

# **Review of Ammonium Chloride–Water Solution Properties**

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**ABSTRACT:** Ammonium chloride is commonly used as a buffer solution to control pH levels in a wide variety of chemical and medical applications and is also used as a fertilizer because it acts as a sufficient source of nitrogen for the soil. More recently it is used to create an experimental benchmark, useful to model/simulate metal solidification. In electronics and metallurgy it is also used for cleaning, to prevent the formation of oxides during welding or smelting of metals. In the literature different values are available for the thermo-physical parameters and in the current paper an overview of measured or calculated values of the most important properties is presented. For an ammonium chloride—water solution different phase diagrams are accessible, and the calculation of the liquidus and solidus line is completed. A comparison of calculated heat capacity values for ammonium chloride is made with the literature values. Measured data for the ammonium chloride density are



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available in the literature, and the values for different temperatures and concentrations are presented here. Thermal conductivity values are gathered in the present work. The viscosity can be estimated in between 283 and 333 K and for mass fraction up to  $0.324 \text{ kg}\cdot\text{kg}^{-1}$ , with a model for the calculation of the aqueous solutions viscosity, based on the viscosity of solute and water. The variation curve of diffusivity values with the concentration, exists only for 293 and 298 K. For this reason an approximation with NH<sub>3</sub> diffusivity values, which are measured for different temperatures and concentrations, can be recommended. Additional analysis of two experimental measurements, performed in order to estimate the ammonium chloride diffusivity in water and further extract the Gibbs–Thomson coefficient, is done.

## 1. INTRODUCTION

Good knowledge of physical properties of a substance is very important to understand its behavior during phase change. In the course of metal's solidification it is not possible to see either the solid structure or the liquid melt behavior because metals are opaque. Ammonium chloride was used extensively in modeling metal solidification because it solidifies like metals, and the liquid melt has the advantage of being transparent.<sup>1–3</sup> Its melting temperature range is considerably lower that metal's melting temperature, making the operating conditions much easier for experimental studies in the laboratory. Other metal analogue alloys were used in modeling solidification, such as SCN (succinonitrile),<sup>4–11</sup> NPG-TRIS,<sup>12–16</sup> or NaCl.<sup>17,18</sup>

Besides experimental work, numerical simulation became an important tool to understand solidification. The two domains developed in parallel in order to obtain a better understanding of the solidification process. Moreover experimental studies on ammonium chloride solidification were used to validate such numerical models. For accurate numerical simulations it is crucial to have precise physical data.

Solidification is a temperature-dependent process and the main parameters in this field such as diffusivity, viscosity, and density are concentration and temperature related. A nonexhaustive list of values found in literature for these physical parameters, concerning the ammonium chloride, will be given in this paper. Recently a series of experiments were performed on the solidification of a hypereutectic ammonium chloride  $alloy^{19-23}$  in a cast cell cooled homogeneously from the three walls. Heterogeneous solidification occurred simultaneously along verticals and horizontal walls where a columnar mushy zone developed. The occurrence of equiaxed crystals was sometimes observed, and a mechanism was proposed to explain the equiaxed crystal's origin and growth in an undercooled melt for which convection is important.<sup>23</sup> With the PIV (particle image velocimetry) technique the investigation of the flow was possible in the same time as the NH<sub>4</sub>Cl columnar/equiaxed growth. Such experimental work constitutes a valuable benchmark for validating numerical models.

One of the phenomena occurring during solidification is the double-diffusive convection due to thermal and solutal buoyancy forces. To estimate the thermos-solutal buoyancy, parameters such as density, thermal and solutal expansion coefficient, and viscosity are very important to know precisely. Experimental studies on the double-diffusive convection during ammonium chloride solidification were performed by Ghenai et al.,<sup>24</sup> Nishimura and Imoto,<sup>25</sup> McCay et al.,<sup>26</sup> and Skudarnov et al.<sup>27</sup>

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The influence of the initial ammonium chloride alloy concentration on the solidification was considered in many studies. Skudarnov et al.<sup>27</sup> considered concentrations from hypo- to hypereutectic and qualitatively quantified the influence on the convection pattern. Once more density, thermal/solutal expansion coefficients, viscosity, and liquid diffusivity are playing an important role. The variation of these parameters with both temperature and concentration is at the origin of the double-diffusive convection, and thus their temperature evolution needs to be well-known.

