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Comprehensive Model of Synthetic *Bayer* Liquors. Part 3. Sodium Aluminate Solutions and the Solubility of Gibbsite and Boehmite[#]

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Summary. A *Pitzer* model representing the thermodynamics of alkaline sodium aluminate solutions is presented. It constitutes a key part of our 10-component synthetic *Bayer* liquor model communicated in this series of papers. The present model calculates thermodynamic properties, such as heat capacities, osmotic coefficients, and densities, of these solutions as well as the solubilities of gibbsite and boehmite over temperature and concentration ranges of industrial interest.

Keywords. Thermodynamics; Solubility; Sodium aluminate; *Bayer* process; *Pitzer* model; Alumina production.

Introduction

The *Bayer* process involves the leaching of bauxite with caustic solution and the subsequent precipitation of purified gibbsite from the supersaturated alkaline aluminate solutions so produced ('*Bayer* liquors'). Enormous quantities of materials are involved, for example in Australia, the world's largest producer, over 17 million tonnes of alumina are produced *per annum*. Dissolution and precipitation of gibbsite are governed by the solubility equilibrium (Eq. (1)).

$$\mathrm{Al(OH)_3(s) + NaOH(aq) \rightleftharpoons `NaAl(OH)_4(aq)'} \qquad (1)$$

Quantitative knowledge of the solubility of gibbsite in *Bayer* liquors is essential to optimise the design and engineering of plant equipment so as to improve yields and product quality.

In this series of papers [1, 2] a comprehensive, thermodynamically consistent model of *Bayer* liquors is presented, from which densities, heat capacities, enthal-

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[#] Dedicated to Professor Dr. *Heinz Sterk* on the occasion of his 65th birthday pies, osmotic and activity coefficients, and solubilities can be calculated simultaneously. The first part of this series provided an overview of a *Pitzer* model [3] for the 10-component system: NaOH–'NaAl(OH)$_4$'–Na_2SO_4–Na_2CO_3–NaCl–NaF–$Na_2C_2O_4$ (sodium oxalate)–NaHCOO (sodium formate)–$NaCH_3COO$ (sodium acetate)–H_2O [1], while in part 2 a volumetric model for the hypothetical binary electrolyte 'NaAl(OH)$_4$(aq)' was derived from density measurements of NaOH/NaAl(OH)$_4$ mixtures [2]. The present communication reports a *Pitzer* model for other thermodynamic properties of 'NaAl(OH)$_4$(aq)'. On the basis of this model, the solubilities of gibbsite and boehmite in liquors containing various amounts of 'impurities' are calculated and compared with experimental data.

Model Calculations

Initially, all calculations and optimizations involving the *Pitzer* model were performed using the ChemSage software [4–6]. To enable the use of functions or models that are not available in the standard version, ChemSage allows for 'user-defined' functions, which can be coded by the user and linked to the main program. This feature, which is explained in detail in part 1 of this series, has been extensively used in the current work.

The models discussed in this series have been incorporated in a 'stand-alone' code based on the ChemApp® Thermodynamic Software Interface [6]. ChemApp is a programmer's library consisting of a comprehensive set of subroutines, based on the thermodynamic phase equilibrium calculation module of ChemSage [4]. It permits the calculation of complex, multicomponent, multiphase chemical equilibria and their associated extensive property balances.

An alternative code has been developed also, which does not require ChemApp to calculate the thermodynamic properties of aqueous solutions and two-phase equilibria between the aqueous phase and stoichiometric solid phases (or the vapour phase). All calculations reported in this paper have been performed using this code. Details of both computer codes are given in part 1 of this series.

Pitzer Model of 'NaAl(OH)$_4$(aq)'

The following user-defined *Gibbs* energy models have been coded as part of the present work:

(a) *Wesolowski* [7], valid for $273 < T/\mathrm{K} < 373$, $P = 1$ bar and $I \leq 5\,\mathrm{mol\,kg^{-1}}$, combined with standard partial molar heat capacities derived in this work from literature data [8, 9];
(b) *Caiani et al.* [9], valid for $323 < T/\mathrm{K} < 523$, $P \approx P_{\mathrm{sat}}$ and $I \leq 2\,\mathrm{mol\,kg^{-1}}$;
(c) *Park* and *Englezos* [10], valid at 298.15 K and $I \leq 4\,\mathrm{mol\,kg^{-1}}$.

