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Isopiestic measurement of the osmotic and activity coefficients for the NaOH-NaAl(OH)₄-H₂O system at 313.2 K

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Abstract—By using a specially designed and constructed isopiestic apparatus, we measured the osmotic coefficients at 313.2 K for the NaOH-NaAl(OH)₄-H₂O system with the total alkali molality, m_{NaOHT} ($m_{\text{NaOH}} + m_{\text{NaAl(OH)}_4}$), from 0.05 mol/kg H₂O to 12 mol/kg H₂O and α_K ($m_{\text{NaOHT}}/m_{\text{NaAl(OH)}_4}$) from 1.64 to 5.53. The mean standard deviation of the measurements is 0.0038. Several sets of the Pitzer model parameters for NaOH-NaAl(OH)₄-H₂O system were then obtained by regressing the measured osmotic coefficients with the Pitzer model and the Pitzer model parameters for NaOH(aq). One set of the results is as follows: $\beta^{(0)}_{\text{NaOH}}$: 0.08669, $\beta^{(1)}_{\text{NaOH}}$: 0.31446, $\beta^{(2)}_{\text{NaOH}}$: -0.00007367, $C^{\text{p}}_{\text{NaOH}}$: 0.003180, $\beta^{(0)}_{\text{NaAl(OH)}_4}$: 0.03507, $\beta^{(1)}_{\text{NaAl(OH)}_4}$: 0.02401, $C^{\text{p}}_{\text{NaAl(OH)}_4}$: -0.001066, $\theta_{\text{OH}^-\text{Al(OH)}_4^-}$: 0.08177, $\Psi_{\text{Na}^+\text{OH}^-\text{Al(OH)}_4^-}$: -0.01162. The mean standard difference between the calculated and the measured osmotic coefficients is 0.0088. With the obtained Pitzer model parameters, we calculated the values of $K' = (\gamma_{\text{NaAl(OH)}_4, \text{cal}} \cdot m_{\text{Al(OH)}_4^-, \text{exp}}) / (\gamma_{\text{NaOH, cal}} \cdot m_{\text{OH}^-, \text{exp}})$ for the gibbsite solubility. The results show that the obtained Pitzer model parameters are reliable, and the relative error of the calculated activity coefficients should be < 2.1%. We also compared the calculated gibbsite solubility data among several activity coefficients models over a range of m_{NaOHT} at various temperatures. The comparison indicates that our activity coefficients model may be approximately applied in the ranges of temperature from 298.2 to 323.2 K and m_{NaOHT} from 0 to 8 mol/kg H₂O. We also calculated the stoichiometric activity coefficients of NaOH and NaAl(OH)₄ and the activity of H₂O for the NaOH-NaAl(OH)₄-H₂O system, and these calculations establish their variations with m_{NaOHT} and α_K . These variations imply that the strengths of the repulsive interactions among various anions are in the following sequence: $\text{Al(OH)}_4^- - \text{Al(OH)}_4^- < \text{Al(OH)}_4^- - \text{OH}^- < \text{OH}^- - \text{OH}^-$, and the attractive interaction between Al(OH)_4^- and H₂O is weaker than that between OH⁻ and H₂O. Copyright © 2003 Elsevier Ltd

1. INTRODUCTION

The physico-chemical properties of sodium aluminate solutions are quite different from those of normal electrolytes, especially the abnormally high metastability of the supersaturated solution. Thus, the rate of the deposition process of the solution is very slow. It results in this process to be the bottleneck in the production of Al₂O₃ by the Bayer method (Yang, 1993), in which the sodium hydroxide is used for the extraction of aluminum from several of its ores. Unfortunately, there are many discrepancies in the views about the mechanism of the deposition process and the structure of the solution (Yang, 1993; Li, 2001). The physico-chemical properties of sodium aluminate solutions are also the important components in the system involving aluminum. Aluminum is the third most abundant element in the Earth's crust. Many of the active Earth processes of interest to geoscientists, such as ore formation, geothermal alteration, sedimentary diagenesis, the remediation of the high level nuclear wastes in leaking underground storage tanks, geochemical transport of the aluminum, and so forth, involve the physico-chemical properties of aluminum in natural systems, especial the aqueous chemistry of dissolved aluminum. However, the aqueous chemistry of dissolved aluminum remains a controversial subject (May et al., 1979; Apps et al.,

1988; Wesolowski, 1992, 2002). Moreover, it has been necessary to substitute concentrations for activities in the thermodynamic analysis of sodium aluminate solutions in most cases, because of the lack of the reliable activity coefficients. But this kind of substitution could result in wrong conclusions. In addition, the osmotic and activity coefficients can provide a theoretical and experimental thermodynamic foundation for the studies of the solubilities of aluminum hydroxides or oxides in solutions, of the deposition processes, and of the structures of sodium aluminate solutions. Therefore, the determination of the osmotic and activity coefficients for the sodium aluminate solution system, especially for the supersaturated solution, is needed for practical and theoretical applications. However, this aim is much more difficult to achieve than for many other electrolytes. Because the forms of existing various species of aluminate anions are very complex and NaOH is very corrosive, an effective reversible electrode responding to the aluminate anion, which could be used to directly determine the activity coefficients of the component NaAl(OH)₄, is not available. The cryoscopic method is difficult to be employed, because the deposition or precipitation of the sodium aluminate solution is prone to occur as the temperature is lowered. Even for the isopiestic method, which has wide applicability and great flexibility, the tendency of the hydroxide to absorb atmospheric carbon dioxide, the high viscosity of the solution, and many other disadvantageous properties, make experiments become difficult. Atranovskiy (1970), Apps et al. (1988), Apps

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and Neil (1990), Zeng (1993), and Pokrovskii and Helgeson (1995) had presented complete reports of the accrued research involving aluminum. Despite of the wealth of experimental data for the system $\text{NaOH-Al}_2\text{O}_3\text{-H}_2\text{O}$, few direct studies of the osmotic and activity coefficients are available. By modeling the solubility of gibbsite with the Pitzer ion interaction treatments, Wesolowski (1992, 2002) gave a set of approximate values of the pure electrolyte Pitzer model parameters for $\text{NaAl(OH)}_4(\text{aq})$ at various temperatures, as well as the mixing parameters for Al(OH)_4^- with OH^- and $\text{OH}^- + \text{Na}^+$. Park and Englezos (1999) measured the osmotic coefficients for $\text{NaOH-NaAl(OH)}_4\text{-NaCl-H}_2\text{O}$ system from ($m_{\text{NaOH}} = 0.85$, $m_{\text{NaAl(OH)}_4} = 0.05$, $m_{\text{NaCl}} = 0.15$) (mol/kg H_2O) to ($m_{\text{NaOH}} = 2.6$, $m_{\text{NaAl(OH)}_4} = 0.35$, $m_{\text{NaCl}} = 1.04$) (mol/kg H_2O) at 298.15 K by an isopiestic method, and modeled the experimental data with the Pitzer model. The temperature of the practical interest to industry for sodium aluminate solutions is usually ~ 313 to 353 K (Yang, 1993). In here, we measured the osmotic coefficients for the $\text{NaOH-NaAl(OH)}_4\text{-H}_2\text{O}$ system at 313.2 K with our isopiestic apparatus. This isopiestic apparatus was specially designed and constructed to be applicable to the $\text{NaOH-NaAl(OH)}_4\text{-H}_2\text{O}$ system and other unstable systems (Zhou and Chen, in press). The experimental data were then modeled with the Pitzer model to give the Pitzer model parameters. The obtained Pitzer model parameters were then used to analyze the solubilities of aluminum hydroxide in the aqueous solution. The activity coefficients were also calculated. These values reflect the interactions between the species in solutions.

2. EXPERIMENTAL

2.1. General

Each of experimental data is usually given with a uncertainty following the datum. The uncertainty is expressed in integer forms with the right-hand digit in the same order as the right-hand digit of the experimental datum. The standard deviation of a calculated datum was calculated from the individual standard deviations of all used data according to the usual propagation of errors method as follows:

$$y = y(x_1, x_2, x_3, \dots), \quad (1)$$

$$\sigma(y)^2 = (\partial y / \partial x_1)^2 \cdot \sigma(x_1)^2 + (\partial y / \partial x_2)^2 \cdot \sigma(x_2)^2 + \dots, \quad (2)$$

where σ is the standard deviation.

Electronic balances of Satorius BP190S ($\leq \pm 0.0001$ g) and Satorius BS2000S ($\leq \pm 0.01$ g) were used in our experiments. They were always calibrated before used. Each weighing was repeated for at least three times, and the average weight was taken as the result. For all weights, except for those of containers, vacuum correction was made when the relative errors arising from air buoyancy were $> 1/8000$.

2.2. Apparatus

The apparatus mainly contains four small silver cups for the reference standard solution samples and one big cup for the sample being investigated. It has been described in detail by Zhou and Chen (in press). Experiments showed that, not only the apparatus was able to ensure a good consistent equilibrium temperature among the samples, but also it had a favorable reliability and stability during the equilibration process. Experiments also showed that the apparatus possessed a fairly fast rate of equilibration, and it was easy and effective to decide when the equilibrium is achieved. Therefore, the apparatus is suitable for complex or unstable solutions that are sluggish to equilibrate or have other disadvantageous properties for the measurements.

The isopiestic apparatus was put on a platform that was rotating during the equilibration process. The platform was in a thermostat. The thermostat was inclined by $\sim \pi/36$, and the temperature was electri-

cally controlled to 313.2 K with a maximum drift of $\sim \pm 0.5$ K over 24 h. Although this kind of temperature was not so precise as usual ($\leq \pm 0.01$ K), our previous work has shown that good results could be obtained with our apparatus (Zhou and Chen, in press).

2.3. Chemical Reagents and the Preparation of the Stock Solutions

Water was prepared by distillation of tap water. A small amount of KMnO_4 and NaOH had been added into the tap water to get rid of organic substances and inorganic acids. The temperature of the distilled water in the outlet was controlled to 348 to 358 K during the distillation. The distilled water was stored in a big glass container, which is connected to a gas-washed bottle first with NaOH solution in it and then a gas-dried tower with soda-lime in it to eliminate CO_2 and the dust in the admitting air.

The concentrated stock solution of reference standard NaCl solution is the same as described by Zhou and Chen (in press). It was prepared by dissolving reagent grade NaCl (GR grade GB1266-86) in the purified water. The density of the NaCl stock solution was measured to be 1191.675 ± 22 g/dm³ at ~ 287.6 K. The impurities in the stock solution were analyzed by using inductive-coupled plasma atomic emission spectroscopy (ICPAES). It was found that the contents of the impurities were: K: 0.000642 mol/mol NaCl ; S: 0.000555 mol/mol NaCl ; Zn: 0.000033 mol/mol NaCl ; each of the remainder: ≤ 0.000043 mol/mol NaCl . These impurities were neglected in our experiments, and the solute was assumed to be only NaCl in the calculation of molalities. The effective molar mass of NaCl was taken to be 58.443 g/mol. The density of the crystalline NaCl was calculated by Archer's (1992) equation to be 2165 g/dm³ at 298.15 K. The molality of the NaCl stock solution was analyzed to be 5.7690 ± 11 mol/kg H_2O (the mass percentage is $25.2146 \pm 49\%$) by the dehydration method. The dehydration method was similar to that used by Rard and Archer (1995) and that presented in the *Handbook of Analytical Chemistry* (Analytical Chemistry Editor Group, Hangzhou University, 1997). The details of the analysis have been described by Zhou and Chen (in press).