Steady state ammonium chloride solidification with mushy zone development was considered by Pepin et al.<sup>28</sup> in a Hele-Shaw cell. Measurement of undercooling and height of the mushy region was performed, and a relation with the velocity growth was extracted. Morphological transitions were observed and a diagram considering initial solution concentration and pulling velocity in the occurrence of different growth regimes was described. Convection in the mushy layer seems to be at the origin of chimneys, and a key parameter to evaluate the convection force is the Rayleigh number. For the calculation of the Rayleigh number the density and viscosity are some of the data needed.

C. F. Chen<sup>29</sup> performed experiments on the effect of viscosity on ammonium chloride direct solidification in a Hele-Shaw cell. Viscosity is another parameter playing an important role in solidification. The melt viscosity changes with temperature and concentration, its influence should be taken into account in the Rayleigh number calculation, which represents a significant parameter in the evaluation of the melt flow.

C. Beckermann and colleagues<sup>30–34</sup> realized a significant work in both experimental and numerical investigations on ammonium chloride solidification. For numerical simulation having thermos-physical property data at desired temperatures and concentrations is required. Approximation or interpolation by linear or polynomial functions is in some cases necessary. Experimental and numerical insight on the solidification of ammonium chloride was also given by Kumar et al.<sup>35</sup>

Beside physical parameters, the phase diagram is fundamental for understanding liquid—solid phase transformation. The phase diagram is characterized by the liquidus and solidus lines and the eutectic point in the case of an alloy (two components melt). The liquidus and solidus lines provide us information about the concentration corresponding to a given temperature at the equilibrium. The liquidus lines are usually approximated with a line but they are actually curved. The slope which can be extracted from the phase diagram is very useful in calculation of liquid concentration at the solid liquid interface or far in the bulk melt. But if the liquidus line is very curved the effect on the slope is dramatic. In this case the liquidus slope is not constant anymore; it is changing with the temperature.

The eutectic point, defined by the  $C_{\rm eut}$  and  $T_{\rm eut}$ , represents the fact that the three phases (liquid and two solid components for a binary alloy) are in thermodynamical equilibrium. When a eutectic alloy will solidify, eutectic growth will occur, which means that the two phases will grow simultaneously. The near eutectic compositions present good casting properties for alloys, almost as pure metals and also excellent final product qualities. For this reason a lot of casting alloys are solidified around eutectic concentration; thus having a well-defined eutectic point is valuable. Review

Some of the above numerated parameters and examples of ammonium chloride phase diagram will be presented in this paper.

# 2. PHASE DIAGRAM, LIQUIDUS/SOLIDUS LINE, EUTECTIC POINT

In literature two phase diagrams for ammonium chloride are available. One phase diagram (Figure 1) presents only a part of



Figure 1. Ammonium chloride phase diagram. Figure reprinted with permission from ref 27. Copyright 2002 Elsevier.

the alloy concentration, where just the liquidus line is shown; the solidus line is supposed to be a vertical line at 100% ammonium chloride.<sup>27,36</sup> All through the paper the solvent for ammonium chloride solution is water. From the liquidus line we can calculate the liquidus line slope  $m_1$  and use eq 1 to calculate the liquidus temperature for any given concentration. The liquidus slope  $m_1$  calculated from the phase diagram in Figure 1 is 534 (K·kg·kg<sup>-1</sup>).

$$T_{\rm l} = m_{\rm l} \cdot (C_{\rm l} - C_{\rm eut}) + T_{\rm eut} \tag{1}$$

The second phase diagram found in the literature is complete (Figure 2) showing a liquidus line and a solidus line.<sup>37,38</sup>

It can be noticed that the liquidus line slope is steeper in the second (Figure 2) than that in the first phase diagram (Figure1). The liquidus slope calculated from the phase diagram in Figure 2 is 476.19 (K·kg·kg<sup>-1</sup>). With eq 1 and



Figure 2. Ammonium chloride complete phase diagram. Figure adapted from refs 37 and 38. Copyright 1998 and 1989 Elsevier.



Figure 3. Ammonium chloride phase diagram calculated with the FactSage<sup>39</sup> software.