The volumetric *Pitzer* model of 'NaAl(OH)$_4$(aq)' is discussed in detail in part 2 of this series. It was incorporated in the present code for density calculations, concentration unit conversions, and calculations of thermodynamic properties at higher pressures.

Table 1. Thermodynamic properties of phases and species in the Al–O–H system used in this work; these data are consistent with CODATA key values [13]

	$\Delta_f G^\circ/\mathrm{kJ\,mol^{-1}}$	$\Delta_f H^\circ/\mathrm{kJ\,mol^{-1}}$	$S^\circ/\mathrm{J\,K^{-1}\,mol^{-1}}$	$C_p{}^\circ/\mathrm{J\,K^{-1}\,mol^{-1}}$
$Al(OH)_3$(cr)	−1154.91	−1293.13	68.44	91.72
AlOOH(cr)	−917.50	−995.50	37.19	54.24
$Al(OH)_4{}^-$(aq)	−1305.64	−1500.645	111.24	97.35

Following a critical comparison of the three models above, it was decided that currently *Wesolowski*'s model is the best available for the calculation of solution thermodynamic properties and solubilities of gibbsite and boehmite. This model is based on a constant difference between the *Pitzer* parameters of sodium hydroxide and aluminate (Eqs. (2)–(4)).

$$\beta^{(0)}{}_{\mathrm{NaOH}} - \beta^{(0)}{}_{\mathrm{NaAl(OH)_4}} = 0.0356 \tag{2}$$

$$\beta^{(1)}{}_{\mathrm{NaOH}} - \beta^{(1)}{}_{\mathrm{NaAl(OH)_4}} = 0 \tag{3}$$

$$C^{\phi}{}_{\mathrm{NaOH}} - C^{\phi}{}_{\mathrm{NaAl(OH)_4}} = 0.00526 \tag{4}$$

This difference is essentially the same as that between sodium hydroxide and perchlorate. In this way, the *Pitzer* model of *Simonson et al.* [11] for sodium hydroxide was coupled with model (a). The standard thermodynamic quantities for gibbsite and '$NaAl(OH)_4$(aq)' (Table 1) as well as the anion–anion ($\theta_{\mathrm{OH,Al(OH)_4}} = 0.014$) and ternary ($\psi_{\mathrm{Na,OH,Al(OH)_4}} = -0.0048$) interaction parameters reported by *Wesolowski* [7] were also used in our calculations. The standard *Gibbs* energy of formation of the aluminate ion at 298.15 K (Table 1) is close to the 'best' value $\Delta_f G^\circ = -(1305.0 \pm 1.3)\ \mathrm{kJ\,mol^{-1}}$ selected by *Hemingway et al.* [12] after performing a comprehensive literature review. The standard thermodynamic quantities for gibbsite used by *Wesolowski* [7] are identical with the values measured by *Hemingway et al.* [14, 15].

Model (b) does not fit the observed thermodynamic and solubility data as well as model (a) below 100°C although it might be useful at temperatures above 100°C. Unfortunately, the ionic strength range for which it is applicable is rather limited. The *Park* and *Englezos* model (c) only appears capable of reproducing the osmotic coefficients measured by those authors at 298.15 K [10].

After an examination of the various sources of thermodynamic data for boehmite, it was decided to incorporate the values reported by *Hemingway et al.* [12] in our chosen *Bayer* liquor model. The standard enthalpy of formation of boehmite [12], $\Delta_f H^\circ = -(996.4 \pm 2.2)\ \mathrm{kJ\,mol^{-1}}$, was slightly adjusted (well within its experimental error, Table 1) to achieve good agreement with experimental solubility data in caustic solutions [16]. It should be noted that these values were recently confirmed ($\Delta_f H^\circ = -(996.1 \pm 1.3)\ \mathrm{kJ\,mol^{-1}}$) by an independent calorimetric study [17]. The standard entropy and heat capacity function for boehmite (Table 1) were also taken from *Hemingway et al.* [12]. All thermodynamic data used in this study are consistent with CODATA key values [13].