The concentrated stock solution of the reference standard CaCl_2 solution was prepared by the reaction between primary standard CaCO_3 (GB12596-90) and reagent grade aqueous HCl (GR grade GB622-89). The method was similar to that used by Rard and Miller (1981). The prepared CaCl_2 solution was stored in contact with excess CaCO_3 for several days, and the excess CaCO_3 was then filtered off to yield the final CaCl_2 stock solution. The density of the stock solution was measured to be 1361.415 ± 49 g/dm³ at ~ 290.0 K. The impurities of the CaCl_2 stock solution were analyzed by ICPAES method: K: 0.000741 mol/mol CaCl_2 ; S: 0.000245 mol/mol CaCl_2 ; Ba: 0.000060 mol/mol CaCl_2 ; each of the remainder: ≤ 0.000011 mol/mol CaCl_2 . All impurities were neglected so that the solute could be assumed to be only CaCl_2 in the calculation of molalities. The effective molar mass of CaCl_2 was taken to be 110.984 g/mol. The density of the solid CaCl_2 is 2150 g/dm³ at room temperature (Dean, 1985). The molality of the CaCl_2 stock solution was analyzed to be 5.3030 ± 12 mol/kg H_2O (mass percentage $37.0496 \pm 74\%$) by the direct dehydration method, which has been discussed by Rard and Miller (1981). The details of the analysis were similar to those of the NaCl stock solution analysis.

The NaOH used was of reagent grade (GR grade GB629-81[84]), its molar mass is taken to be 39.9971 g/mol. The NaOH stock solution was prepared by the method similar to those used by Stokes (1945), Simonson et al. (1989), and *Handbook of Analytical Chemistry* (Analytical Chemistry Editor Group, Hangzhou University, 1997). The preparation method was described in detail by Zhou and Chen (in press). The density was measured to be 1456.6 ± 15 g/dm³ at ~ 291.6 K. According to the method of GB629-81(84) (Quality Monitoring Center for Chemical Reagents, Chemical Department of China, 1996), the content of Na_2CO_3 in one sample was analyzed. This sample was prepared from the stock solution and had been stored for > 1 month. The analysis showed that the presence of $1/2(\text{Na}_2\text{CO}_3)$ was equivalent to 0.177 ± 70 mol.% of the total alkali. In Stokes's (1945) opinion, the presence of 0.2% carbonate is not likely to affect the isopiestic molality ratios of $m_{\text{H}_2\text{SO}_4}/m_{\text{NaOH}}$ by > 0.0005 in isopiestic experiments. Therefore, the presence of Na_2CO_3 was ignored in our experiments. The NaOH contents in the stock solutions were analyzed by an improved titration method, which was described in detailed in the reference

Table 1. The obtained compositions of the sodium aluminate stock solutions (NaOH-NaAl(OH)₄-H₂O).

Number	1	2	3	4
α_K^a	1.6481 ± 18	2.1951 ± 23	3.2500 ± 28	5.5236 ± 45
NaOHT (%) ^b	26.571 ± 28	27.477 ± 29	25.883 ± 22	34.520 ± 27
Al(OH) ₃ (%)	31.4434 ± 55	24.4119 ± 55	15.53125 ± 31	12.1881 ± 29
m_{NaOHT} (mol/kg H ₂ O) ^c	15.823 ± 20	14.279 ± 17	11.0044 ± 104	16.195 ± 15
ρ (g/dm ³)	1505.3 ± 15 (302.0 K)	1466.3 ± 15 (293.0 K)	1388.5 ± 14 (289.0 K)	1454.3 ± 15 (298.2 K)

^a $\alpha_K = m_{\text{NaOHT}}/m_{\text{Al(OH)}_3} = m_{\text{NaOHT}}/m_{\text{NaAl(OH)}_4}$.

^b NaOHT denotes the total alkali which includes the free alkali NaOH and the alkali NaOH in NaAl(OH)₄ (namely the alkali NaOH reacting with the aluminum hydroxide Al[OH]₃).

^c $m_{\text{NaOHT}} = m_{\text{NaOH}} + m_{\text{NaAl(OH)}_4}$.

(Zhou and Chen, in press). The analyses yielded the follows: stock solution I: NaOH% = 42.640 ± 37 , $m_{\text{NaOH}} = 18.586 \pm 20$ mol/kg H₂O, $\rho_{\text{NaOH}} = 1456.6 \pm 15$ g/dm³ at ~ 291.6 K; stock solution II: NaOH% = 43.115 ± 46 , $m_{\text{NaOH}} = 18.950 \pm 25$ mol/kg H₂O, $\rho_{\text{NaOH}} = 1465.9 \pm 15$ g/dm³ at ~ 286.0 K.

The Al wire is of ultrapure grade >99.999% (Q/CYDZ-184-97, lot number Shanghai SCR-F990506). The density is 2.6989 g/cm³ at 293 K (Weast and Astle, 1983). Molar masses of Al and Al(OH)₃ are taken to be 26.98154 g/mol and 78.0036 g/mol, respectively.

Sodium aluminate stock solutions were prepared in the following steps: (1) According to the method similar to that used in GB32571-82 (The National Standard of the People's Republic of China, 1982), a certain amount of Al wires was first boiled in aqueous HCl (1:1) for at least 5 to 10 min. Then they were washed with distilled water for at least five times and with CH₃CH₂OH for at least three times. Subsequently, they were blown to be completely dry by a hair dryer and cooled in a desiccator. Finally they were accurately weighed. (2) An amount of the NaOH stock solution in a 500-cm³ measuring flask was accurately weighed. The measuring flask had been weighed accurately in advance. (3) The lower part of the measuring flask was inserted into a water bath, whose temperature was controlled in the range of 353 to 373 K. Then the Al wires, along with an appropriate amount of water, were added to the NaOH solution gradually. At the same time, the measuring flask was being wagged in the water bath so that the temperature of the sodium aluminate solution in it was approximately equal to that in the water bath. (4) The prepared sodium aluminate solution was adjusted to a fixed volume of 500 cm³ by adding some water. Subsequently, the sodium aluminate solution was mixed thoroughly and weighed accurately, and then transferred into an 800-cm³ polyethylene bottle. (5) After being capped hermetically and weighed, the bottle was stored in a desiccator containing soda-lime. The bottle was always re-weighed before used. The weight difference from that when the bottle was placed in the desiccator should be < 0.01 g. By this experimental technique, we can calculate the compositions of the stock solutions accurately and avoid chemical analyses of the aluminum contents of the solutions. According to the standard chemical analysis methods described in GB32571-82 (The National Standard of the People's Republic of China, 1982) and ISO 6994-1986(1) (1986), the relative error is nearly 0.5%. However, accurate analyses of the stock solutions are very important for isopiestic measurements as pointed out by Rard and Platford (1991).

The obtained compositions of the prepared sodium aluminate stock solutions are given in Table 1.

The compositions of the stock solutions, except for number 4, are approximately in the stable regions according to the phase diagrams of Na₂O-Al₂O₃-H₂O systems (Atrantovskiy, 1970). Number 4 was prepared from number 2 and the NaOH stock solution several days before the isopiestic experiments. They were always examined carefully to check whether there was any deposition before use. In our experiments, no deposition was found.

The Si contents of the sodium aluminate stock solutions were analyzed by spectrophotometry. We had found that when the lower part of the measuring flask was not inserted into the water in step (3) of the preparation of an aluminate solution, the temperature of the aluminate solution was ~ 393 K while the Al wires were being dissolved into the NaOH solution. When the time of dissolving Al is ~ 6 to 12 h, the Si

content of the solution is ~ 111 mg/dm³. Therefore, the lower part of the measuring flask was always inserted into the water during the preparation of the stock aluminate solutions. For number 3, the water in the water bath was controlled to be 373 K, and the time of dissolving Al wires was ~ 6 to 12 h. The Si content was found to be 32.8 mg/dm³ (0.00013 mol/mol NaOH). For stock solution 2, the temperature of the water was controlled to ~ 353 K, and the time was ~ 4 h, and the Si content was found to be < 1 mg/dm³ (0.000004 mol/mol NaOH). For number 1, the water was controlled to 353 K, and the time was < 10 h. The Si content was assumed to be < 32.8 mg/dm³ (0.00013 mol/mol NaOH). One sample was prepared from stock aluminate solution 3 by mass dilution. The molality of NaOH was 0.88360 ± 88 mol/kg H₂O. The impurities were analyzed by ICPAES: S: 0.000636 mol/mol NaOH, Si: 0.0000584 mol/mol NaOH, each of remainder: ≤ 0.0000289 mol/mol NaOH. These impurities should be equivalent in the other stock aluminate solutions. All these impurities, including Si, were neglected in our experiments.

2.4. Array of the Experimental Molalities

As we know, one important reason for the measurement of the osmotic coefficients Φ is to calculate the activity coefficients of solutes. For the binary system of water and the solute i , there is

$$\ln \gamma_i = \int_0^{m_i} d\Phi + \int_0^{m_i} (\Phi - 1) d \ln m_i, \quad (3)$$

where γ_i is the activity coefficient of the solute i , the m_i is the stoichiometric molality. From Eqn. 3, it can be seen that the relative error in γ_i depends on the absolute error in Φ , and the error in the second part of the right side, which is an integration error. The array of the experimental molalities was designed basically according to Eqn. 3, being more closely spaced in the dilute solutions and more widely spaced in the concentrated solutions.

2.5. Experimental Procedure

The adopted experimental procedure was the same as described in detail by Zhou and Chen (in press). (1) The experimental solutions were prepared by mass dilution from the stock solutions. Two small cups were used for the reference standard solutions of higher initial molality, the other two small cups were used for the solutions of lower initial molality. The relative difference between the higher and lower initial molalities was $\sim 25\%$. The masses of the reference standard solutions were 0.2 to 1.0 g. About 100 cm³ sodium aluminate solution was put into the big cup. (2) All cups were put into the isopiestic apparatus, then, the isopiestic apparatus was closed and evacuated with our evacuation system. (3) The whole apparatus was put on the platform in the thermostat, and the equilibration experiment commenced. In general terms, the water activity of the initial sodium aluminate solution was easily maintained between those of the reference standard solutions of the higher and lower initial molalities because of the great relative difference in the initial molalities of the reference standard solutions. As the equilibration progressed, the higher and lower initial molalities approached together. In the end of the equilibration process,

Table 2. Isopiestic molalities of the equilibration experiments for NaOH-NaAl(OH)₄-H₂O system at 313.2 K.

