



HAL
open science

Thermodynamic approach of the NH₄-dawsonite solubility

Robin Lafficher, Mathieu Digne, Fabien Salvatori, Malika Boualleg, Didier Colson, Francois Puel

► **To cite this version:**

Robin Lafficher, Mathieu Digne, Fabien Salvatori, Malika Boualleg, Didier Colson, et al.. Thermodynamic approach of the NH₄-dawsonite solubility. Proceeding of the 9th workshop of French Industrial Crystallization CRISTAL9, May 2019, Nancy, France. hal-02142338

HAL Id: hal-02142338

<https://hal.science/hal-02142338>

Submitted on 28 May 2019

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

To cite this article: R. Lafficher, M. Digne, F. Salvatori, M. Boualleg, D. Colson, F. Puel (2019) Thermodynamic approach of the NH₄-dawsonite solubility, Proceeding of the 9th workshop of French Industrial Crystallization CRISTAL9, Nancy 16-17 May 2019, France

Thermodynamic approach of the NH₄-dawsonite solubility

LAFFICHER Robin^{a,b,*}, DIGNE Mathieu^a, SALVATORI Fabien^a, BOUALLEG Malika^a, COLSON Didier^b and PUEL Francois^{c*}

^aIFP Energies Nouvelles

BP 3, F-69360 Solaize, France

^bUniv Lyon, Université Claude Bernard Lyon 1, CNRS, LAGEPP UMR 5007,
43 boulevard du 11 novembre 1918, F-69100, VILLEURBANNE, France

^cLGPM, CentraleSupélec, Université Paris-Saclay
3 rue Joliot-Curie, 91192 Gif-sur-Yvette, France

Abstract

NH₄-dawsonite is a promising alternative precursor for the preparation of alumina catalyst supports. Since generally prepared by precipitation, a good knowledge of its thermodynamic properties and its solubility would allow a better control over its synthesis. However, only few research efforts have focused on this material aspect until now. We propose in this study to estimate the order of magnitude of the NH₄-dawsonite Gibbs free energy at 25 °C by combining experimental solubility measurements and theoretical solubility calculations. The latter were performed within the pH range 3–14 and considering the predominant Al species Al³⁺, Al(OH)₃⁰ and Al(OH)₄⁻. The NH₄-dawsonite Gibbs free energy obtained with this method was $-1564 \pm 2 \text{ kJ}\cdot\text{mol}^{-1}$.

Keywords: Solubility, Gibbs free energy, NH₄-dawsonite

1. Introduction

Dawsonite is a crystalline mineral that can generally be found in nature as sodium aluminum carbonate hydroxide (NaAl(OH)₂CO₃), also called Na-dawsonite. Over the last two decades, a significant research effort has focused on the importance of Na-dawsonite in CO₂ sequestration by mineral trapping, leading to a better understanding of the equilibrium and kinetics that control its precipitation: in particular, Bénézeth *et al.* (2007) performed solubility experiments based on in situ pH measurements to reevaluate its thermodynamic properties, then confirming previous experimental measurements from the literature (Ferrante *et al.* 1976).

Dawsonite does not only exist as NaAl(OH)₂CO₃: numerous analogues can be synthesized by changing the nature of sodium or aluminum cations in the structure (Hernandez *et al.* 1985, Ali *et al.* 2005, Yalfani *et al.* 2007). Ammonium aluminium carbonate hydroxide (NH₄Al(OH)₂CO₃), also called NH₄-dawsonite, is one of the most studied analogues. Its main interest comes from the fact that it represents a promising alternative for preparation of alumina-based catalyst supports with high purity level and new textural properties. Various methods can be used to synthesize NH₄-dawsonite (Ali *et al.* 2005), the main one remaining the precipitation of aluminium salts (Al(NO₃)₃, (NH₄)Al(SO₄)₂, or AlCl₃) in aqueous phase with precipitating agents such as (NH₄)₂CO₃ or NH₄HCO₃ (Vogel *et al.* 1984, Pitsch *et al.* 2001). Influence of several

* Corresponding authors : robin.lafficher@gmail.com (Robin Lafficher), francois.puel@centralesupelec.fr (Prof. François Puel)

parameters on the product properties have been studied so far: reactants (Shin *et al.* 2014), contacting mode (Ma *et al.* 2001, Santiago *et al.* 2006, Dubert *et al.* 2011, Hu *et al.* 2012), pH (Liu *et al.* 2012a, 2012b), molar ratio (Vogel *et al.* 1984, Hu *et al.* 2012, Li *et al.* 2012), alternative medias (Liu *et al.* 2012b, Duan *et al.* 2013).