Results and Discussion

Heat Capacities of NaOH/NaAl(OH)$_4$ Solutions

Heat capacities of aqueous NaOH/NaAl(OH)$_4$ solutions at a total stoichiometric ionic strength of up to 6 mol kg^{-1} and with up to 60 mol% substitution of OH$^-$ by $\mathrm{Al(OH)_4}^-$ have been measured in this laboratory at 25°C by flow calorimetry [18]. The mean apparent molar heat capacities ($^{\phi}C_p$) of the NaOH/NaAl(OH)$_4$ mixtures were linear with respect to $\mathrm{Al(OH)_4}^-$ substitution, consistent with *Young*'s rule [18].

As recently reviewed by *Magalhães et al.* [18], the $^{\phi}C_p$ data by *Hovey et al.* [8] and *Caiani et al.* [9] are probably the most reliable of those reported earlier. From these data, the following standard partial molar heat capacity function, $C_p{}^{\circ}(T)$, was derived for 'NaAl(OH)$_4$(aq)' (Eq. (5)) and combined with *Wesolowski*'s model [7]. The last two terms in Eq. (5), which is valid in the temperature range 283 to 518 K, take into account that $C_p{}^{\circ}(T)$ functions of aqueous electrolytes change rapidly when approaching 227 K, where supercooled water exhibits a singularity, and the critical point of water at 647 K, respectively. The standard partial molar heat capacity of the aluminate ion at 298.15 K (Table 1) was calculated from Eq. (5) and the value of 43.01 J K^{-1} mol^{-1} for Na$^+$(aq) given by *Criss* and *Millero* [19].

$$\begin{aligned} C_p{}^{\circ}(T) = {} & 65671.169 - 550158.92\,(\mathrm{K}/T) - 13464.009\ln(T/\mathrm{K}) \\ & + 55.509011\,(T/\mathrm{K}) - 0.03292435\,(T/\mathrm{K})^2 \\ & - 31384.1/(T/\mathrm{K} - 227) - 54151.1512/(647 - T/\mathrm{K}) \qquad (5) \end{aligned}$$

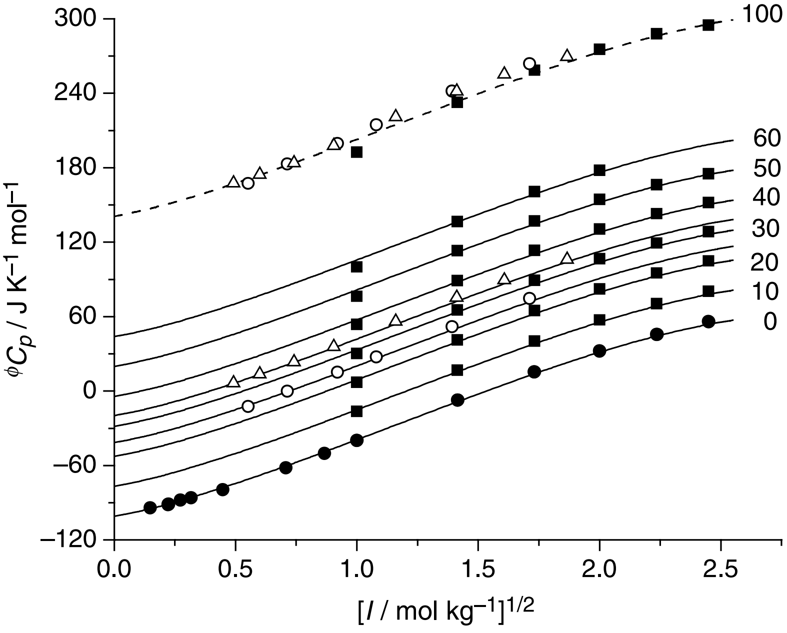

Fig. 1. Mean apparent molar heat capacities $^{\phi}C_p$ of NaOH/NaAl(OH)$_4$ solutions at 25°C; the numbers indicate the mol% substitution of OH$^-$ by $\mathrm{Al(OH)_4}^-$; the values for pure, hypothetical 'NaAl(OH)$_4$(aq)' (100 mol% substitution) were obtained by extrapolation; experimental data: filled circles [20] (NaOH(aq)), filled squares [18], open circles [8] (24.6 mol% substitution), open triangles [8] (33.6 mol% substitution); the lines were calculated from the present model

Figure 1 shows that the present model reproduces ${}^{\phi}C_p$ data at 25°C with high accuracy. This indicates that *Wesolowski*'s assumption of constant (*i.e.* temperature independent) differences between the *Pitzer* parameters of NaOH and 'NaAl(OH)$_4$'