Experiment	$m_{\text{NaOHT}}^{\text{a,b}}$ (mol/kg H ₂ O)	$m_{\text{NaAl(OH)}_4}^{\text{a}}$ (mol/kg H ₂ O)	α_K^{c}	$m_{\text{NaCl}}^{\text{a}}$ (mol/kg H ₂ O)	$m_{\text{CaCl}_2}^{\text{a}}$ (mol/kg H ₂ O)
1	0.10416 ± 16	0	/	0.10398 ± 28	/
2	2.9704 ± 34	0	/	3.0603 ± 20	/
3	5.1849 ± 47	0	/	5.5150 ± 78	2.7777 ± 78
4	9.7215 ± 91	2.9911 ± 14	3.2500 ± 28	/	4.4246 ± 25
5	6.4286 ± 58	1.97800 ± 65	3.2500 ± 28	/	3.1522 ± 19
6	4.6166 ± 40	1.42048 ± 46	3.2500 ± 28	4.6251 ± 25	2.4106 ± 26
7	3.1680 ± 27	0.97475 ± 30	3.2500 ± 28	3.1427 ± 29	/
8	1.5053 ± 13	0.46315 ± 16	3.2500 ± 28	1.5043 ± 16	/
9	1.01702 ± 88	0.31292 ± 11	3.2500 ± 28	1.01777 ± 65	/
10	0.50388 ± 43	0.155034 ± 59	3.2500 ± 28	0.50358 ± 35	/
11	0.26342 ± 23	0.081050 ± 34	3.2500 ± 28	0.26329 ± 19	/
12	0.105245 ± 91	0.032382 ± 14	3.2500 ± 28	0.10480 ± 12	/
13	0.052547 ± 45	0.0161679 ± 71	3.2500 ± 28	0.05236 ± 19	/
14	11.755 ± 14	5.3548 ± 34	2.1951 ± 23	/	4.7969 ± 37
15	8.5922 ± 101	3.9141 ± 21	2.1951 ± 23	/	3.7718 ± 47
16	5.9247 ± 67	2.6991 ± 12	2.1951 ± 23	/	2.8404 ± 31
17	3.9204 ± 43	1.78589 ± 74	2.1951 ± 23	3.7988 ± 34	/
18	2.5622 ± 29	1.16717 ± 48	2.1951 ± 23	2.4967 ± 33	/
19	1.4663 ± 16	0.66799 ± 27	2.1951 ± 23	1.4382 ± 20	/
20	0.9988 ± 11	0.45499 ± 18	2.1951 ± 23	0.9834 ± 14	/
21	0.46922 ± 54	0.213758 ± 88	2.1951 ± 23	0.46162 ± 104	/
22	0.23753 ± 25	0.108207 ± 44	2.1951 ± 23	0.23405 ± 52	/
23	0.098104 ± 111	0.044693 ± 19	2.1951 ± 23	0.09675 ± 35	/
24	10.337 ± 12	6.2725 ± 37	1.6481 ± 18	/	4.1095 ± 48
25	0.45190 ± 49	0.274239 ± 97	1.6481 ± 18	0.44201 ± 84	/
26	0.23919 ± 26	0.145136 ± 52	1.6481 ± 18	0.23389 ± 263	/
27	0.095199 ± 106	0.057762 ± 23	1.6481 ± 18	0.09359 ± 29	/
28	0.047406 ± 55	0.028763 ± 12	1.6481 ± 18	0.046482 ± 46	/
29 ^d	0.97152 ± 106	0.58950 ± 20	1.6481 ± 18	0.94096 ± 134	/
30	7.5502 ± 83	4.5813 ± 20	1.6481 ± 18	/	3.2852 ± 41
31 ^e	2.5533 ± 28	1.54928 ± 52	1.6481 ± 18	2.4093 ± 61	/
32 ^f	1.4931 ± 16	0.90600 ± 30	1.6481 ± 18	1.4275 ± 55	/
33	9.4308 ± 85	1.7074 ± 16	5.5236 ± 45	/	4.4848 ± 84
34	7.2377 ± 62	1.31033 ± 50	5.5236 ± 45	/	3.5773 ± 28
35	5.5417 ± 48	1.00328 ± 43	5.5236 ± 45	5.6871 ± 67	/
36	4.0179 ± 34	0.72740 ± 27	5.5236 ± 45	4.0580 ± 89	/
37	2.5116 ± 22	0.45470 ± 17	5.5236 ± 45	2.4952 ± 93	/
38	1.4574 ± 13	0.26384 ± 10	5.5236 ± 45	1.43861 ± 488	/
39	0.96454 ± 84	0.174621 ± 65	5.5236 ± 45	0.9498 ± 14	/
40	0.46274 ± 41	0.084314 ± 33	5.5236 ± 45	0.45654 ± 62	/
41	0.23858 ± 21	0.043194 ± 18	5.5236 ± 45	0.23311 ± 37	/
42	0.096064 ± 83	0.0173912 ± 75	5.5236 ± 45	0.09457 ± 12	/

^a All m values are the stoichiometric molalities.

^b m_{NaOHT} is the molality of total alkali, i.e., $m_{\text{NaOHT}} = m_{\text{NaOH}} + m_{\text{NaAl(OH)}_4}$.

^c $\alpha_K = m_{\text{NaOHT}}/m_{\text{NaAl(OH)}_4}$.

^d The sodium-D-gluconate (C₆H₁₁O₇Na) content is 25 mg/dm³ (see text).

^e The sodium-D-gluconate (C₆H₁₁O₇Na) content is 15 mg/dm³ (see text).

^f The sodium-D-gluconate (C₆H₁₁O₇Na) content is 16 mg/dm³ (see text).

the mean molality of all reference standard solution samples was accepted as the equilibrium molality. The final standard deviation was calculated from the individual standard deviations of all molalities used in the calculation and the limit difference of all molalities. The sodium aluminate solutions were always examined carefully, and only those experiments, in which there was no evidence of precipitation, were accepted as the equilibrium results. More experimental details can be found in our paper (Zhou and Chen, in press).

3. RESULTS AND DISCUSSION

3.1. Osmotic Coefficient Measurements

Results of the isopiestic molalities of the equilibration experiments are listed in Table 2.

In experiments 29, 30 and 31, a small amount of sodium-D-

gluconate (C₆H₁₁O₇Na) of 25 mg/dm³, 15 mg/dm³, and 16 mg/dm³, respectively, was added into the sodium aluminate solutions during their preparation, as C₆H₁₁O₇Na can effectively inhibit the crystallization of gibbsite from the sodium aluminate solution according to Watling et al. (2000) and Watling (2000). Because the amounts of C₆H₁₁O₇Na added were very small in comparison with the main compositions of the solutions, they would have little effect on the whole thermodynamic properties of the solutions.

The osmotic coefficients of the NaOH solutions, which were prepared from the same NaOH stock solutions to those described in this paper, were measured at 298.2 K, and the measured osmotic coefficients were basically within the range

Table 3. The osmotic coefficients of CaCl₂ and NaOH solutions at 313.2 K and 0.1 MPa.

Experiments		1	2	3	6
NaCl	m	0.10398 ± 28	3.0603 ± 20	5.5150 ± 78	4.6251 ± 25
	$\Phi_{\text{Archer}} (1992)$	0.930625 ± 39	1.06218 ± 14	1.23383 ± 56	1.16999 ± 18
	$\Phi \cdot m^a$	0.09677 ± 26	3.2506 ± 25	6.8046 ± 127	5.4111 ± 40
CaCl ₂	m	/	/	2.7777 ± 78	2.4106 ± 26
	Φ_{meas}	/	/	1.6331 ± 65	1.4965 ± 22
	$\Phi_{\text{Phutela, Pitzer}} (1983)$	/	/	1.6337	1.49832
	$\Phi_{\text{Ananthaswamy, Atkinson}} (1985)$	/	/	1.6371	1.49928
	$\Phi_{\text{Møller}} (1988)$	/	/	1.6374	1.50130
NaOH	m	0.10416 ± 16	2.9704 ± 34	5.1849 ± 47	/
	Φ_{meas}	0.9290 ± 29	1.09433 ± 151	1.3124 ± 27	/
	$\Phi_{\text{Pabalan, Pitzer}} (1987, 1991)$	0.93156	1.0990	1.3209	/
	$\Phi_{\text{Simonson, Mesmer, Rogers}} (1989)$	0.93265	1.0893	1.3067	/
	$\Phi_{\text{Holmes, Mesmer}} (1998)$	0.93262	1.0899	1.3080	/

^a The standard deviation is calculated from the greatest and the smallest values of $\Phi \cdot m$ corresponding to m with the standard deviation.

of the various reference values (Zhou and Chen, in press). Table 3 gives the osmotic coefficients of the NaOH solutions and CaCl₂ solutions, which were measured at 313.2 K with the NaCl solution as the reference standard solutions.

From Table 3, we can draw the conclusion that our measured osmotic coefficients are reliable. It further implies that the analyzed molalities of the stock solutions are reliable and consistent with each other.

Table 4 lists the measured osmotic coefficients Φ_{meas} for the NaOH-NaAl(OH)₄-H₂O system. The standard deviations of the measured osmotic coefficients are usually ~ 0.001 to 0.005 , and the mean standard deviation is calculated to be 0.0038 . The value of Φ_{meas} was usually calculated according to the osmotic coefficient of NaCl reference standard solution. The osmotic coefficient of NaCl solution was calculated with the equations and parameters given by Archer (1992). For an experiment, where only the CaCl₂ reference standard solution was employed, the value of Φ_{meas} was calculated from the average osmotic coefficient of the CaCl₂ reference standard solution. The average osmotic coefficient of the CaCl₂ solution was the average of those values calculated with the sets of parameters given by Phutela and Pitzer (1983), Ananthaswamy and Atkinson (1985), and Møller (1988). The difference among those reference osmotic coefficients of CaCl₂ solution was considered in the calculation of the standard deviation of the average value.

3.2. Modeling of the Osmotic Coefficients for the NaOH-NaAl(OH)₄-H₂O System With the Pitzer Model

It is known that aluminum in sodium hydroxide solutions occurs as various kinds of species, such as Al(OH)₄⁻, Al(OH)₄⁻OH⁻, Al₂O(OH)₆²⁻, AlO(OH)₂⁻, (Al[OH]₄)₆⁶⁻, NaAl(OH)₄⁰, and so forth. According to the research of Lippincott et al. (1952), Mal'tsev et al. (1965), Moolenaar et al. (1970), Zambo (1986), and Barcza and Palfalvi-Rozsahegyi (1989), it is generally accepted that the tetrahedral Al(OH)₄⁻ ion is the only important species in hydroxide solutions of less than moderate concentration (2–4 mol/kg H₂O) below 373 K. On the basis of the possible equilibria among the various species, the Al(OH)₄⁻ ion would be the only possible aluminum species in an infinitely dilute hydroxide solution. As a

result, in many recent studies, such as those of Wesolowski (1992, 2002), Verdes et al. (1992), Zeng (1993), and Park and Englezos (1999), the Al(OH)₄⁻ ion is assumed to be the major species in dilute sodium aluminate solutions. Here, we adopted NaAl(OH)₄, NaOH and H₂O as the basic components of the sodium aluminate system. These components can be consistent in formula with the actually existing species of Na⁺, Al(OH)₄⁻, OH⁻, and H₂O in an infinitely dilute sodium aluminate solution. The molalities of these components are stoichiometric molalities. Only on this basis, we can use the Pitzer model to regress the experimental osmotic coefficients.