It is interesting to note that most of these works focus on NH₄-dawsonite synthesis from a “material” point of view, without any consideration of the “precipitation” aspects. Precipitation is a complex phenomenon combining reaction and mixing, and involving several mechanisms depending on many factors (temperature, surface energy, molecular diffusivity, solubility, etc.) (Karpinsky and Wey 2002). Among these mechanisms, both nucleation and growth are highly dependent on the supersaturation level. Supersaturation control could therefore allow a better control over nucleation and growth kinetics, and, consequently, over the precipitated materials properties (Mersmann 1999). From a theoretical point of view, this requires a good understanding of the material thermodynamic properties, to evaluate its solubility over the synthesis conditions. However, in NH₄-dawsonite case, only very few studies have focused on its thermodynamic properties and, consequently, on its solubility on aqueous media, as previously reported (Lodziana *et al.* 2011). A reason could be the relatively recent interest of this material.

The goal of this study was to estimate the NH₄-dawsonite Gibbs free energy. This material was synthesized in a stirred tank reactor and, for the first time, an experimental measurement of its solubility was realized and reported. This measurement, combined with a theoretical solubility model, was used to assess the probable order of magnitude of the NH₄-dawsonite Gibbs free energy value at 25 °C.

2. Materials and Method

The synthesis of NH₄-dawsonite was carried out in a stirred tank reactor equipped with a mechanical stirrer and containing an initial 667 mL water volume. Reagent grade aluminium nitrate (Alfa Aesar) and carbonate ammonium (Alfa Aesar) were used as starting materials without further purification. Precipitation was realized by simultaneous dosing of an aluminium nitrate solution (1.2 mol.L⁻¹, 21.8 mL.min⁻¹) and a carbonate ammonium solution (2.0 mol.L⁻¹, 39.3 mL.min⁻¹) over 30 minutes. The molar ratio R_{b/a} (defined as the molar ratio of (NH₄)₂CO₃ over Al(NO₃)₃) was 3.0, and the suspension temperature was controlled at 60 °C. pH was monitored between 7 and 8. After synthesis, the suspension was filtered and washed once using hot demineralized water. Then the cake was dried at 120 °C overnight and ground. The obtaining of pure NH₄-dawsonite was validated using powder XRD (Lafficher *et al.* 2017). 0.12 g of the synthesized NH₄-dawsonite was poured into 50 mL of an aqueous solution of (NH₄)₂CO₃ (2 mol.L⁻¹). The preparation was allowed to equilibrate at 25 °C under magnetic stirring, for more than 15 days. It was then ultrafiltered at 25 °C, under stirring, with a pressure of 2 bar and through a 5 kDa Ultracel™ membrane (PLCC06210, Millipore). The ultrafiltered solution then exhibited a pH of 8.7. The aluminium content was measured using AAS with a Polarized Zeeman Graphite Furnace Atomic Absorption Spectrophotometer (GTA 120, Varian). The protocol was repeated on two identical suspensions and analyses were conducted on two aliquots of each ultrafiltered solution. The mean value of the obtained measurements was taken as Al concentration.

3. Theoretical expression of NH₄-dawsonite solubility at 25 °C

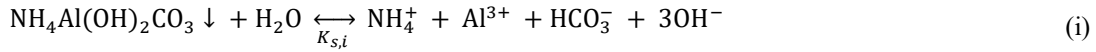
Solubility C* of a sparingly soluble salt A_mB_n is usually expressed based upon its solubility constant K_s, as shown in Eq. (1). However, this relation is only valid if salts solubility is independent of the pH (Schwartz and Myerson 2002). This is not the case for aluminium, as its speciation involves numerous species equilibriums depending on the pH (Bénézeth *et al.* 1997, Paniais and Krestou 2007). Consequently, those different species must be considered to the extent possible – at least the main ones – to evaluate the aluminium solubility in equilibrium with NH₄-dawsonite, as a function of pH. Thereafter, we will refer to this solubility as “NH₄-dawsonite solubility”.