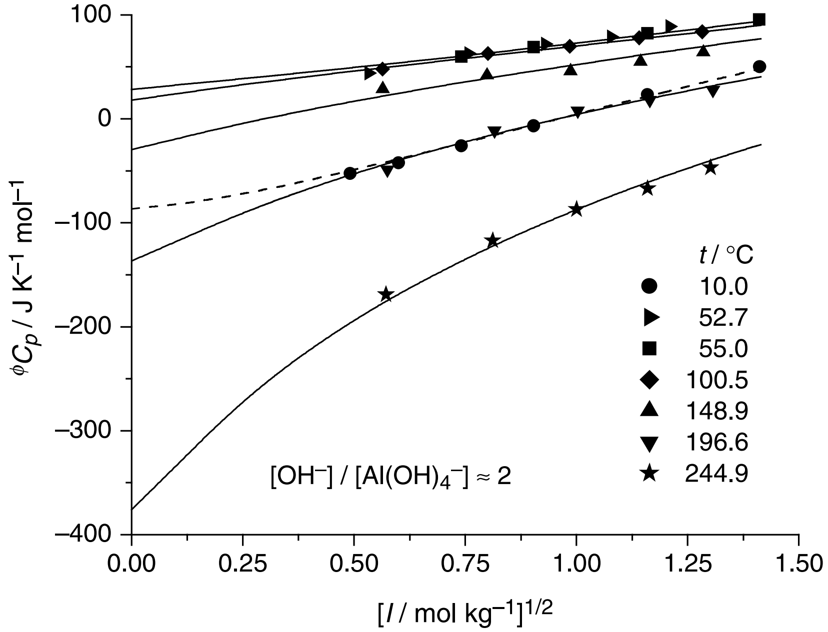

Fig. 2. Mean apparent molar heat capacities ${}^{\phi}C_p$ of NaOH/NaAl(OH)$_4$ solutions at various temperatures for a stoichiometric [OH$^-$]/[Al(OH)$_4^-$] ratio of *ca.* 2; experimental data: circles and squares [8], all other symbols [9]; lines: calculated from the present model (dashed line, 10°C)

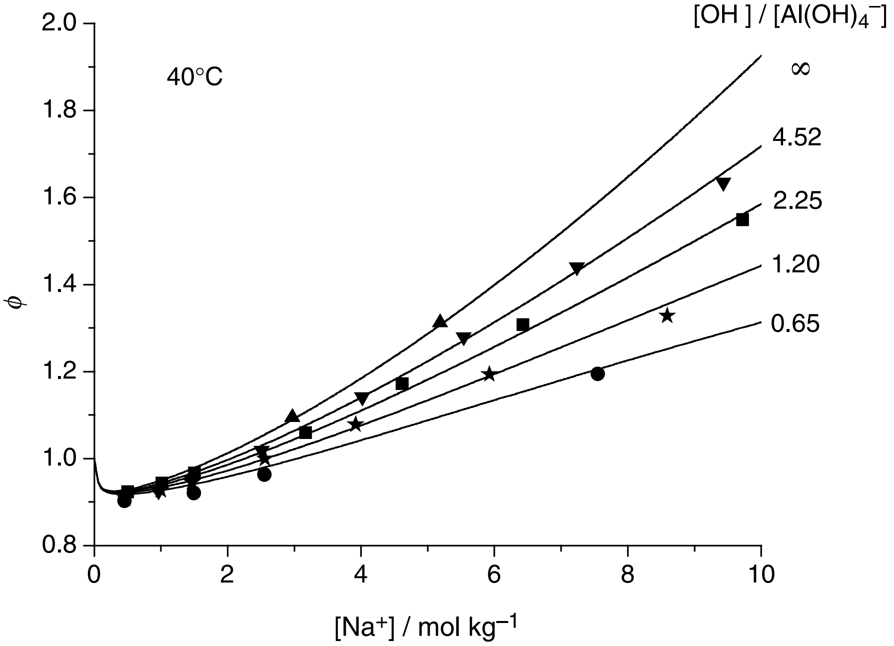

Fig. 3. Comparison of experimental osmotic coefficient data at 40°C [21] for NaOH/NaAl(OH)$_4$ solutions of various stoichiometric [OH$^-$]/[Al(OH)$_4^-$] ratios with model predictions

is reasonable. Since ${}^{\phi}C_p$ is related to the first and second derivatives of *Pitzer* parameters, these constant differences do not contribute to ${}^{\phi}C_p$ of 'NaAl(OH)$_4$(aq)'. The calculated lines in Fig. 1 therefore have the same curvature as the ${}^{\phi}C_p$ function for NaOH(aq) and are only shifted by constant amounts. These are calculated using *Young*'s pro-rata additivity rule, *i.e.* the C_p° values of the ternary mixtures are linearly interpolated (according to the molality fractions) between the C_p° values of binary NaOH(aq) and 'NaAl(OH)$_4$(aq)'.