According to the equation of Pitzer (1991), the osmotic coefficient Φ of the NaOH-NaAl(OH)₄-H₂O system is given by

$$\begin{aligned} \Phi - 1 = & -A_{\Phi} m^{1/2} / (1 + b m^{1/2}) + \\ & (1 - 1/\alpha_k) m [\beta_{\text{NaOH}}^{(0)} + \beta_{\text{NaOH}}^{(1)} \exp(-\alpha_1 m^{1/2}) \\ & + \beta_{\text{NaOH}}^{(2)} \exp(-\alpha_2 m^{1/2}) + m C_{\text{NaOH}}^{\Phi}] + \\ & (m/\alpha_k) \beta_{\text{NaAl(OH)}_4}^{(0)} + (m/\alpha_k) \exp(-\alpha_1 m^{1/2}) \beta_{\text{NaAl(OH)}_4}^{(1)} \\ & + (m/\alpha_k) \exp(-\alpha_2 m^{1/2}) \beta_{\text{NaAl(OH)}_4}^{(2)} + \\ & (m^2/\alpha_k) C_{\text{NaAl(OH)}_4} + (1 - 1/\alpha_k)(1/\alpha_k) m \theta_{\text{OH-Al(OH)}_4^-} \\ & + (1 - 1/\alpha_k)(1/\alpha_k) m^2 \Psi_{\text{Na}^+\text{OH-Al(OH)}_4^-} \quad (4) \end{aligned}$$

where $m = m_{\text{NaOHT}} = m_{\text{NaOH}} + m_{\text{NaAl(OH)}_4}$; $\alpha_K = m_{\text{NaOHT}}/m_{\text{NaAl(OH)}_4}$; A_{Φ} is Debye-Hückel limiting-law slope equal to $0.4023 \text{ (kg mol}^{-1}\text{)}^{1/2}$ at 313.15 K (Pitzer, 1991); b is a universal parameter generally considered to be $1.2 \text{ (kg mol}^{-1}\text{)}^{1/2}$ (Pitzer, 1991); α_1 and α_2 are also universal parameters usually taken as $2.0 \text{ (kg mol}^{-1}\text{)}^{1/2}$ and $8.0 \text{ (kg mol}^{-1}\text{)}^{1/2}$, respectively, and these values were also previously used by Simonson et al. (1989) for sodium hydroxide solutions. $(\beta_{\text{NaOH}}^{(0)}, \beta_{\text{NaOH}}^{(1)}, \beta_{\text{NaOH}}^{(2)}, C_{\text{NaOH}}^{\Phi})$ and $(\beta_{\text{NaAl(OH)}_4}^{(0)}, \beta_{\text{NaAl(OH)}_4}^{(1)}, \beta_{\text{NaAl(OH)}_4}^{(2)}, C_{\text{NaAl(OH)}_4}^{\Phi})$ are the Pitzer model parameters for NaOH and NaAl(OH)₄, respectively. $\theta_{\text{OH-Al(OH)}_4^-}$ and $\Psi_{\text{Na}^+\text{OH-Al(OH)}_4^-}$ are the Pitzer model mixing parameters. For symmetrical mixed solutes, the Pitzer model mixing terms ${}^e\theta(\text{I})$, ${}^e\theta'(\text{I})$ are taken to be zero (Pitzer, 1991); therefore, they do not appear in Eqn. 4. After two sets of the values of $(\beta_{\text{NaOH}}^{(0)}, \beta_{\text{NaOH}}^{(1)}, \beta_{\text{NaOH}}^{(2)}, C_{\text{NaOH}}^{\Phi})$ were calculated from the equations and the parameters given by Simonson et al. (1989) and Pabalan and Pitzer

Table 4. The osmotic coefficients for the NaOH-NaAl(OH)₄-H₂O system and the comparison between the measured osmotic coefficients and the calculated osmotic coefficients at 313.2 K and 0.1 MPa.

Experiment	$m_{\text{NaOHT}}^{\text{a}}$ (mol/kg H ₂ O)	α_K^{b}	Φ_{meas}	$\Phi_{\text{cal},1}^{\text{c}}$	δ_1^{d}	$\Phi_{\text{cal},3}^{\text{e}}$
4	9.7215 ± 91	3.2500 ± 28	1.5487 ± 46	1.5406	0.0081	1.5577
5	6.4286 ± 58	3.2500 ± 28	1.3079 ± 37	1.2991	0.0088	1.2887
6	4.6166 ± 40	3.2500 ± 28	1.1721 ± 13	1.1671	0.0051	1.1531
7	3.1680 ± 27	3.2500 ± 28	1.0591 ± 15	1.0654	-0.0063	1.0548
8	1.5053 ± 13	3.2500 ± 28	0.9665 ± 14	0.9609	0.0056	0.9608
9	1.01702 ± 88	3.2500 ± 28	0.9434 ± 10	0.9360	0.0074	0.9396
10	0.50388 ± 43	3.2500 ± 28	0.9230 ± 10	0.9175	0.0055	0.9239
11	0.26342 ± 23	3.2500 ± 28	0.9209 ± 10	0.9167	0.0042	0.9227
12	0.105245 ± 91	3.2500 ± 28	0.9266 ± 13	0.9277	-0.0011	0.9316
13	0.052547 ± 45	3.2500 ± 28	0.9381 ± 34	0.9398	-0.0016	0.9423
14	11.755 ± 14	2.1951 ± 23	1.4750 ± 82	1.4876	-0.0126	1.5473
15	8.5922 ± 101	2.1951 ± 23	1.3282 ± 53	1.3397	-0.0116	1.3520
16	5.9247 ± 67	2.1951 ± 23	1.1935 ± 35	1.1956	-0.0021	1.1884
17	3.9204 ± 43	2.1951 ± 23	1.0776 ± 17	1.0797	-0.0021	1.0712
18	2.5622 ± 29	2.1951 ± 23	0.9995 ± 19	1.0016	-0.0021	0.9991
19	1.4663 ± 16	2.1951 ± 23	0.9452 ± 18	0.9440	0.0012	0.9499
20	0.9988 ± 11	2.1951 ± 23	0.9267 ± 17	0.9236	0.0031	0.9332
21	0.46922 ± 54	2.1951 ± 23	0.9077 ± 23	0.9093	-0.0016	0.9209
22	0.23753 ± 25	2.1951 ± 23	0.9084 ± 22	0.9123	-0.0039	0.9220
23	0.098104 ± 111	2.1951 ± 23	0.9188 ± 34	0.9261	-0.0073	0.9322
24	10.337 ± 12	1.6481 ± 18	1.2806 ± 46	1.2784	0.0022	1.3228
25	0.45190 ± 49	1.6481 ± 18	0.9021 ± 20	0.9000	0.0021	0.9180
26	0.23919 ± 26	1.6481 ± 18	0.9015 ± 101	0.9062	-0.0047	0.9206
27	0.095199 ± 106	1.6481 ± 18	0.9164 ± 29	0.9236	-0.0072	0.9321
28	0.047406 ± 55	1.6481 ± 18	0.9251 ± 14	0.9383	-0.0132	0.9434
29	0.97152 ± 106	1.6481 ± 18	0.9097 ± 17	0.9077	0.0020	0.9263
30	7.5502 ± 83	1.6481 ± 18	1.1939 ± 44	1.1888	0.0051	1.2033
31	2.5533 ± 28	1.6481 ± 18	0.9627 ± 30	0.9712	-0.0084	0.9797
32	1.4931 ± 16	1.6481 ± 18	0.9207 ± 40	0.9256	-0.0048	0.9410
33	9.4308 ± 85	5.5236 ± 45	1.6346 ± 75	1.6467	-0.0121	1.6539
34	7.2377 ± 62	5.5236 ± 45	1.4397 ± 50	1.4364	0.0033	1.4298
35	5.5417 ± 48	5.5236 ± 45	1.2790 ± 23	1.2825	-0.0035	1.2709
36	4.0179 ± 34	5.5236 ± 45	1.1414 ± 33	1.1529	-0.0115	1.1414
37	2.5116 ± 22	5.5236 ± 45	1.0189 ± 45	1.0370	-0.0180	1.0298
38	1.4574 ± 13	5.5236 ± 45	0.9512 ± 36	0.9676	-0.0164	0.9658
39	0.96454 ± 84	5.5236 ± 45	0.9253 ± 16	0.9410	-0.0157	0.9420
40	0.46274 ± 41	5.5236 ± 45	0.9102 ± 15	0.9220	-0.0118	0.9251
41	0.23858 ± 21	5.5236 ± 45	0.9008 ± 16	0.9210	-0.0202	0.9241
42	0.096064 ± 83	5.5236 ± 45	0.9175 ± 14	0.9312	-0.0137	0.9333

^a m_{NaOHT} is the molality of total alkali, i.e., $m_{\text{NaOHT}} = m_{\text{NaOH}} + m_{\text{NaAl(OH)}_4}$.

^b $\alpha_K = m_{\text{NaOHT}}/m_{\text{NaAl(OH)}_4}$.

^c $\Phi_{\text{cal},1}$ is calculated with set 1 of Pitzer parameters in Table 5.

^d $\delta_1 = \Phi_{\text{meas}} - \Phi_{\text{cal},1}$.

^e $\Phi_{\text{cal},3}$ is calculated with Pitzer parameters generated from Wesolowski's (1992, 2002) equations coupled with NaOH equations of Simonson et al. (1989).

(1987, 1991), the Φ_{meas} values in Table 4 were regressed according to Eqn. 4 by the least-squares linear method with the standard deviations of Φ_{meas} as the weights. In the regression analysis, $\beta^{(2)}_{\text{NaAl(OH)}_4}$ was taken to be zero. The regression analysis readily gave the Pitzer model parameters for NaAl(OH)₄ and the mixing parameters. These parameters are given in Table 5.

Table 4 illustrates the comparison between the measured osmotic coefficients Φ_{meas} and the osmotic coefficients Φ_{cal} calculated with set 1 of Pitzer model parameters in Table 5. From Table 4, the mean standard difference between Φ_{meas} and Φ_{cal} was calculated to be 0.0088. It is obviously larger than the mean standard deviation of the measured osmotic coefficients that is 0.0038. The situation is similar when set 2 of Pitzer model parameters in Table 5 is used. We have also regressed the experimental data with consideration of $\beta^{(2)}_{\text{NaAl(OH)}_4}$, and

the value of the mean standard difference was still ~ 0.0087 . Generally speaking, the differences, δ , are usually < 0.01 . This is adequate for most applications. More important, the fit of the Pitzer model to our experimental data at 313.2 K extends to almost $> m_{\text{NaOHT}} = 10$ mol/kg H₂O, so it would appear that, not only our experimental data are fully consistent with the current thermodynamic model, but also the current thermodynamic model is valid over broader ranges of NaOH-NaAl(OH)₄-H₂O system than expected. In addition, it is reasonable to suppose that the Pitzer model could be applied to the sodium aluminate solution at other temperatures. That is very beneficial to the study on the sodium aluminate solution at other temperatures, since the Pitzer model parameters could be obtained by various methods.

Wesolowski (1992, 2002) had proposed a set of equations to calculate the Pitzer parameters for NaAl(OH)₄(aq) at various

Table 5. The Pitzer model parameters for NaOH-NaAl(OH)₄-H₂O system at 313.2 K and 0.1 MPa.