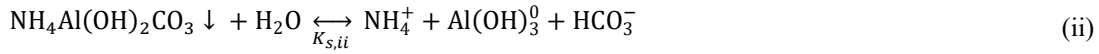
Considering the speciation of aluminium in aqueous media at 25 °C presented by Paniais and Krestou (2007), and in order to simplify the calculations, we considered only Al^{3+} , $Al(OH)_3^0$ and $Al(OH)_4^-$, which are the predominant species in the pH range 3–14. This leads to Eq. (2) giving the expression of the NH_4 -dawsonite solubility as a function of the different aluminium species.

$$C_{Al}^* = [Al^{3+}] + [Al(OH)_3^0] + [Al(OH)_4^-] \quad (2)$$

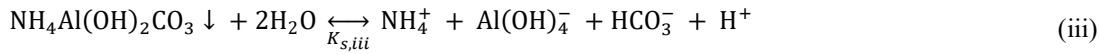
Reactions (i) to (iii) present the equilibria involved and their respective solubility constant. For simplification purposes, we have likened activities to concentrations, assuming activity coefficients equal to unity.



$$K_{s,i} = [Al^{3+}] \cdot [NH_4^+] \cdot [HCO_3^-] \cdot \frac{K_W^3}{[H^+]^3} \quad (3)$$



$$K_{s,ii} = [Al(OH)_3^0] \cdot [NH_4^+] \cdot [HCO_3^-] \quad (4)$$



$$K_{s,iii} = [Al(OH)_4^-] \cdot [NH_4^+] \cdot [HCO_3^-] \cdot [H^+] \quad (5)$$



$$K_W = [H^+] \cdot [OH^-] \quad (7)$$

Solubility constant K_S at 25 °C can be deduced from the equilibrium constant K_r of the precipitation reaction leading to A_mB_n , as $K_S = K_r^{-1}$. This equilibrium constant can be calculated from the Gibbs free energy of the precipitation reaction (Eq. (8)), itself obtained from the standard Gibbs free energy of the species involved (Eq. (9)).

$$K_r(T) = \exp\left(-\frac{\Delta G_r^0}{RT}\right) \quad (8)$$

$$\Delta G_r^0 = \sum_j \nu_j \Delta G_{f,j}^0 \quad (9)$$

The solubility products at 25 °C of the reactions (i) and (iii) ($K_{S,i}$ and $K_{S,iii}$, respectively) can easily be calculated using the above-mentioned method, if the standard Gibbs free energies of the species considered are known (see Table 1). In the absence – to the best of our knowledge – of standard Gibbs free energy for $Al(OH)_3^0$ in the literature, the solubility product $K_{S,ii}$ of the reaction (ii) can be calculated indirectly, taking into account the aluminium hydrolysis reaction (10). Eq. (11) and Eq. (12) give respectively the expressions for the hydrolysis constant β_3 and for $K_{S,ii}$ as a function of β_3 . β_3 value at 25 °C was determined according to Eq. (13) proposed by Bourcier *et al.* (1993) (with T in Kelvin): $\log \beta_3 = -16.12$. This value is consistent with those generally referenced in the literature (Nordstrom and May 1996, Brown and Allison 1987);



$$\beta_3 = \frac{[Al(OH)_3^0] \cdot [H^+]^3}{[Al^{3+}]} \quad (11)$$

$$K_{S,ii} = \frac{\beta_3 \cdot K_{S,i}}{K_W^3} \quad (12)$$

$$\log \beta_3 = 41.943 - 10.1134 \cdot \log T - \frac{9851.53}{T} \quad (13)$$

Table 1. Standard Gibbs free energy at 298.15 K

Substance	State	ΔG_f^0 (kJ.mol ⁻¹)	Reference
OH ⁻	aq	-157,2	Wagman <i>et al.</i> 1982
H ⁺	aq	0,0	Wagman <i>et al.</i> 1982
H ₂ O	l	-237,1	Wagman <i>et al.</i> 1982
Na ⁺	aq	-261,9	Wagman <i>et al.</i> 1982
NH ₄ ⁺	aq	-79,3	Wagman <i>et al.</i> 1982
NH ₃	aq	-26,5	Wagman <i>et al.</i> 1982
H ₂ CO ₃	aq	-623,1	Wagman <i>et al.</i> 1982
HCO ₃ ⁻	aq	-586,8	Wagman <i>et al.</i> 1982
CO ₃ ²⁻	aq	-527,8	Wagman <i>et al.</i> 1982
Al ³⁺	aq	-489,4	Robie <i>et al.</i> 1979
Al(OH) ₄ ⁻	aq	-1305,0	Chen <i>et al.</i> 1991
NaAl(OH) ₂ CO ₃	s	-1782,0	Bénezet <i>et al.</i> 2007

However, aluminium is not the only element in NH₄-dawsonite of which speciation is a function of pH. Ammonium and carbonate ions present the following equilibria (reactions (iv) to (vi)). Their acidic dissociation constants are listed in Table 2.



$$K_{a,iv} = \frac{[\text{NH}_3] \cdot [\text{H}^+]}{[\text{NH}_4^+]} \quad (14)$$



$$K_{a,v} = \frac{[\text{HCO}_3^-] \cdot [\text{H}^+]}{[\text{H}_2\text{CO}_3]} \quad (15)$$



$$K_{a,vi} = \frac{[\text{CO}_3^{2-}] \cdot [\text{H}^+]}{[\text{HCO}_3^-]} \quad (16)$$