It is noteworthy that the ${}^{\phi}C_p$ predictions are in good agreement with the observed data to temperatures as high as 245°C [9] (Fig. 2).

Osmotic Coefficients of NaOH/NaAl(OH)$_4$ Solutions

Although no osmotic coefficient data were used in the parameterisation, the model agrees very well with data measured recently at 40°C [21] (Fig. 3), while isopiestic data obtained in our laboratory at 125°C [22] are reproduced reasonably well (Fig. 4).

Enthalpies of Dissolution of Gibbsite

Chen et al. [23] have measured the enthalpy of dissolution of gibbsite in 1 to 5 mol kg^{-1} NaOH(aq) in the temperature range 100 to 150°C. The values calculated from the current model are *ca.* 2 kJ mol^{-1} higher than the experimental data, which is within the combined uncertainties of the thermodynamic quantities reported by *Wesolowski* [7] and *Chen et al.* [23]. Whereas the standard thermo-

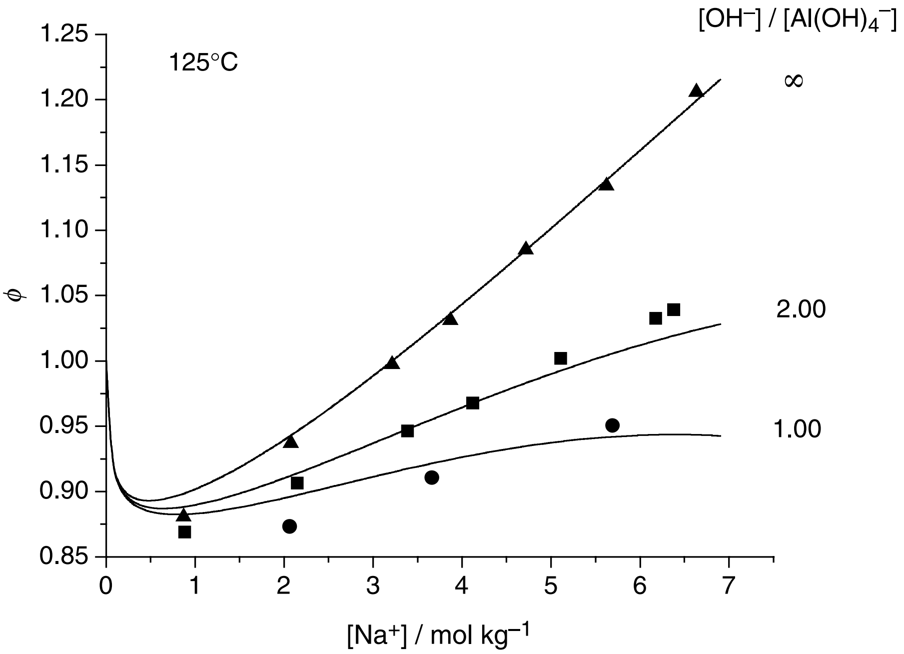

Fig. 4. Comparison of experimental osmotic coefficient data at 125°C [22] for NaOH/NaAl(OH)$_4$ solutions of various stoichiometric [OH$^-$]/[Al(OH)$_4^-$] ratios with model predictions

dynamic data for gibbsite [14, 15, 17, 24] and NaOH(aq) [13] are well established, those for the aluminate ion are rather uncertain. *Wu et al.* [25] have reviewed the literature and found $\Delta_f H^\circ$ ranging from -1486.3 to $-1503.65\,\text{kJ mol}^{-1}$, while their own measurements suggest $\Delta_f H^\circ = -1501.7\,\text{kJ mol}^{-1}$, in close agreement with the value selected by *Wesolowski* [7] and used in this work. The average between this value [25] and the one recommended by *Zeng et al.* [26], $\Delta_f H^\circ = -(1503.61 \pm 1.00)\ \text{kJ mol}^{-1}$, leads to an almost perfect agreement with the enthalpy of dissolution of gibbsite measured by *Chen et al.* [23]. In this work however, *Wesolowski*'s thermodynamic quantities for the aluminate ion were selected for reasons of consistency with the other data reported in his study [7].