Figure 4. Evolution of the ammonium chloride liquidus slope.

using  $m_{\rm b}$ ,  $T_{\rm l}$  can be calculated again. For mass fraction 0.3 NH<sub>4</sub>Cl, the liquidus temperature  $T_{\rm l}$  can be 312 K, if  $m_{\rm l}$  is extracted from first phase diagram, or 303 K, if the second phase diagram is used. These 9 K represent a large difference

and can change much in the simulation of the solidification process.

In Table 1 some values for  $m_{\rm b}$  used in the literature are gathered. The minimum value found is 461 (K·kg·kg<sup>-1</sup>)

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Table 2. Experimental <b>`</b>	Values of the Ammonium Cl	hloride Density $ ho$ , Measured	d at Different Mass Fractions and	l Temperatures <sup>**</sup>
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$w/kg\cdot kg^{-1}$	273.15 K	283.15 K	293.15 K	303.15 K	323.15 K	353.15 K	373.15 K
0.01	1003.3	1002.9	1001.3	998.7	991.0	974.9	961.7
0.02	1006.7	1006.2	1004.5	1001.8	994.0	978.0	965.1
0.04	1013.5	1012.6	1010.7	1007.7	999.9	984.2	971.8
0.08	1026.6	1025.1	1022.7	1019.5	1011.6	996.3	984.9
0.12	1039.1	1037.0	1034.4	1031.0	1023.1	1008.1	997.5
0.16	1051.0	1048.5	1045.7	1042.2	1034.3	1019.8	1009.6
0.20	1062.5	1059.6	1056.7	1053.2	1045.4	1031.2	1021.3
0.24	1073.6	1070.5	1067.4	1064.1	1056.4	1042.6	1032.7

(Beckermann and Wang<sup>31</sup> in their paper from 1996) and the maximum value is 490 (K·kg·kg<sup>-1</sup>) (Worster et al.<sup>28</sup>).

For further comparison concerning  $T_1$  and  $m_1$  we used FactSage,<sup>39</sup> a software designed for thermodynamic calculations. The phase diagram calculated with FactSage<sup>39</sup> is presented in Figure 3. The  $T_1$  calculated with FactSage<sup>39</sup> for a mass fraction of 0.3 NH<sub>4</sub>Cl is 306.58 K. Anyway the solidification temperature observed during our experimental studies is lower and respectively 300.95 K for this alloy concentration ( $w = 0.3 \text{ kg} \cdot \text{kg}^{-1}$ ).

It is very important to note that the "liquidus line" is not a straight line in the phase diagram given by FactSage.<sup>39</sup> This can explain the existence in the literature of different liquidus slopes, as for a different temperature a different liquidus slope will be obtained. The eutectic temperature and concentration are 266.361 K and 0.157 NH<sub>4</sub>Cl/H<sub>2</sub>O + NH<sub>4</sub>Cl (kg·kg<sup>-1</sup>). The liquidus line between the eutectic point and 0.40 NH<sub>4</sub>Cl/H<sub>2</sub>O + NH<sub>4</sub>Cl (kg·kg<sup>-1</sup>) was approximated by the polynomial function shown in eq 2:

$$T_l = -79.15 + 915.47C - 4593.379C^2 + 12444.29C^3 - 10448.116C^4$$
(2)

where C is the mass fraction  $NH_4Cl/H_2O + NH_4Cl (kg \cdot kg^{-1})$ (C = 1 for 100%  $NH_4Cl$ ).

Using the derivative of eq 2 we can calculate the slope of the liquidus line, and its evolution versus the temperature is plotted in Figure 4.

From Figure 4 it can be noticed that the slope is strongly changing with temperature, from a value of 230 (K·kg·kg<sup>-1</sup>) to a value of 530 (K·kg·kg<sup>-1</sup>).

The phase diagram shown in Figure 1 supposes that the solidus line is a vertical line at 1 mass fraction NH<sub>4</sub>Cl, which gives  $C_s = 1$ . The second phase diagram presented in Figure 2 gives a solidus line which is almost a vertical line at approximately 0.8 mass fraction NH<sub>4</sub>Cl, which means that the solid formed does not contain 100% NH<sub>4</sub>Cl but a mixture of water and ammonium chloride of a concentration  $C_s$  defined by the solidus line  $m_s$ . The solidus line slope is  $m_s = 1386.38$  (K· kg·kg<sup>-1</sup>). In literature papers most of the numerical simulations consider  $C_s$  (solid concentration) to be equal to 1, except Rady and Nada<sup>37</sup> and Christerson and Incropera.<sup>38</sup> The FactSage<sup>39</sup> software calculations give also  $C_s = 1$ .