Table 2. Acidic dissociation constants at 25 °C of ammonium and carbonate ions

Reaction	pK _a	Reference
(iv)	9.24	Bates <i>et al.</i> 1949
(v)	6.35	Lide 2003
(vi)	10.33	Lide 2003

As aqueous ammonia and carbonic acid can adopt various solubilized forms, the total concentrations in their respective species have been noted C_N and C_{CO} , respectively.

$$C_N = [NH_3] + [NH_4^+] \quad (17)$$

$$C_{CO} = [H_2CO_3] + [HCO_3^-] + [CO_3^{2-}] \quad (18)$$

Eq. (19) gives the concentration in NH_4^+ , obtained from Eq. (14) and (17). Eq. (20) gives the concentration in HCO_3^- , obtained from Eq. (15), (16) and (18).

$$[NH_4^+] = \frac{C_N}{1 + \frac{K_{a,iv}}{[H^+]}} \quad (19)$$

$$[HCO_3^-] = \frac{C_{CO} \cdot K_{a,v} \cdot [H^+]}{[H^+]^2 + [H^+] \cdot K_{a,v} + K_{a,v} \cdot K_{a,vi}} \quad (20)$$

Finally, the theoretical expression of the NH_4 -dawsonite solubility at 25 °C as a function of pH was obtained from Eq. (21).

$$C_{Al}^* = \frac{10^{(3pK_W - pK_{S,i} - 3pH)}}{[NH_4^+] \cdot [HCO_3^-]} + \frac{10^{-pK_{S,ii}}}{[NH_4^+] \cdot [HCO_3^-]} + \frac{10^{(pH - pK_{S,iii})}}{[NH_4^+] \cdot [HCO_3^-]} \quad (21)$$

with:

$$[NH_4^+] = \frac{C_N}{1 + 10^{pH - pK_{a,iv}}} \quad (22)$$

$$[HCO_3^-] = \frac{C_{CO} \cdot 10^{-pK_{a,v} - pH}}{10^{-2pH} + 10^{-pH - pK_{a,v}} + 10^{-pK_{a,v} - pK_{a,vi}}} \quad (23)$$

4. Results

Since NH_4 -dawsonite is unstable in deionized water (Stoica and Perez-Ramirez 2010), the aluminium solubility was evaluated at 25 °C in an aqueous solution of $(NH_4)_2CO_3$ (2 mol.L⁻¹), with pH = 8.7 once the equilibrium was reached. In these conditions, we measured a solubility of $C_{Al}^* = 1.94 \cdot 10^{-4}$ mol.L⁻¹ with an uncertainty of $\pm 1.29 \cdot 10^{-4}$ mol.L⁻¹. From this single solubility measurement, we aimed at assessing the order of magnitude of the NH_4 -dawsonite Gibbs free energy value at 25 °C. Assuming that the theoretical solubility curve for NH_4 -dawsonite actually passes through our experimentally determined solubility value, and considering the above-mentioned uncertainty of $\pm 1.29 \cdot 10^{-4}$ mol.L⁻¹, we found a Gibbs free energy of -1564 ± 2 kJ.mol⁻¹ (see Figure 1). It can be noted that for the considered experimental pH, the only species contributing to the total aluminium concentration are $Al(OH)_3^0$ and $Al(OH)_4^-$, the latter being very predominant. Thus, the starting hypothesis to consider only the major species in the pH range 3–14 did not lead to any uncertainty for this indirect estimation of the NH_4 -dawsonite Gibbs free energy from a measured solubility value.

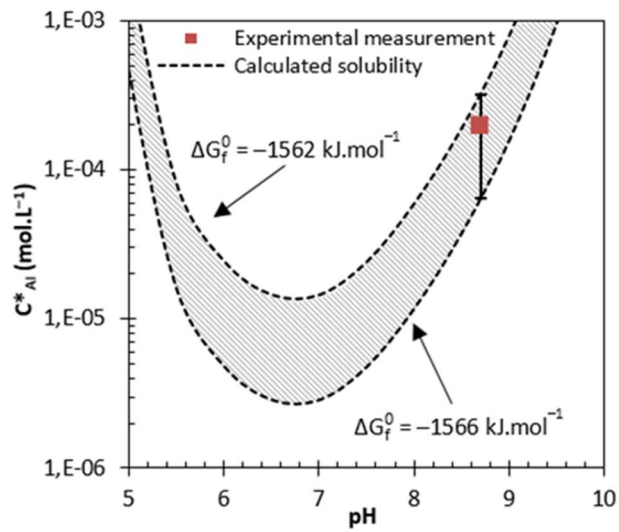


Figure 1. Potential NH_4 -dawsonite solubility curves at 25 °C (with $C_N = 4.0 \text{ mol.L}^{-1}$ and $C_{\text{CO}} = 2.0 \text{ mol.L}^{-1}$) and their corresponding Gibbs free energy values.