Solubilities of Gibbsite and Boehmite in the $Al(OH)_3$–NaOH–H_2O System

Wesolowski's model [7] very closely reproduces his experimental gibbsite solubilities in NaOH solution, which is expected because these data were used to parameterise the model. Our solubility calculations also agree very well with earlier results reported by *Russell et al.* [16] (Fig. 5b), which constitutes an independent test of the present model.

Figure 5a compares boehmite solubility data in NaOH solutions [16] with those calculated from the present model. The satisfactory agreement indicates thermodynamic consistency between the calorimetric [12, 17] and solubility [16] data for boehmite. In other studies, *e.g.* Ref. [24], the thermodynamic quantities were derived exclusively from solubility data and the resulting values are inconsistent with calorimetric data. It is therefore surprising that the quantities given by *Verdes*

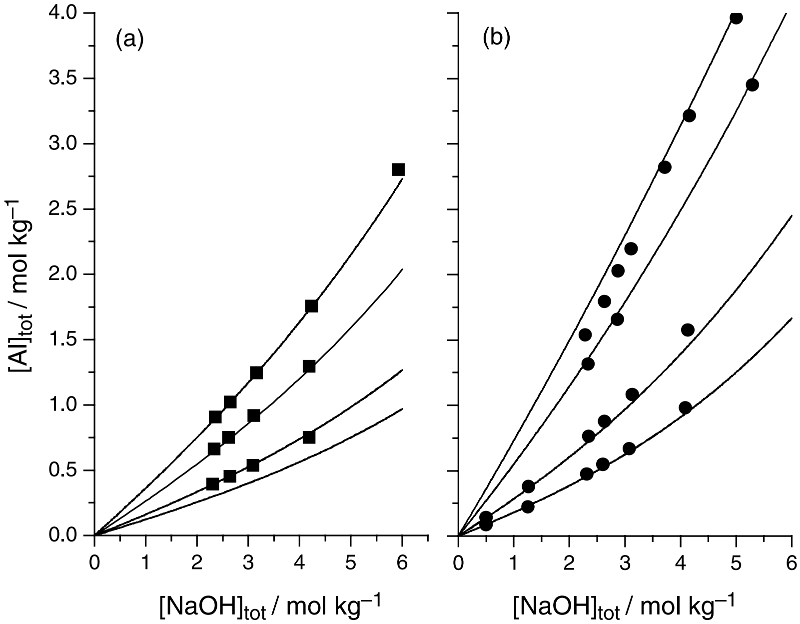

Fig. 5. Solubility of boehmite (a) and gibbsite (b) in NaOH solutions at 60, 80, 120, and 150°C (in the order of increasing solubility); experimental data [16]: squares, boehmite; dots, gibbsite; lines, present model

et al. [24] were found to be reliable in an authoritative study [27]. It has been stressed recently [28] that various kinds of experimental data have to be considered in optimisations of thermodynamic quantities to reduce such inconsistencies.

The stability of boehmite with respect to gibbsite increases with temperature and concentration of NaOH, as can be seen from the increasing differences in their solubilities. Our model predicts that gibbsite becomes more stable than boehmite below 32°C at a water activity (a_w) of 1. This transition temperature is predicted to shift to 18°C in 5 mol kg^{-1} NaCl ($a_w \approx 0.8$). Presumably due to kinetic restrictions, such transition temperatures do not appear to have been observed directly. However, some researchers report that gibbsite does not convert to boehmite even after several months at temperatures <80°C [27], while others have succeeded in a seeded precipitation of boehmite from *Bayer* liquors at 90°C [29]. *Skoufadis et al.* [29] conclude from their kinetic study that the difficulties in boehmite precipitation at lower temperatures can be attributed to its much higher activation energy of precipitation compared to that for gibbsite, even though boehmite formation is thermodynamically favoured.

