Wesolowski ^[3]	App et al. ^[1]	Chang ^[7]		Russell et al. ^[11]
				Case 1	Case 2	
25	-1.040	-1.143	-1.276	-1.260	-1.276	-1.272
30	-1.012	-1.076		-1.171	-1.189	-1.183
40	-0.932	-0.945		-1.003	-1.024	-1.014
50	-0.826	-0.814	-0.889	-0.845	-0.869	-0.856
60	-0.703	-0.684	-0.740	-0.700	-0.724	-0.707
70	-0.572	-0.556		-0.557	-0.586	-0.566
80	-0.438	-0.430		-0.425	-0.457	-0.434
90	-0.306	-0.306		-0.300	-0.335	-0.309
100	-0.183	-0.184	-0.184	-0.183	-0.219	-0.190

The comparison indicates that the current results from Eq.(11) are in close agreement with those of the work employing the Pitzer model reported by Wesolowski^[3]. The tendency of approximation becomes especially obvious with the increase of temperature, and our results are almost completely identical with the Wesolowski's above 90 °C. This strongly supports the laws reported by Helgeson et al.^[8] that Debye–Hückel equation has an outstanding applicability at high temperatures. In contrast, it shows some deviation at 25 °C. But fortunately, the deviation is not significant, as only the temperatures above 40 °C are meaningful for the alumina industry, so the discrepancy at lower temperatures would not hold back the application of

extended Debye–Hückel equation in NaAl(OH)₄–NaOH–H₂O system.

According to what mentioned above, the close approximate results are obtained by using the extended Debye–Hückel equation which is much simpler than the Pitzer model. This indicates that applying the extended Debye–Hückel equation to calculate activity coefficients of sodium aluminate solution is suitable and accurate. Debye–Hückel model has an excellent applicability in NaAl(OH)₄–NaOH–H₂O system.

3.2.2 Discussion of $b_{\gamma, \text{NaAl(OH)}_4}$

In the activity calculation equation provided by Helgeson et al.^[8], b_γ is one of the key parameters. The use of b_γ makes the activity coefficients calculation with

Debye–Hückel equation be more approximate to the actual values. As $b_{\gamma}I$ represents the main part of errors in the work of establishing the calculation model. Its analysis can also illuminate the applicability of Debye–Hückel model.

From Eq.(10) and the values of parameters listed in Table 1, the empirical relationship between $b_{\gamma, \text{NaAl(OH)}_4^-}$ – $b_{\gamma, \text{NaOH}}$ and temperature is expressed as:

$$b_{\gamma, \text{NaAl(OH)}_4^-} - b_{\gamma, \text{NaOH}} = -12060 + 255500/T + 2264.8 \ln T - 6.6850T + 0.0033T^2. \quad (12)$$

The values of b_{γ} are usually tested by experimental data according to the method provided by Helgeson et al.^[13]. There is no report about b_{γ} of sodium aluminate solution. But at certain temperature, when the value of $b_{\gamma, \text{NaOH}}$ is known, the value of $b_{\gamma, \text{NaAl(OH)}_4^-}$ can be calculated by Eq.(12). Combining the values of $b_{\gamma, \text{NaOH}}$ selected from Pokrovskii and Helgeson^[2], a series of $b_{\gamma, \text{NaAl(OH)}_4^-}$ are calculated at some temperature points, being listed in Table 3.

Table 3 The extended-term parameter b_{γ} (with temperature)

T (°C)	$b_{\gamma, \text{NaOH}}$ ^[2]	$b_{\gamma, \text{NaAl(OH)}_4^-}$
50	0.102	0.044
75	0.099	0.039
100	0.093	0.035

The results show that along with the increase of temperature, the value of $b_{\gamma, \text{NaAl(OH)}_4^-}$ decreases. The change of $b_{\gamma, \text{NaAl(OH)}_4^-}$ with the temperature is identical with other systems^[8,13] in the principles and ranges. In another point of view, it also testifies the success in establishing a calculation model based on Debye–Hückel model by regression of solubility data of gibbsite in NaOH solution.

4 CONCLUSIONS

(1) Debye–Hückel model for calculation of activity coefficients has an excellent applicability in NaAl(OH)_4^- – NaOH – H_2O system. Therefore, based on Debye–Hückel equation and equilibrium solubility data, establishing a calculation model of activity coefficients for NaAl(OH)_4^- – NaOH – H_2O system is feasible.

(2) The parameter $\hat{a}_{\text{NaAl(OH)}_4^-}$ can be deduced from the radii of Na^+ and of OH^- ions along with the radius discrepancy of Al(OH)_4^- and OH^- . Its value is determined as 0.3595 nm.

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