5. Discussion

To the best of our knowledge, the only NH_4 -dawsonite Gibbs free energy value previously reported in the literature is $-1483,0 \text{ kJ.mol}^{-1}$, from the work of Stoica and Pérez-Ramírez (2010). Nevertheless, it must be noticed that their work did not aim at determining precisely that thermodynamic data, but rather to compare its order of magnitude with that of other substances; since no data was available, the NH_4 -dawsonite Gibbs free energy was calculated from the tables provided by Wagman *et al.* (1982). This value presents a slight variation of -5.2% compared to our experimentally determined one ($-1564 \pm 2 \text{ kJ.mol}^{-1}$). However, this slight difference has a significant impact on the NH_4 -dawsonite calculated solubility. Indeed, considering $\Delta G_{f,\text{NH}_4\text{-daw}}^0 = -1483 \text{ kJ.mol}^{-1}$ leads to very high theoretical solubility values ($C_{\text{Al}}^* > 10^9 \text{ mol.L}^{-1}$) in the pH range 3–14 (see Figure 2), which are totally inconsistent for a product known to precipitate immediately (at least in the classical concentration and pH ranges of $0.05\text{--}2 \text{ mol.L}^{-1}$ and 7–11, respectively).

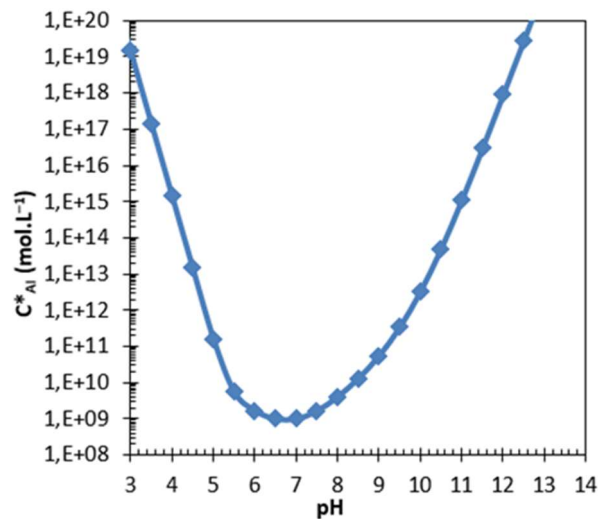


Figure 2. NH_4 -dawsonite calculated solubility at 25 °C versus pH, considering $\Delta G_{f,\text{NH}_4\text{-daw}}^0 = -1483 \text{ kJ.mol}^{-1}$ (with $C_N = 4.0 \text{ mol.L}^{-1}$ and $C_{\text{CO}} = 2.0 \text{ mol.L}^{-1}$)

According to the DFT study of Łodziana *et al.* (2011), Na-dawsonite stability would be slightly higher than that of NH_4 -dawsonite, meaning that NH_4 -dawsonite is more soluble than Na-dawsonite. It can easily be deduced from the previously developed theoretical expression of the NH_4 -dawsonite solubility (Eq. (21))

that an equivalent solubility level between NH_4 -dawsonite and Na -dawsonite would be achievable if considering a NH_4 -dawsonite Gibbs free energy in the order of $-1600.0 \text{ kJ}\cdot\text{mol}^{-1}$, anything else being equal (Figure 3) (see Appendix A for the determination of the Na -dawsonite theoretical solubility curve). Consequently, a higher solubility level for NH_4 -dawsonite can only be achievable with a Gibbs free energy above $-1600.0 \text{ kJ}\cdot\text{mol}^{-1}$, which is in agreement with our experimentally determined value (Figure 3.a).