Finally, Fig. 5 also shows that, consistent with industry practice, much higher digestion temperatures are needed for boehmitic than gibbsitic ores: the solubility of boehmite at 150°C is only slightly higher than the solubility of gibbsite at 80°C.

Solubility of Gibbsite in the $Al(OH)_3$–NaOH–NaCl–H_2O System

Wesolowski [7] has also studied gibbsite solubilities in NaOH/NaCl solutions extensively and concluded that no ternary *Pitzer* parameters were necessary to model the solubilities in these electrolyte mixtures. However, a careful re-exam-

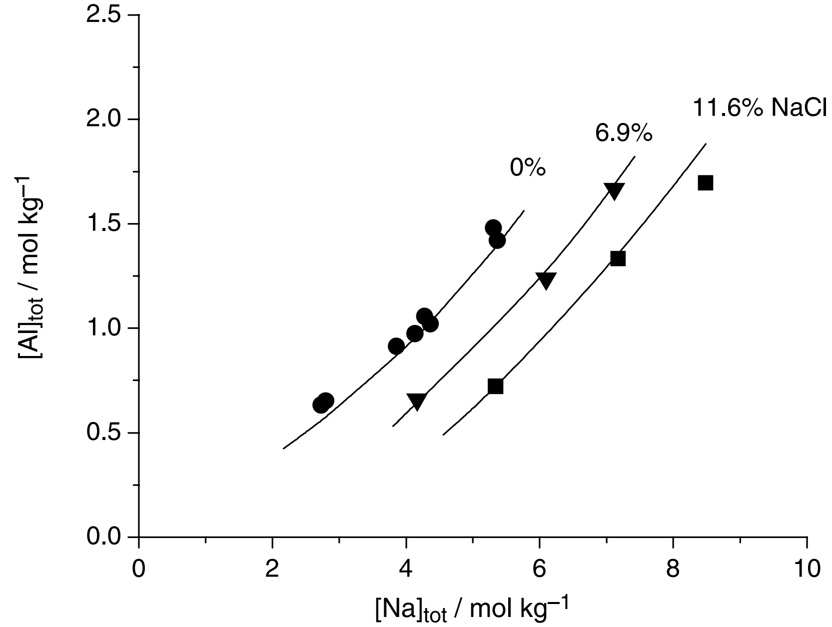

Fig. 6. Gibbsite solubilities [30] at 60°C in NaOH solutions containing various amounts of sodium chloride (in mass%) as compared to the present *Pitzer* model (lines)

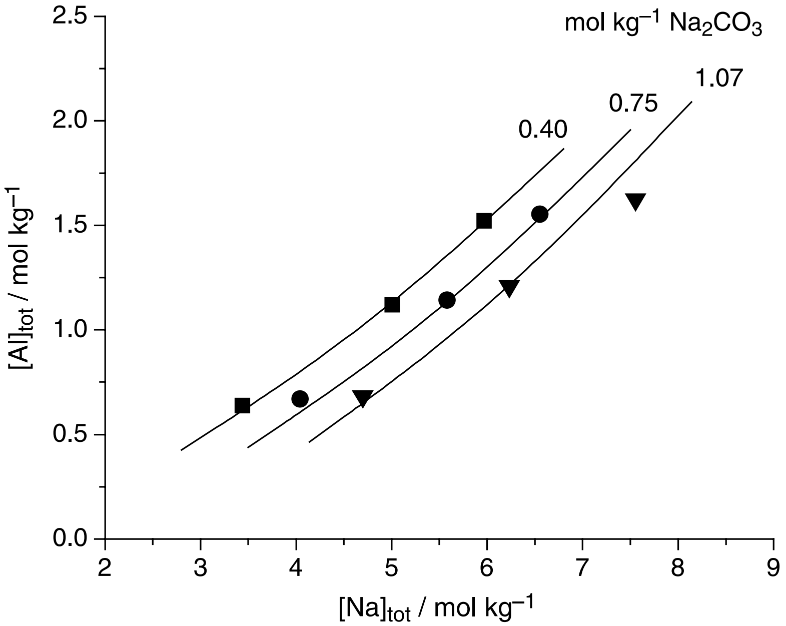

Fig. 7. Gibbsite solubilities [30] at 60°C in NaOH solutions containing varying amounts of Na_2CO_3 as compared to the predictions of the present *Pitzer* model (lines)

ination of these solubility data revealed that an anion-anion parameter $\theta_{Cl,Al(OH)_4} = -0.055$ reproduces the experimental data almost perfectly, giving a much better result than if this parameter is omitted. Figure 6 compares model predictions for gibbsite solubilities in NaOH/NaCl mixtures with experimental data by *Lyapunov et al.* [30], which have not been used in the current parameterisation. The agreement is excellent.