Other important information that we can extract from the phase diagram are the temperature and the concentration of the eutectic point. For the  $C_{\text{eut}}$  and  $T_{\text{eut}}$  the values found in literature are  $C_{\text{eut}} = 0.197 \text{ kg} \cdot \text{kg}^{-1}$  and  $T_{\text{eut}} = 257.75 \text{ K}$ , but other values can be found too (see Table 1).

#### 3. DENSITY

The ammonium chloride density was measured for different temperatures and concentrations. The density is not a constant; it varies with temperature and concentration. The experimental values found in the literature<sup>43</sup> are presented in Table 2.

The plot of the density versus concentration, at different temperatures, is shown in Figure 5.



**Figure 5.** Evolution of the ammonium chloride density vs concentration, measured at different temperatures<sup>43</sup> ( $\blacksquare$ ) 273.15 K, ( $\bullet$ ) 283.15 K, ( $\blacktriangle$ ) 293.15 K, ( $\bigtriangleup$ ) 303.15 K, ( $\bigcirc$ ) 323.15 K, ( $\Box$ ) 353.15 K). The lines represent the linear fit to the experimental data.

For each temperature the density varies linearly with the concentration. Thus, each set of data (dots of same shape) corresponding to a certain temperature, were fitted with a linear equation (strait line).

$$\rho = \rho_T + \beta_C(T) \cdot \rho_{\text{ref}} \cdot C \tag{3}$$

where  $\rho_T$  and  $\beta_C$  (solutal expansion coefficient) are depending on the temperature. The reference density  $\rho_{ref}$  is taken constant and equal to 1000 (kg·m<sup>-3</sup>). From the linear eq 3 we extracted the values of  $\rho_T$  and  $\beta_C$ . Their evolution with the temperature is reported in Figure 6, and values are given in Table 3.

To fit the extracted values for  $\rho_T(T)$  and respectively  $\beta_C(T)$  the following polynomial functions presented in eq 4 and correspondingly eq 5 were employed:

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Figure 6. (a)  $\rho_T$  and (b) solutal expansion coefficient  $\beta_C$  values (dots), extracted from the linear fit of density with concentration, at different temperatures and their fitted polynomial functions (line).

Table 3. $\rho_T$ and Solutal Expansion Coefficient $\beta_C$ Values
Extracted from the Linear Fit of Density with Concentration,
at Different Temperatures

temp	$ ho_{\mathrm{T}}$ (T)	$\beta_{C}$ (T)
273.15 K	1001.16	0.306
283.15 K	1000.76	0.294
293.15 K	999.095	0.287
303.15 K	996.315	0.284
323.15 K	988.503	0.284
353.15 K	972.35	0.294

 $\rho_T(T) =$ 

$$1001.15503 + 0.03854 \cdot (T - 273.15) - 0.00824$$
$$\cdot (T - 273.15)^{2} + 6.06948 \cdot 10^{-5} \cdot (T - 273.15)^{3}$$
$$- 2.48971 \cdot 10^{-7} \cdot (T - 273.15)^{4}$$
(4)

$$\beta_{\rm C}(T) = 0.30602 - 0.0154 \cdot (T - 273.15) + 3.63497$$
$$\cdot 10^{-5} \cdot (T - 273.15)^2 - 3.72741 \cdot 10^{-7} \cdot (T - 273.15)^3 + 1.68757 \cdot 10^{-9} \cdot (T - 273.15)^4 \quad (5)$$

# 4. HEAT CAPACITY AND THERMAL CONDUCTIVITY

The ammonium chloride heat capacity  $c_p$  was extracted from the FactSage<sup>39</sup> software calculations. In Figure 7 a plot of the NH<sub>4</sub>Cl heat capacity for three concentrations at different temperatures is presented. It can be observed that in the solid state only small differences exist for a given concentration versus the temperature (average value  $c_p$  (solid) = 1861 (J·kg<sup>-1</sup>· K<sup>-1</sup>)). In the liquid state values are more spread. For 0.15 mass fraction NH<sub>4</sub>Cl hypoeutectic aqueous solution the heat capacity is almost constant after the eutectic point ( $T_{eut} = 266.361$  K) with an average value of  $c_p$  (liquid) = 3925 (J·kg<sup>-1</sup>·K<sup>-1</sup>). For the case of 0.30 mass fraction ammonium chloride (hypereutectic alloy the heat capacity values in the liquid are slowly descending until T = 306.55 K when the phase change (liquid—solid) takes