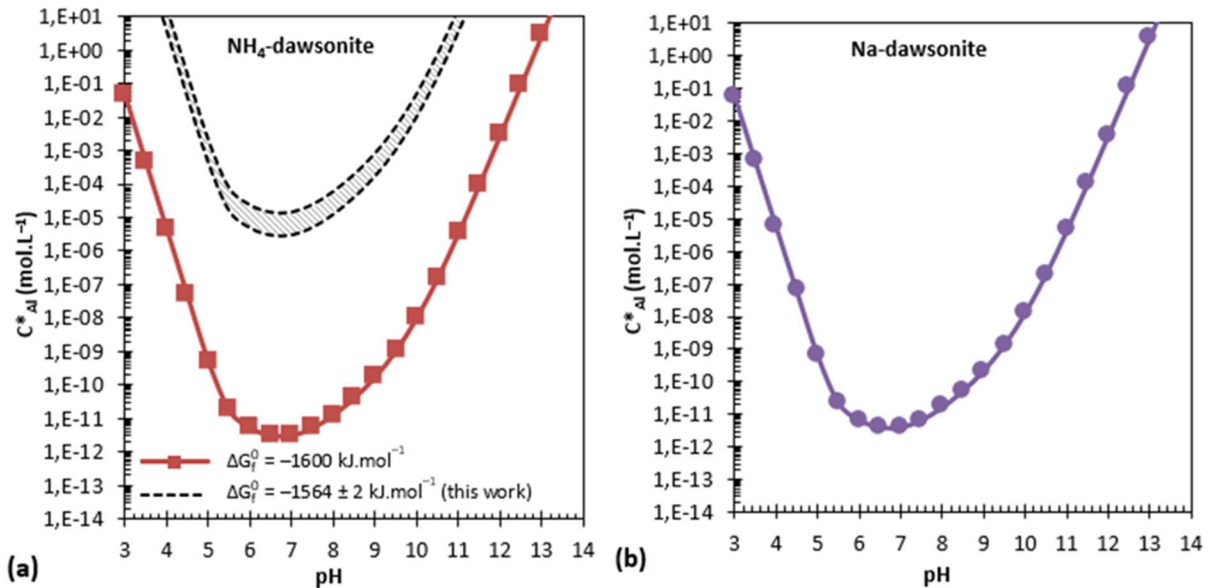


Figure 3. (a) NH_4 -dawsonite calculated solubility at $25 \text{ }^\circ\text{C}$ versus pH , considering $\Delta G_{f,NH4-daw}^0 = -1600 \text{ kJ}\cdot\text{mol}^{-1}$ (with $C_N = 4.0 \text{ mol}\cdot\text{L}^{-1}$ and $C_{CO} = 2.0 \text{ mol}\cdot\text{L}^{-1}$) (NH_4 -dawsonite calculated solubility from Figure 1 is represented for information purpose) and (b) Na -dawsonite calculated solubility at $25 \text{ }^\circ\text{C}$ versus pH (with $C_{Na} = 4.0 \text{ mol}\cdot\text{L}^{-1}$ and $C_{CO} = 2.0 \text{ mol}\cdot\text{L}^{-1}$)

6. Conclusion

NH_4 -dawsonite is a promising alternative precursor for the preparation of alumina catalyst supports. However, only few research efforts have focused on its thermodynamic properties and its solubility until now. This study focused on the evaluation of the NH_4 -dawsonite solubility at $25 \text{ }^\circ\text{C}$. First, a theoretical expression of its solubility within the pH range 3–14 has been proposed, considering the predominant Al species (Al^{3+} , $\text{Al}(\text{OH})_3^0$ and $\text{Al}(\text{OH})_4^-$) and based on the Gibbs free energy. Combined with an experimental measurement of the NH_4 -dawsonite solubility at $25 \text{ }^\circ\text{C}$ and pH 8.7, this allowed us to determine a probable order of magnitude of the NH_4 -dawsonite Gibbs free energy ($-1564 \pm 2 \text{ kJ}\cdot\text{mol}^{-1}$). This order of magnitude is all the more probable since a comparison between NH_4 -dawsonite and Na -dawsonite respective theoretical solubility curves led us to conclude that NH_4 -dawsonite Gibbs free energy should be higher than $-1600 \text{ kJ}\cdot\text{mol}^{-1}$. However, further studies will be needed to validate the actual value of this thermodynamic data: for example, a better accuracy could be achieved by determining the Gibbs free energy value from a regression of $\log(K_S) = f(T)$ after several NH_4 -dawsonite solubility measurements at various temperature and pH .