Solubility of Gibbsite in the $Al(OH)_3$–NaOH–Na_2CO_3–H_2O System

The predictions of the present model also agree very well with gibbsite solubilities in NaOH/Na_2CO_3 solutions measured by *Lyapunov et al.* [30] (Fig. 7). No additional ternary parameters were required.

Gibbsite Solubilities in Synthetic Bayer Liquors

The model predicts gibbsite solubilities in synthetic *Bayer* liquors containing all of the common major inorganic impurities: Cl^-, CO_3^{2-} and SO_4^{2-} [31] (Fig. 8). The agreement is very good at 50°C and quite reasonable at 60°C. No additional ternary parameters were used.

Gibbsite Solubilities in Bayer Plant Liquors

Since the solubility of gibbsite under refinery conditions is one of the most important *Bayer* process parameters, model predictions for gibbsite solubilities in plant liquors (containing all components of the present model) were compared with

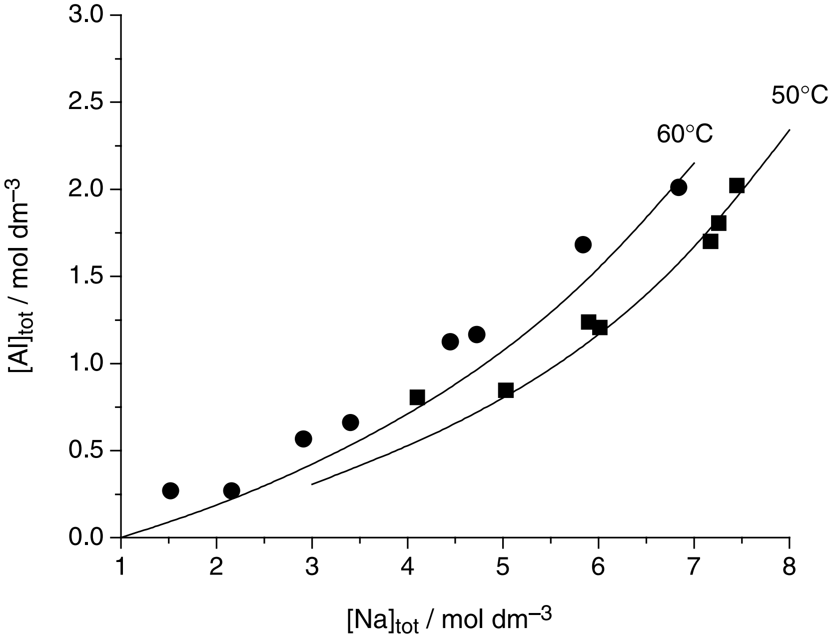

Fig. 8. Solubility of gibbsite in synthetic *Bayer* liquors containing $[Cl^-] = 0.24\,mol\,dm^{-3}$, $[SO_4^{2-}] = 0.22\,mol\,dm^{-3}$, and $[CO_3^{2-}] = 0.22\,mol\,dm^{-3}$ [31] compared with the predictions of the present *Pitzer* model (lines); the calculated molarities refer to 25°C, since the analyses are usually performed close to this temperature

carefully measured values [32]. After an assumption was made regarding the modelling of organic species [33], an excellent agreement was found indicating that the model can be applied favourably to *Bayer* plant liquors under realistic industrial conditions [1, 33].

Conclusions

The present *Pitzer* model calculates, in a thermodynamically consistent manner, the thermodynamic properties (*e.g.* C_p, ϕ, ρ) of alkaline sodium aluminate solutions together with solubilities of gibbsite and boehmite over concentration and temperature ranges of industrial interest. However, accurate computer simulations of the *Bayer* process at conditions far exceeding the current plant operating ranges are seen by alumina producers as an important way to increase future productivity, minimise energy consumption, and cut greenhouse emissions. To overcome possible model inaccuracies at high temperatures, heat capacity and density data are being measured in our laboratory to 300°C so as to develop hitherto unavailable modelling capabilities of the thermodynamics of *Bayer* liquors.

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