Set	1			2			3 ^a
	NaOH ^b	NaAl(OH) ₄	δ ^c	NaOH ^d	NaAl(OH) ₄	δ ^c	NaAl(OH) ₄
β ⁽⁰⁾	0.08669	0.03507	0.05162	0.09257	0.03959	0.05298	0.05109
β ⁽¹⁾	0.31446	0.02401	0.29045	0.28339	0.07036	0.21303	0.31446
β ⁽²⁾	-7.367 · 10 ⁻⁵	0 ^e	/	0	0 ^e	/	0
C ^Φ	0.003180	-0.001066	0.004246	0.002636	-0.001268	0.003904	-0.002080
θ _{OH⁻Al(OH)₄⁻}	0.08177			0.05848			0.014
Ψ _{Na⁺OH⁻Al(OH)₄⁻}	-0.01162			-0.009934			-0.0048

^a Generated from Wesolowski's (1992, 2002) equations coupled with the equations given by Simonson et al. (1989).

^b The Pitzer model parameters for NaOH are calculated from the equations and parameters given by Simonson et al. (1989).

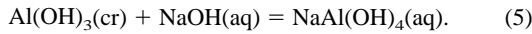
^c δ = parameter (NaOH)-parameter (NaAl(OH)₄).

^d The Pitzer model parameters for NaOH are calculated from the equations and parameters given by Pabalan and Pitzer (1987, 1991).

^e β⁽²⁾_{NaAl(OH)₄} is taken to be zero in the regression analysis.

temperatures, as well as the mixing parameters for Al(OH)₄⁻ with OH⁻ and OH⁻ + Na⁺. Those equations were obtained by modeling his own experimental data of gibbsite solubilities and those of Russell et al. (1955). We can then generate a set of Pitzer model parameters for NaAl(OH)₄ at 313.2 K and 0.1 MPa from Wesolowski's (1992, 2002) equations, coupled with the equations given by Simonson et al. (1989). This set of Pitzer model parameters is also given in Table 5. The comparison between our Pitzer model parameters (set 1 in Table 5) and those derived from Wesolowski (1992, 2002) (set 3 in Table 5) shows that there is actually a reasonable agreement between the two sets of values of β⁽⁰⁾_{NaAl(OH)₄} and C^Φ_{NaAl(OH)₄}, although the value of β⁽¹⁾_{NaAl(OH)₄} and the mixing parameters from two studies are fairly different. Table 4 also includes the comparison between the measured osmotic coefficients and the osmotic coefficients calculated with set 3 Pitzer parameters. The mean standard difference is 0.0187. In fact, this magnitude of difference should be acceptable as the sodium aluminate solution is quite complicate.

After the Pitzer model parameters for NaOH-NaAl(OH)₄-H₂O are obtained, the gibbsite solubilities in sodium hydroxide solutions can be discussed. The dissolving reaction between gibbsite and sodium hydroxide solutions can be expressed as follows:



The equilibrium constant K is

$$K = \frac{a_{\text{NaAl(OH)}_4, \text{equ}}^2}{\alpha_{\text{NaOH, equ}}^2} = \frac{\gamma_{\text{NaAl(OH)}_4}^2 m_{\text{Na}^+, \text{equ}} m_{\text{Al(OH)}_4^-, \text{equ}}}{\gamma_{\text{NaOH}}^2 m_{\text{Na}^+, \text{equ}} m_{\text{OH}^-, \text{equ}}} = \frac{\gamma_{\text{NaAl(OH)}_4}^2 (1/\alpha_{K, \text{equ}})}{\gamma_{\text{NaOH}}^2 (1-1/\alpha_{K, \text{equ}})}. \quad (6)$$

According to the Pitzer equation, there is

$$\begin{aligned} \ln \gamma_{\text{NaAl(OH)}_4, \text{cal}} - \ln \gamma_{\text{NaOH, cal}} &= m(\beta_{\text{NaAl(OH)}_4}^{(0)} - \beta_{\text{NaOH}}^{(0)}) + \\ & m \frac{2[1 - (1 + \alpha_1 m^{1/2}) \exp(-\alpha_1 m^{1/2})]}{(\alpha_1 m^{1/2})^2} (\beta_{\text{NaAl(OH)}_4}^{(1)} - \beta_{\text{NaOH}}^{(1)}) + \\ & m \frac{2[1 - (1 + \alpha_2 m^{1/2}) \exp(-\alpha_2 m^{1/2})]}{(\alpha_2 m^{1/2})^2} (\beta_{\text{NaAl(OH)}_4}^{(2)} - \beta_{\text{NaOH}}^{(2)}) + \\ & (m^2/2)(C_{\text{NaAl(OH)}_4}^{\Phi} - C_{\text{NaOH}}^{\Phi}) - \Phi[m(1/\alpha_K) - m(1-1/\alpha_K)] - \\ & (\Psi/2)[m^2(1/\alpha_K) - m^2(1-1/\alpha_K)], \quad (7) \end{aligned}$$

where the symbols are similar to those in Eqn. 4. We can then use the solubility data of gibbsite in hydroxide solution and Eqn. 6 and 7 to calculate the equilibrium constant. However, due to deviations in the experimental solubility data and the calculated activity coefficients from the true values, the "calculated equilibrium constant" from solubility data will not be exactly equal to the true equilibrium constant. So we represent these calculated values by K' . The K' is defined by Eqn. 8 as

$$K' = \frac{\gamma_{\text{NaAl(OH)}_4, \text{cal}}^2 m_{\text{Al(OH)}_4^-, \text{exp}}}{\gamma_{\text{NaOH, cal}}^2 m_{\text{OH}^-, \text{exp}}} = \frac{\gamma_{\text{NaAl(OH)}_4, \text{cal}}^2 (1/\alpha_{K, \text{exp}})}{\gamma_{\text{NaOH, cal}}^2 (1-1/\alpha_{K, \text{exp}})} \quad (8)$$

For the solubility data of gibbsite in sodium hydroxide solutions at 313.15 K given by Russell et al. (1955) and Ikkatai and Okada (1963) the values of K' are calculated and given in Tables 6 and 7.

From Table 6 it can be seen that there is a generally good consistency among the values of K'_1 calculated from the different molalities of the solubility experiments. However, numbers (1, 2, and 9) are somewhat smaller than the others. The regularity of K'_3 is similar. The same phenomena also occurred in the analysis of these solubility data performed by Wesolowski (1992, 2002) and Pokrovskii and Helgeson (1995). As pointed out by Wesolowski (1992, 2002) and Atravovskiy (1970), it might be due to the lack of complete equilibration in some experiments of Russell et al. (1955), especially at low ionic strengths. Therefore the mean value of K' in Table 6 does not include the numbers (1, 2, and 9). In fact, the mean value of K'_1 , 0.1074 ± 23 , is in the range of the equilibrium constants given by different references: 0.097 (Russell et al., 1955), ~ 0.091 (calculated from the tabulated values given by Apps and Neil, 1990, with an interpolation method; the error of the calculation is estimated to be $\sim 1-2\%$), 0.114 (Wesolowski, 1992, 2002), 0.119 (Verdes et al., 1992). Most of these investigators have also used the solubility data of Russell et al. (1955) in their analyses; therefore, our mean value of K'_1 should be reasonable. Since our Pitzer model parameters are used in the calculation of K'_1 , the good consistency among the values of K'_1 from the different molalities of the solubility experiments and the mean value of K'_1 in the range of the various reference equilibrium constants indicate that our Pitzer model parameters are reliable. The standard variance of the mean value of K'_1 is 0.0023, and the relative error is 2.1%. It may imply that the relative error of the calculated activity

Table 6. The values of K' for the solubility data at 313.2 K of Russell et al. (1955).

Number	$m_{\text{NaOHT,exp}}^{\text{a}}$ (mol/kg H ₂ O)	$\alpha_{K,\text{exp}}^{\text{a,b}}$	$K'_1{}^{\text{c,d}}$	$\log K'_1{}^{\text{c,d}}$	$K'_3{}^{\text{c,e}}$	$\log K'_3{}^{\text{c,e}}$
1	0.5016	10.35	0.09592	1.0181	0.1042	0.9822
2	1.250	10.55	0.08797	1.0557	0.09720	1.0123
3	2.295	8.225	0.1072	0.9698	0.1177	0.9290
4	2.565	7.909	0.1097	0.9598	0.1200	0.9207
5	3.057	7.687	0.1090	0.9628	0.1180	0.9280
6	4.092	7.060	0.1086	0.9641	0.1157	0.9366
7	5.068	6.451	0.1070	0.9706	0.1132	0.9463
8	7.888	4.399	0.1027	0.9886	0.1159	0.9358
9	10.75	3.092	0.08387	1.0764	0.1108	0.9556
Mean	/	/	$0.1074 \pm 23^{\text{f}}$	$0.9693 \pm 94^{\text{f}}$	$0.1168 \pm 22^{\text{f}}$	$0.9328 \pm 81^{\text{f}}$

^a Calculated from the values of Na₂O (g/dm³), density, and Al₂O₃/Na₂O (g/g) given in the reference (Russell et al., 1955).

^b $\alpha_{K,\text{exp}} = m_{\text{NaOHT,exp}}/m_{\text{NaAl(OH)}_4,\text{exp}}$.

^c K' is defined by Eqn. 8.

^d Calculated with our Pitzer model parameters (the set 1 in Table 5).

^e Calculated with the Pitzer model parameters derived from Wesolowski (1992, 2002) (the set 3 in Table 5).

^f The calculation of the mean value of K' does not include the numbers (1, 2, and 9) value (see text).

coefficients of NaAl(OH)₄ and NaOH with our Pitzer model parameters may be < 2.1%.

In Table 7 there is also a generally good consistency among the values of K' calculated from the different molalities. However, the mean values of K' in Table 7 are obviously greater than those in Table 6. The same phenomenon occurred in the treatments of these solubility data performed by Wesolowski (1992, 2002) and Pokrovskii and Helgeson (1995). Wesolowski (1992, 2002) calculated the values of $\log(m_{\text{OH}^-}/m_{\text{Al(OH)}_4^-})$ with the parameters obtained by regressing the solubility data from his own experiments and those of Russell et al. (1955). The comparisons between the calculated values of $\log(m_{\text{OH}^-}/m_{\text{Al(OH)}_4^-})$ and the experimental values of Russell et al. (1955) and Ikkatai and Okada (1963), respectively, showed that the calculated values agreed well with most of the values of Russell et al. (1955); however, the values of Ikkatai and Okada (1963) were obviously smaller than the calculated values. Pokrovskii

and Helgeson (1995) modeled all of the previous experimental work with HKF model, and calculated out $\log(Q \cdot a_w^2)$, which is equivalent to $\log K'$ in our paper. The results showed that the values $\log(Q \cdot a_w^2)$ of Russell et al. (1955) were greater than those of Ikkatai and Okada (1963). Therefore, there is indeed some kind of difference between those two sets of solubility data.

From Tables 6 and 7, we could see that there are some differences between the values of K' calculated by us and those derived from Wesolowski (1992, 2002). However, the differences are generally within 0.05 log units. Pokrovskii and Helgeson (1995) have reported that the predicted solubilities of gibbsite in concentrated NaCl + NaOH solution in their analysis were within ± 0.05 log units. So we consider that the difference of 0.05 log units in our analysis would be acceptable.

When the Pitzer model parameters for NaOH-NaAl(OH)₄-H₂O system and the equilibrium constant for the dissolving

Table 7. The values of K' for the solubility data at 313.2 K of Ikkatai and Okada (1963).