Nomenclature

C	concentration ($\text{mol}\cdot\text{L}^{-1}$)
C^*	solubility ($\text{mol}\cdot\text{L}^{-1}$)
ΔG_f^0	standard Gibbs free energy at 298.15 K ($\text{kJ}\cdot\text{mol}^{-1}$)
ΔG_r^0	Gibbs free energy of reaction at 298.15 K ($\text{kJ}\cdot\text{mol}^{-1}$)
K_a	acidic dissociation constant
K_r	equilibrium constant
K_s	solubility constant
K_w	water equilibrium constant
T	temperature (K)

Greek letters

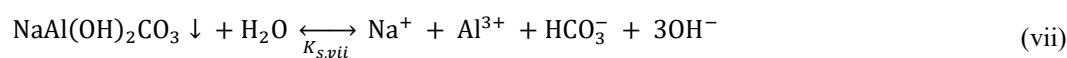
β_3 third hydrolysis constant of Al^{3+}
 ν stoichiometric number

Acknowledgements

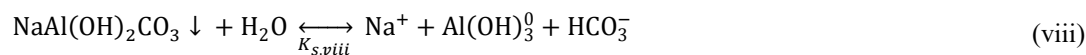
The authors would like to thank the Physics and Analysis Division (IFPEN), as well as Nathalie Palazzo, for technical assistance. This research did not receive any specific grant from funding agencies in the public, commercial, or not-for-profit sectors.

Appendix A. Calculation of Na-dawsonite solubility

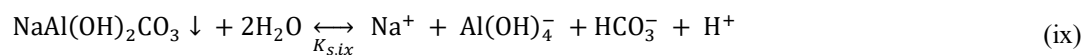
Na-dawsonite solubility was determined considering the equilibria (vii) to (ix) and following the same procedure as for NH_4 -dawsonite solubility. The total concentrations in Na^+ , noted C_{Na} , remains constant within the pH range 3–14.



$$K_{s,vii} = [Al^{3+}] \cdot [Na^+] \cdot [HCO_3^-] \cdot \frac{K_W^3}{[H^+]^3} \quad (24)$$



$$K_{s,viii} = [Al(OH)_3^0] \cdot [Na^+] \cdot [HCO_3^-] \quad (25)$$



$$K_{s,ix} = [Al(OH)_4^-] \cdot [Na^+] \cdot [HCO_3^-] \cdot [H^+] \quad (26)$$

References

- Ali, A.A., M.A. Hasan and M.I. Zaki, 2005, Dawsonite-Type Precursors for Catalytic Al, Cr, and Fe Oxides: Synthesis and Characterization, *Chem. Mater.* 17, 6797–6804.
- Bates, R. G. and G.D. Pinching, 1949, Acidic dissociation constant of ammonium ion at 0 to 50 C, and the base strength of ammonia, *J. Res. Natl. Bur. Stand.* 42, 419.
- Bénézech, P., D.A. Palmer and D.J. Wesolowski, 1997, The aqueous chemistry of aluminum. A new approach to high-temperature solubility measurements, *Geothermics* 26, 465–481.
- Bénézech, P., D.A. Palmer, L.M. Anovitz and J. Horita, 2007, Dawsonite synthesis and reevaluation of its thermodynamic properties from solubility measurements: Implications for mineral trapping of CO₂. *Geochim. Cosmochim. Acta* 71, 4438–4455.
- Bourcier, W. L., K.G. Knauss and K. J. Jackson, 1993, Aluminum hydrolysis constants to 250°C from boehmite solubility measurements, *Geochim. Cosmochim. Acta* 57, 747–762.
- Brown, D. S. and J.D. Allison, 1987, MINTEQA1, an equilibrium metal speciation model: users manual, *Environmental Prot. Agency* 92
- Chen, Q., Y. Xu and L.G. Hepler, 1991, Calorimetric study of the digestion of gibbsite, $Al(OH)_3$ (cr), and thermodynamics of aqueous aluminate ion, $Al(OH)_4^-$ (aq). *Can. J. Chem.* 69, 1685–1690.
- Duan, X., T. Kim, D. Li, J. Ma, J. and W. Zheng, 2013, Understanding the Effect Models of Ionic Liquids in the Synthesis of NH_4 -Dw and γ -AlOOH Nanostructures and Their Conversion into Porous γ -Al₂O₃, *Chem. - A Eur. J.* 19, 5924–5937.
- Dubert, D. C., J. Pérez-Ramírez and R. Garcia-Valls, 2011, Continuous Synthesis of Porous Ammonium Dawsonite Within a New Microstructured System, *Chem. Eng. Trans.* 25, 231–236.
- Ferrante, M.J., J.M. Stuve and D.W. Richardson, 1976, Thermodynamic data for synthetic dawsonite. (U.S. Bureau of Mines Report Investigation, 8129.
- Hernandez, M.J., M.A. Ulbarri, J. Cornejo, M.J. Peña and C.J. Serna, 1985, Thermal stability of aluminium hydroxycarbonates with monovalent cations, *Thermochim. Acta* 94, 257–266.