Number	$m_{\text{NaOHT,exp}}^{\text{a}}$ (mol/kg H ₂ O)	$\alpha_{K,\text{exp}}^{\text{a,b}}$	$K'_1{}^{\text{c,d}}$	$-\log K'_1{}^{\text{c,d}}$	$K'_3{}^{\text{c,e}}$	$-\log K'_3{}^{\text{c,e}}$
1 ^f	1.271	7.12	$0.1279 \pm 68^{\text{h}}$	0.893	$0.1431 \pm 78^{\text{h}}$	0.8444
2 ^g	1.260	7.84				
3 ^f	2.564	7.1	$0.1317 \pm 87^{\text{h}}$	0.880	$0.1463 \pm 105^{\text{h}}$	0.8348
4 ^g	2.559	6.28				
5 ^f	3.993	6.26	$0.1314 \pm 72^{\text{h}}$	0.881	$0.1436 \pm 89^{\text{h}}$	0.8428
6 ^g	3.924	5.68				
7 ^f	5.439	5.24	$0.1366 \pm 103^{\text{h}}$	0.865	$0.1515 \pm 135^{\text{h}}$	0.8196
8 ^g	5.284	4.62				
Mean	/	/	$0.1319 \pm 89^{\text{i}}$	0.8798	$0.1461 \pm 109^{\text{i}}$	0.8354

^a Calculated from the values of Na₂O (g/L), density, and Al₂O₃/Na₂O (mol/mol) given in the reference (Ikkatai and Okada, 1963).

^b $\alpha_{K,\text{exp}} = m_{\text{NaOHT,exp}}/m_{\text{NaAl(OH)}_4,\text{exp}}$.

^c K' is defined by Eqn. 8.

^d Calculated with our Pitzer model parameters (the set 1 in Table 5).

^e Calculated with the Pitzer model parameters derived from Wesolowski (1992, 2002) (the set 3 in Table 5).

^f Measured by dissolution.

^g Measured by crystallization.

^h The average value of K' is calculated from the corresponding experimental data of (f) and (g), respectively, and the deviation is calculated from the greater and smaller values.

ⁱ The deviation is calculated from variation of all K' and their individual deviations.

reaction (Eqn. 5) are known, gibbsite solubilities can be calculated by solving Eqn. 6 and 7 with the help of computer. The compare of the calculated gibbsite solubilities over a range of $m_{\text{NaOHT}} = m_{\text{NaOH}} + m_{\text{NaAl(OH)}_4}$ between our activity coefficients model and that derived from Wesolowski (1992, 2002) at 313.2 K is then obtained. In addition, though our Pitzer model parameters for NaOH-NaAl(OH)₄-H₂O system are at 313.2 K, which is an industrially important but very specific temperature, we are able to estimate the NaAl(OH)₄(aq) Pitzer model parameters at other temperatures basing on our results. As pointed out by Wesolowski (1992, 2002), the OH⁻/Al(OH)₄⁻ activity coefficient ratio for the isocoulombic reaction (Eqn. 5) is nearly independent of the temperature in the 273.15 to 373.15 K range, namely, these values, $\beta_{\text{NaOH}}^{(0)}\beta_{\text{NaAl(OH)}_4}^{(0)}$, $\beta_{\text{NaOH}}^{(1)}\beta_{\text{NaAl(OH)}_4}^{(1)}$, $\beta_{\text{NaOH}}^{(2)}\beta_{\text{NaAl(OH)}_4}^{(2)}$, $C_{\text{NaOH}}^{\Phi}C_{\text{NaAl(OH)}_4}^{\Phi}$, would be nearly unchangeable at least in the 273.15 to 373.15 K range. Therefore, we could approximately calculate the NaAl(OH)₄(aq) Pitzer model parameters at other temperatures by using our difference quantities (δ) in Table 5, coupled with the NaOH Pitzer model parameters. The mixing parameters could be taken as those at 313.2 K. Therefore, we can then carry out the comparison at other temperatures between our activity coefficients model and that derived from Wesolowski (1992, 2002), as well as the activity coefficients model of Park and Englezos (1999), to see what range of temperature our activity coefficients model is able to apply to. All these comparisons are given in Table 8 and Figure 1.

From Table 8 and Figure 1, it can be found that the values of $m_{\text{NaAl(OH)}_4}(\text{III})$ are systematically larger than those of $m_{\text{NaAl(OH)}_4}(\text{I})$, and the differences between the two sets of values increase with increasing m_{NaOHT} and temperature. However, the agreement between the two sets of values is within 10% when the molality extends to 6 mol/kg H₂O at 323.2 K. Even when m_{NaOHT} extends to 8 mol/kg H₂O, the agreement is within 20%. The values of $m_{\text{NaAl(OH)}_4}(\text{II})$ are systematically smaller than those of $m_{\text{NaAl(OH)}_4}(\text{I})$ from 298.2 to 323.2 K. However, when the temperature reaches 333.2 K or the higher, $m_{\text{NaAl(OH)}_4}(\text{II})$ turns to larger than $m_{\text{NaAl(OH)}_4}(\text{I})$. At 298.2 K, $m_{\text{NaAl(OH)}_4}(\text{III})$ agrees well with $m_{\text{NaAl(OH)}_4}(\text{I})$, and the values of $m_{\text{NaAl(OH)}_4}(\text{III})$ are between those of $m_{\text{NaAl(OH)}_4}(\text{I})$ and $m_{\text{NaAl(OH)}_4}(\text{IV})$. Therefore, we estimate that our activity coefficients model may be effective from 298.2 K or lower temperatures to 323.2 K.

3.3. Stoichiometric Activity Coefficients of NaOH and NaAl(OH)₄ and the Activity of H₂O

According to the equation given by Pitzer (1991), the following equations for NaOH-NaAl(OH)₄-H₂O system are derived:

$$\begin{aligned} \ln \gamma_{\text{NaOH, cal}} = & -A_{\Phi} [m^{1/2}/(1 + bm^{1/2}) + (2/b)\ln(1 + bm^{1/2})] \\ & + m \left\{ \beta_{\text{NaOH}}^{(0)} + \beta_{\text{NaOH}}^{(1)} \frac{2[1 - (1 + \alpha_1 m^{1/2})\exp(-\alpha_1 m^{1/2})]}{(\alpha_1 m^{1/2})^2} \right. \\ & \left. + \beta_{\text{NaOH}}^{(2)} \frac{2[1 - (1 + \alpha_2 m^{1/2})\exp(-\alpha_2 m^{1/2})]}{(\alpha_2 m^{1/2})^2} \right\} \end{aligned}$$

$$\begin{aligned} & + (1 - 1/\alpha_K)[\beta_{\text{NaOH}}^{(0)} + \beta_{\text{NaOH}}^{(1)} \exp(-\alpha_1 m^{1/2}) \\ & \quad + \beta_{\text{NaOH}}^{(2)} \exp(-\alpha_2 m^{1/2})] \\ & + (1/\alpha_K)[\beta_{\text{NaAl(OH)}_4}^{(0)} + \beta_{\text{NaAl(OH)}_4}^{(1)} \exp(-\alpha_1 m^{1/2}) \\ & \quad + \beta_{\text{NaAl(OH)}_4}^{(2)} \exp(-\alpha_2 m^{1/2})] \\ & + m[(1/2 + 1 - 1/\alpha_K)C_{\text{NaOH}}^{\Phi} + (1/\alpha_K)C_{\text{NaAl(OH)}_4}^{\Phi}] \\ & + (1/\alpha_K)[\Phi_{\text{OH-Al(OH)}_4} + (1 - (1/\alpha_K)/2)m\Psi_{\text{Na}^+\text{OH-Al(OH)}_4}] \end{aligned} \quad (9)$$

$$\begin{aligned} \ln \gamma_{\text{NaAl(OH)}_4, \text{cal}} = & -A_{\Phi} [m^{1/2}/(1 + bm^{1/2}) + (2/b)\ln(1 + bm^{1/2})] \\ & + m \left\{ \beta_{\text{NaAl(OH)}_4}^{(0)} + \beta_{\text{NaAl(OH)}_4}^{(1)} \right. \\ & \quad \frac{2[1 - (1 + \alpha_1 m^{1/2})\exp(-\alpha_1 m^{1/2})]}{(\alpha_1 m^{1/2})^2} \\ & \quad + \beta_{\text{NaAl(OH)}_4}^{(2)} \frac{2[1 - (1 + \alpha_2 m^{1/2})\exp(-\alpha_2 m^{1/2})]}{(\alpha_2 m^{1/2})^2} \\ & \quad + (1 - 1/\alpha_K)[\beta_{\text{NaOH}}^{(0)} + \beta_{\text{NaOH}}^{(1)} \exp(-\alpha_1 m^{1/2}) \\ & \quad \quad + \beta_{\text{NaOH}}^{(2)} \exp(-\alpha_2 m^{1/2})] \\ & \quad + (1/\alpha_K)[\beta_{\text{NaAl(OH)}_4}^{(0)} + \beta_{\text{NaAl(OH)}_4}^{(1)} \exp(-\alpha_1 m^{1/2}) \\ & \quad \quad + \beta_{\text{NaAl(OH)}_4}^{(2)} \exp(-\alpha_2 m^{1/2})] \\ & \quad + m[(1/2 + 1/\alpha_K)C_{\text{NaAl(OH)}_4}^{\Phi} + (1 - 1/\alpha_K)C_{\text{NaOH}}^{\Phi}] \\ & \quad + (1 - 1/\alpha_K)[\Phi_{\text{OH-Al(OH)}_4} \\ & \quad \quad + (1 - (1 - 1/\alpha_K)/2)m\Psi_{\text{Na}^+\text{OH-Al(OH)}_4}] \end{aligned} \quad (10)$$

where the symbols are similar to those in Eqn. 4. The relation between Φ and the activity of water a_w for NaOH-NaAl(OH)₄-H₂O is

$$\Phi = -\frac{m_w \ln a_w}{2m_{\text{NaOHT}}} \quad (11)$$

where m_w is equal to 55.508 mol/kg H₂O. Using set 1 of Pitzer model parameters in Table 5 and Equations 4, 9, 10, and 11, we calculated the stoichiometric osmotic and activity coefficients for the NaOH-NaAl(OH)₄-H₂O system. The relative errors of the calculated stoichiometric activity coefficients of NaOH and NaAl(OH)₄ are expected to be < 2.1%. The results are given in Table 9 and Figure 2.

From Table 9 and Figure 2 the following conclusions can be obtained

1. With the decreasing value of α_K , namely the increase in the NaAl(OH)₄ content in the total alkali m_{NaOHT} , the activity of water a_w at constant m_{NaOHT} increases. It implies that the attractive interaction between Al(OH)₄⁻ and H₂O may be weaker than that between OH⁻ and H₂O.
2. Initially the stoichiometric activity coefficients of NaOH, r_{NaOH} , decrease steeply with the increasing molality of the total alkali m_{NaOHT} . When m_{NaOHT} is > 1 mol/kg H₂O, γ_{NaOH} turns to increase with m_{NaOHT} up to high concentrations. The value of r_{NaOH} at the higher α_K is greater than the corresponding r_{NaOH} value at the lower α_K , and the extent of the increase in γ_{NaOH} in concentrated solutions is more

Table 8. The comparison of the calculated gibbsite solubility data between several activity coefficients models over a range of the molality of the total alkali and at various temperatures.

T (K)	m_{NaOHT}^a	$m_{\text{NaAl(OH)}_4(\text{exp})}^b$	$m_{\text{NaAl(OH)}_4(\text{I})}^c$	$m_{\text{NaAl(OH)}_4(\text{II})}^d$	$m_{\text{NaAl(OH)}_4(\text{III})}^e$	$m_{\text{NaAl(OH)}_4(\text{IV})}^f$
298.2	0.1		0.006742	0.005197	0.006934	0.007243
298.2	0.5		0.03438	0.02772	0.03702	0.04681
298.2	0.5142	0.03533	0.03538	0.02855	0.03813	0.04855
298.2	1		0.07075	0.05774	0.07725	0.1232
298.2	1.019	0.0725	0.07217	0.05891	0.07882	0.1267
298.2	2		0.1518	0.1217	0.1636	0.3808
298.2	3.045	0.2490	0.2532	0.1966	0.2652	0.7929
298.2	4		0.3673	0.2774	0.3754	1.263
298.2	6		0.7079	0.5209	0.7077	2.398
298.2	8		1.269	0.9664	1.310	3.617
298.2	10		2.174	1.833	2.440	4.855
313.2	0.1		0.01024	0.01002	0.01053	
313.2	0.5016	0.04848	0.05237	0.05374	0.05649	
313.2	1.250	0.1185	0.1363	0.1426	0.1500	
313.2	2.295	0.2790	0.2701	0.2795	0.2944	
313.2	2.565	0.3243	0.3086	0.3179	0.3349	
313.2	3.057	0.3976	0.3842	0.3923	0.4134	
313.2	4.092	0.5796	0.5700	0.5733	0.6048	
313.2	5.068	0.7856	0.7876	0.7885	0.8323	
313.2	7.888	1.793	1.765	1.873	1.974	
313.2	10.75	3.475	3.527	4.228	4.407	
313.2	6		1.045	1.054	1.112	
313.2	10		2.979	3.469	3.631	
323.2	0.1		0.01336	0.01181	0.01374	
323.2	0.5022	0.06655	0.06844	0.06349	0.07391	
323.2	0.5143	0.06941	0.07013	0.06511	0.07580	
323.2	1.019	0.1426	0.1429	0.1353	0.1577	
323.2	1.2706	0.1715	0.1810	0.1718	0.2005	
323.2	3.045	0.4976	0.4963	0.4649	0.5464	
323.2	6		1.331	1.262	1.490	
323.2	8		2.260	2.304	2.695	
323.2	10		3.590	4.023	4.573	
333.2	0.1		0.01723	0.01589	0.01770	
333.2	0.5036	0.08601	0.08845	0.08581	0.09562	
333.2	1.2572	0.2224	0.2304	0.2302	0.2570	
333.2	2.3178	0.4762	0.4565	0.4591	0.5144	
333.2	2.6109	0.5491	0.5259	0.5288	0.5931	
333.2	3.0831	0.6728	0.6453	0.6490	0.7288	
333.2	4.0994	0.9843	0.9393	0.9492	1.0681	
333.2	6		1.666	1.748	1.966	
333.2	8		2.757	3.121	3.465	
333.2	10		4.240	5.130	5.550	

^a $m_{\text{NaOHT}} = m_{\text{NaOH}} + m_{\text{NaAl(OH)}_4}$.

^b $m_{\text{NaAl(OH)}_4(\text{exp})}$ is the experimental gibbsite solubility data taken from Wesolowski (1992, 2002) and Russell et al. (1955).

^c Calculated with the Pitzer model parameters (set 3 in Table 5) and the equilibrium constant of the dissolving reaction (Eqn. 5) given by Wesolowski (1992, 2002).

^d Calculated with our Pitzer model parameters (set 1 in Table 5) and the equilibrium constant of the dissolving reaction (Eqn. 5) given by Apps and Neil (1990), while for $T = 313.2$ K, the equilibrium constant is taken as 0.1074, from the mean value of K'_1 in Table 6.

^e Calculated with our Pitzer model parameters (set 1 in Table 5) and the equilibrium constant of the dissolving reaction (Eqn. 5) given by Wesolowski (1992, 2002).

^f Calculated with the Pitzer model parameters proposed by Park and Englezos (1999) and the equilibrium constant of the dissolving reaction (Eqn. 5) given by Wesolowski (1992, 2002).

obvious at the higher α_K . These observations imply that the repulsive interaction between OH^- and OH^- may be stronger than that between OH^- and Al(OH)_4^- .

- Initially the stoichiometric activity coefficients of NaAl(OH)_4 , $\gamma_{\text{NaAl(OH)}_4}$, decrease steeply with the increasing molality of the total alkali m_{NaOHT} . At the lower α_K , $\gamma_{\text{NaAl(OH)}_4}$ turns to increase when m_{NaOHT} is ~ 2 to 5 mol/kg H_2O . However, the extent of the increase is small in contrast to that of γ_{NaOH} . With increasing α_K , the molality, at which the minimum occurs, decreases to the lower m_{NaOHT} of ~ 1

to 2.5 mol/kg H_2O . The extent of the increase in $\gamma_{\text{NaAl(OH)}_4}$ in the region of high concentration is also enlarged. The values of $\gamma_{\text{NaAl(OH)}_4}$ at higher α_K are greater than the corresponding values at lower α_K in a similar manner to that of r_{NaOH} . These regularities show that the repulsive interaction between OH^- and Al(OH)_4^- may be greater than that between Al(OH)_4^- and Al(OH)_4^- , from the other point of view, the attractive interaction between OH^- and Al(OH)_4^- may be weaker than that between Al(OH)_4^- and Al(OH)_4^- .

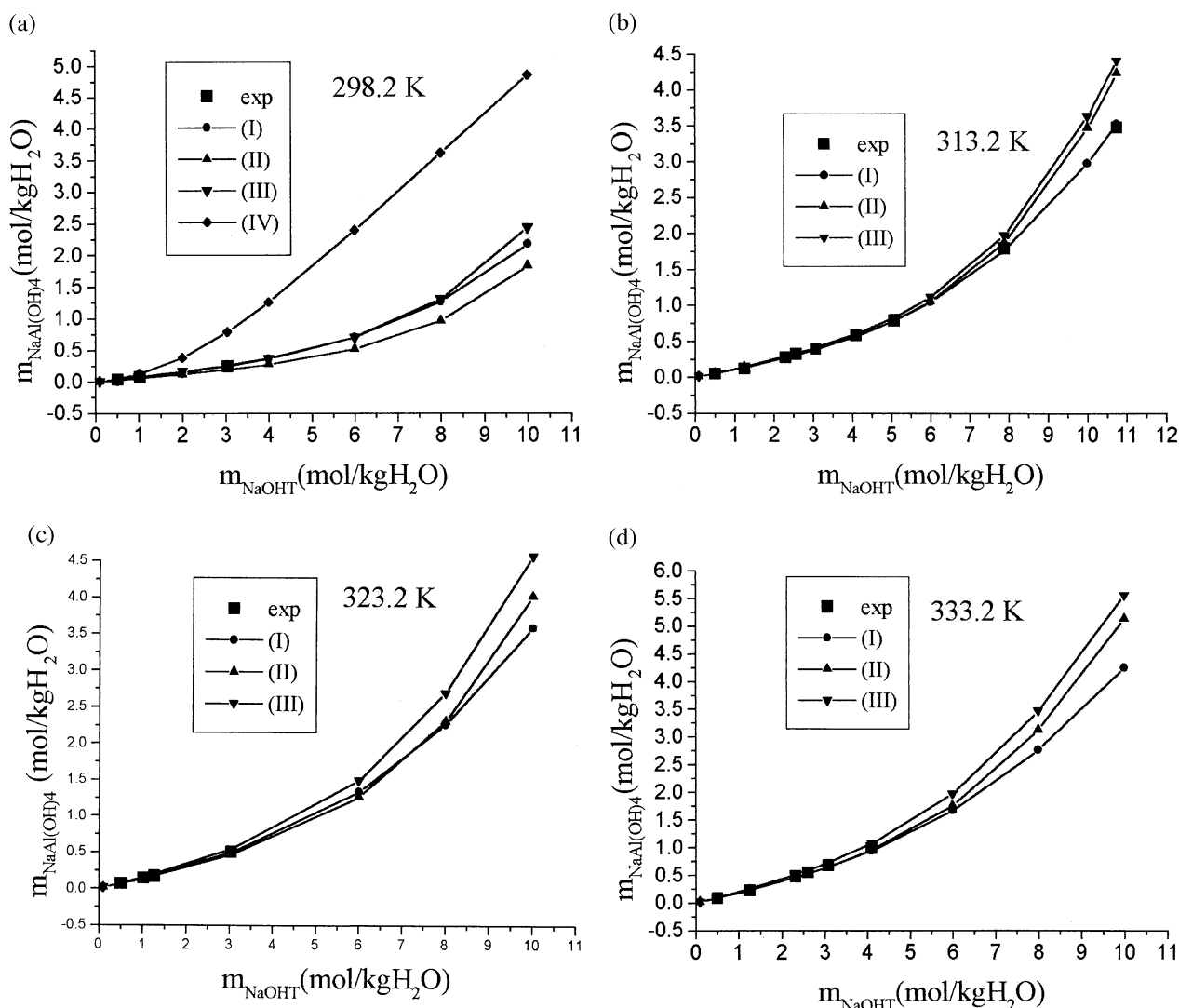


Fig. 1. The comparison of the calculated gibbsite solubility data between several activity coefficients models over a range of the molality of the total alkali and at various temperatures. $m_{\text{NaOH}} = m_{\text{NaOH}} + m_{\text{NaAl(OH)}_4}$. $m_{\text{NaAl(OH)}_4}(\text{exp})$ is the experimental gibbsite solubility data taken from Wesolowski (1992, 2002) and Russell et al. (1955). $m_{\text{NaAl(OH)}_4}(\text{I})$ is calculated with the Pitzer model parameters (set 3 in Table 5) and the equilibrium constant of the dissolving reaction (Eqn. 5) given by Wesolowski (1992, 2002). $m_{\text{NaAl(OH)}_4}(\text{II})$ is calculated with our Pitzer model parameters (set 1 in Table 5) and the equilibrium constant of the dissolving reaction (Eqn. 5) given by Apps and Neil (1990), while for $T = 313.2$ K, the equilibrium constant is taken as 0.1074, from the mean value of K'_1 in Table 6. $m_{\text{NaAl(OH)}_4}(\text{III})$ calculated with our Pitzer model parameters (set 1 in Table 5) and the equilibrium constant of the dissolving reaction (Eqn. 5) given by Wesolowski (1992, 2002). $m_{\text{NaAl(OH)}_4}(\text{IV})$ is calculated with the Pitzer model parameters proposed by Park and Englezos (1999) and the equilibrium constant of the dissolving reaction (Eqn. 5) given by Wesolowski (1992, 2002). (a) 298.2 K; (b) 313.2 K; (c) 323.2 K; (d) 333.2 K.