- Hu, X., Y. Liu, Z. Tang, G. Li, R. Zhao and C. Liu, 2012, Fabrication of high-surface-area γ -alumina by thermal decomposition of AACH precursor using low-temperature solid-state reaction, *Mater. Res. Bull.* 47, 4271–4277.
- Karpinski, P. H. and J.S. Wey, 2002, in *Handbook of Industrial Crystallization* 141–160
- Lafficher, R., M. Digne, F. Salvatori, M. Boualleg, D. colson and F. Puel, 2017, Ammonium aluminium carbonate hydroxide $\text{NH}_4\text{Al}(\text{OH})_2\text{CO}_3$ as an alternative route for alumina preparation: Comparison with the classical boehmite precursor, *Powder Technol.* 320, 565–573.
- Li, G.C., Y.Q. Liu, L.L. Guan, X.F. Hu and C.G. Liu, 2012 Meso/macroporous γ - Al_2O_3 fabricated by thermal decomposition of nanorods ammonium aluminium carbonate hydroxide. *Mater. Res. Bull.* 47, 1073–1079.
- Lide, D. R., 2003, *CRC Handbook of Chemistry and Physics*, 84th Edition. *Handbook of Chemistry and Physics* (CRC Press)
- Liu, H., H. Sun, J. Li, X. He and Z. Zhu, 2012a, pH-dependent formation of AACH fibers with tunable diameters and their in situ transformation to alumina nanocrystals with mesoporous structure. *Adv. Powder Technol.* 23, 164–169.
- Liu, C., J. Li, K. Liew, J. Zhu, M.R. Nordin and M. R. Bin, 2012b, An environmentally friendly method for the synthesis of nano-alumina with controllable morphologies, *RSC Adv.* 2, 8352.
- Łodziana, Z., G. Stoica and J. Pérez-Ramírez, 2011, Reevaluation of the Structure and Fundamental Physical Properties of Dawsonites by DFT Studies, *Inorg. Chem.* 50, 2590–2598.
- Ma, C.-C., X.X. Zhou, X. Xu and T. Zhu, 2001, Synthesis and thermal decomposition of ammonium aluminum carbonate hydroxide (AACH). *Mater. Chem. Phys.* 72, 374–379.
- Mersmann, A., 1999, Crystallization and precipitation. *Chem. Eng. Process. Process Intensif.* 38, 345–353.
- Nordstrom, D. K. and H.M. May, 1996, in *The Environmental Chemistry of Aluminum*, 2nd edition (ed. Sposito, G.) 39–80 (CRC Press)
- Panias, D. and A. Krestou, 2007, Effect of synthesis parameters on precipitation of nanocrystalline boehmite from aluminate solutions, *Powder Technol.* 175, 163–173.
- Pitsch, I., W. Gessner, A. Bruckner, H. Mehner, S. Mohmel, D.C. Uecker and P.P. Pohl, 2001, Synthesis and characterization of Fe_2O_3 containing aluminas by thermal decomposition of modified ammonium dawsonite, *J. Mater. Chem.* 11, 2498–2503.
- Robie, R. A., B.S. Hemingway and J.R. Fisher, 1979, *Thermodynamic Properties of Minerals and Related Substances at 198.15 K and 1 bar and at high temperatures*, USGS Bull. 1452.
- Santiago, M., M.S. Yalfani and J. Pérez-Ramírez, 2006, In-line dispersion–precipitation method for the synthesis of metal-substituted dawsonites. Genesis of oxide materials with superior properties, *J. Mater. Chem.* 16, 2886–2889.
- Schwartz, A. M. and A.S. Myerson, 2002, in *Handbook of Industrial Crystallization* 7, 1–31.
- Shin, D.-C., S.S. Park, J.H. Kim, S.S. Hong, J.M. Park, S.H. Lee, D.S. Kim and G.D. Lee, 2014, Study on α -alumina precursors prepared using different ammonium salt precipitants, *J. Ind. Eng. Chem.* 20, 1269–1275
- Stoica, G. and J. Pérez-Ramírez, 2010, Stability and inter-conversion of synthetic dawsonites in aqueous media, *Geochim. Cosmochim. Acta* 74, 7048–7058.
- Vogel, R. F., G. Marcelin and W.L. Kehl, 1984, The preparation of controlled pore alumina, *Appl. Catal.* 12, 237–248.
- Wagman, D D; W.H. Evans, V.B. Parker, R.H. Schumm and I. Halow, 1982, The NBS tables of chemical thermodynamic properties. Selected values for inorganic C1 and C2 organic substances in SI units, *J. Phys. Chem. Ref. Data* 11, 1–392.
- Yalfani, M.S., M. Santiago and J. Pérez-Ramírez, 2007 In situ studies during thermal activation of dawsonite-type compounds to oxide catalysts, *J. Mater. Chem.* 17, 1222–1229.