4. CONCLUSION

1. The osmotic coefficients at 313.2 K were measured for the NaOH-NaAl(OH)₄-H₂O system with the total alkali molality, $m_{\text{NaOH}} (m_{\text{NaOH}} + m_{\text{NaAl(OH)}_4})$, from 0.05 to 12 mol/kg H₂O and $\alpha_K (m_{\text{NaOH}}/m_{\text{NaAl(OH)}_4})$ from 1.64 to 5.53. The measurement covers most range of the composition of the supersaturated sodium aluminate solutions in the production of Al₂O₃. The standard deviations of the measured osmotic coefficients are usually ~ 0.001 to 0.005 , and the mean standard deviation is 0.0038 .

2. The Pitzer model was used to regress the measured osmotic coefficients with two sets of reference Pitzer model parameters for NaOH from different references. One set of the obtained Pitzer model parameters for NaOH-NaAl(OH)₄-H₂O system are in the following: $\beta_{\text{NaOH}}^{(0)}$: 0.08669, $\beta_{\text{NaOH}}^{(1)}$: 0.31446, $\beta_{\text{NaOH}}^{(2)}$: -0.00007367 , C_{NaOH}^{Φ} : 0.003180, $\beta_{\text{NaAl(OH)}_4}^{(0)}$: 0.03507, $\beta_{\text{NaAl(OH)}_4}^{(1)}$: 0.02401, $C_{\text{NaAl(OH)}_4}^{\Phi}$: -0.001066 , $\theta_{\text{OH}^-\text{Al(OH)}_4^-}$: 0.08177, $\Psi_{\text{Na}^+\text{OH}^-\text{Al(OH)}_4^-}$: -0.01162 . The mean standard difference between the calculated osmotic coefficients Φ_{cal} and the

Table 9. The osmotic and activity coefficients for the NaOH-NaAl(OH)₄-H₂O system calculated with set 1 of Pitzer model parameters at 313.2 K and 0.1 MPa in Table 5.

$m_{\text{NaOHT}}(\text{mol/kg H}_2\text{O})^a$	α_K^b	Φ_{cal}	$a_{\text{w,cal}}$	$\gamma_{\text{NaOH,cal}}$	$\gamma_{\text{NaAl(OH)}_4\text{,cal}}$
0.001	1 ^c	0.9878	0.99996	0.964	0.964
0.01	1 ^c	0.9646	0.99965	0.899	0.895
0.1	1 ^c	0.9126	0.99672	0.767	0.742
0.5	1 ^c	0.8663	0.98451	0.672	0.593
1	1 ^c	0.8544	0.96968	0.659	0.531
1.5	1 ^c	0.8538	0.95490	0.671	0.500
2	1 ^c	0.8578	0.94006	0.694	0.482
3	1 ^c	0.8715	0.91010	0.756	0.462
5	1 ^c	0.9058	0.84943	0.919	0.452
7	1 ^c	0.9392	0.78909	1.112	0.455
10	1 ^c	0.9792	0.70270	1.414	0.466
0.001	1.5	0.9879	0.99996	0.964	0.964
0.01	1.5	0.9658	0.99965	0.899	0.896
0.1	1.5	0.9212	0.99669	0.770	0.749
0.5	1.5	0.8955	0.98400	0.677	0.613
1	1.5	0.9017	0.96803	0.663	0.562
1.5	1.5	0.9168	0.95166	0.673	0.539
2	1.5	0.9353	0.93482	0.693	0.529
3	1.5	0.9763	0.89985	0.754	0.524
5	1.5	1.0591	0.82630	0.926	0.542
7	1.5	1.1331	0.75143	1.150	0.570
10	1.5	1.2181	0.64475	1.574	0.608
0.001	3	0.9880	0.99996	0.964	0.964
0.01	3	0.9667	0.99965	0.900	0.897
0.1	3	0.9281	0.99666	0.773	0.757
0.5	3	0.9162	0.98363	0.682	0.634
1	3	0.9334	0.96693	0.667	0.595
1.5	3	0.9583	0.94952	0.676	0.583
2	3	0.9868	0.93136	0.697	0.584
3	3	1.0497	0.89274	0.761	0.602
5	3	1.1861	0.80761	0.962	0.672
7	3	1.3263	0.71569	1.268	0.761
10	3	1.5334	0.57550	1.993	0.902
0.001	5	0.9881	0.99996	0.964	0.964
0.01	5	0.9671	0.99965	0.900	0.898
0.1	5	0.9304	0.99665	0.774	0.760
0.5	5	0.9221	0.98352	0.684	0.643
1	5	0.9418	0.96664	0.669	0.609
1.5	5	0.9689	0.94898	0.678	0.602
2	5	1.0002	0.93046	0.699	0.608
3	5	1.0703	0.89075	0.766	0.638
5	5	1.2295	0.80132	0.986	0.739
7	5	1.4034	0.70191	1.341	0.870
10	5	1.6810	0.54570	2.272	1.095

^a $m_{\text{NaOHT}} = m_{\text{NaOH}} + m_{\text{NaAl(OH)}_4}$.^b $\alpha_K = m_{\text{NaOHT}}/m_{\text{NaAl(OH)}_4}$.^c A pseudo-state which presumes that all solutes are NaAl(OH)₄.

measured osmotic coefficients Φ_{meas} is 0.0088. With the data for the gibbsite solubility in sodium hydroxide solutions and the obtained Pitzer model parameters, we calculated the values of $K'_1 = (\gamma_{\text{NaAl(OH)}_4\text{,cal}}^2 m_{\text{Al(OH)}_4\text{,exp}}) / (\gamma_{\text{NaOH,cal}}^2 m_{\text{OH}^-\text{,exp}})$. The mean value of K'_1 is in the range of the various reference equilibrium constants for the dissolution reaction of gibbsite. The relative standard deviation of the calculated values of K'_1 is only 2.1%, which implies that the relative error of the calculated activity coefficients could be < 2.1%. These results indicate that our Pitzer model parameters are reliable. We also estimated the NaAl(OH)₄(aq) Pitzer model parameters at other temperatures and calculated the gibbsite solubility data with several activity coefficients models over a range of the molality of the total alkali and at various temperatures. The comparison

between these activity coefficients models indicates that our activity coefficients model may be approximately applied to the temperature from 298.2 to 323.2 K and $m_{\text{NaOHT}} = m_{\text{NaOH}} + m_{\text{NaAl(OH)}_4}$ from 0 to 8 mol/kg H₂O.

3. The stoichiometric activity coefficients of NaOH and NaAl(OH)₄ and the activity of H₂O for the NaOH-NaAl(OH)₄-H₂O system were calculated with our Pitzer model parameters, respectively. The results show the regularities of the activity coefficients with the m_{NaOHT} and α_K . All of these regularities imply that the strengths of the repulsive interactions among various anions follow the sequence of $\text{Al(OH)}_4^- - \text{Al(OH)}_4^- < \text{Al(OH)}_4^- - \text{OH}^- < \text{OH}^- - \text{OH}^-$, and the attractive interaction between Al(OH)_4^- and H₂O is weaker than that between OH⁻ and H₂O.

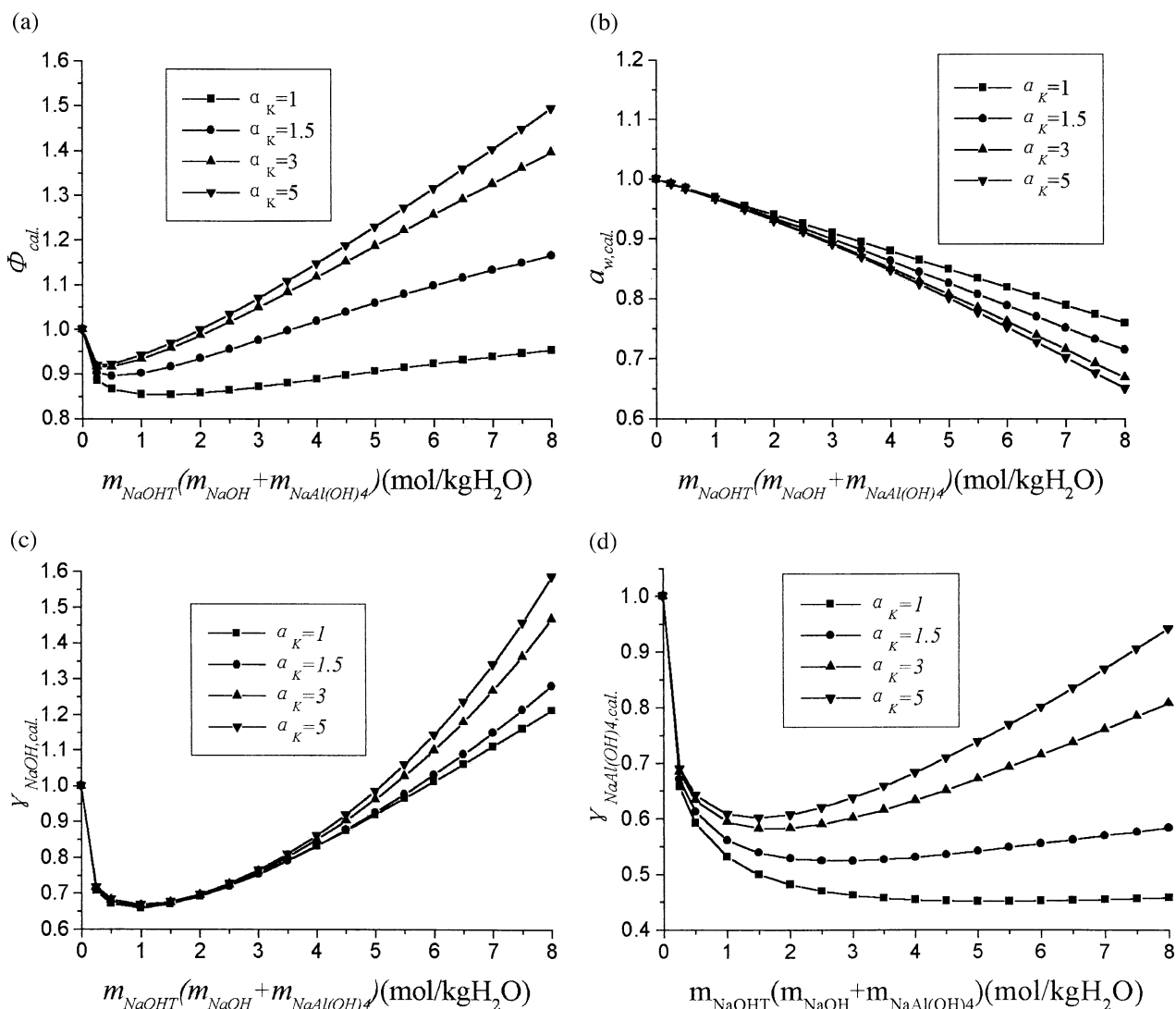


Fig. 2. The changes in the calculated osmotic coefficients of the solution (plot a), the calculated water activity of the solution (plot b), the calculated activity coefficients of NaOH (plot c), and the calculated activity coefficients of NaAl(OH)₄ (plot d) with the solution composition (the plots of $\alpha_K = 1$ are the pseudostates which presume that all solutes are NaAl(OH)₄).

- The calculated osmotic and activity coefficients, and the obtained Pitzer model parameters for the NaOH-NaAl(OH)₄-H₂O system provide a reliable thermodynamic basis for the theoretical analysis of the solubilities of aluminum hydroxides or oxides in solution, the thermodynamic calculations of the deposition process from the supersaturated sodium aluminate solutions, and the study on the structure of the solution.

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