Figure 7. FactSage<sup>39</sup> calculations for ammonium chloride heat capacity at different mass fractions: ( $\blacktriangle$ ) 0.15, ( $\blacksquare$ ) 0.30, ( $\bigcirc$ ) 0.40, and comparison with water heat capacity ( $\Box$  H<sub>2</sub>O).

authors	$c_{p \text{ (solid)}} (J \cdot kg^{1-} \cdot K^{-1})$	$c_{p \text{ (liquid)}} (J \cdot kg^{1-} \cdot K^{-1})$	$k_{\rm s} \; ({\rm W} \cdot {\rm m}^{-1} \cdot {\rm K}^{-1})$	$k_1 (W \cdot m^{-1} \cdot K^{-1})$
Zabaras and Samanta <sup>45</sup>	1870	3249	0.393	0.468
Sanyal et al. <sup>46</sup>	1870	3249	0.393	0.468
Beckermann and Wang <sup>31</sup>	1827	3249	2.7	0.468
Pepin et al. <sup>28</sup>	$2.28 \times 10^6 (\text{J} \cdot \text{m}^{-3} \cdot \text{K}^{-1})$	$3.68 \times 10^6 (\text{J} \cdot \text{m}^{-3} \cdot \text{K}^{-1})$	2.2	0.54
		-		
	0.8904 –	-		
	0.8902			
	0.8900 -			
9	• 0.8898 – 🗖		•	
	0.8896 -	_		
	<b>6</b> 0.8894 –	U		
	0.8892 -			
	0.8890 -			
	0.8888 -			
	0.000 0.002	0.004 0.006 0.008	0.010 0.012	
		NH Cl w /kg·kg <sup>-1</sup>		

# Table 4. Specific Heat Capacity $c_p$ and Thermal Conductivity $k_s$ , $k_1$ Values Gathered from Literature

Figure 8. Viscosity measured (■) for diluted ammonium chloride solution<sup>47</sup> and comparison with calculation (□) at 298.15 K.



Figure 9. Viscosity-concentration curve for dilute solution of ammonium chloride at 308.15 K: ( $\blacksquare$ ) measurement,<sup>48</sup> ( $\bullet$ ) calculation,<sup>48</sup> ( $\square$ ) calculation,<sup>57</sup>).

place with release of latent heat and the heat capacity decreases drastically. After the complete solid change took place, the heat capacity has a constant value ( $c_p$  (solid) = 3600 (J·kg<sup>1-</sup>·K<sup>-1</sup>)). For 0.4 mass fraction NH<sub>4</sub>Cl, the  $c_p$  (liquid) values descend slowly until complete phase change (liquid–solid) will take place ( $\sim T$  = 354.15 K not shown here). Water's heat capacity values are also plotted in Figure 7, and its values are almost constant in

between 273.15 K (liquid phase) and 333.15 K (the average value for  $c_{p \text{ (liquid)}}$  is 4186 (J·kg<sup>-1</sup>·K<sup>-1</sup>)).

The National Institute of Standard and Technology (NIST) makes accessible a data plot for the heat capacity of ammonium chloride.<sup>44</sup> In some papers treating the numerical simulation of ammonium chloride, two values for the heat capacity are given, one for solid state 1870 ( $J\cdot kg^{-1}\cdot K^{-1}$ ), and one for liquid state, 3249 ( $J\cdot kg^{-1}\cdot K^{-1}$ ).<sup>45,46</sup> Beckermann and Wang<sup>31</sup> used the same



Figure 10. Ammonium chloride viscosity measured: ( $\blacksquare$ ) Sahu and Behera,<sup>49</sup> ( $\blacktriangle$ ) Monica et al.,<sup>50</sup> ( $\bigstar$ ) Getman.<sup>51</sup> Comparison with calculation: ( $\Box$ ) Sahu and Behera,<sup>49</sup> ( $\bigcirc$ ) Laliberte <sup>57</sup>, at 298.15 K.



Figure 11. Absolute ammonium chloride viscosity–concentration curves, measurements at: (a) 313.15 K and (b) 323.15 K:  $(\Box)$  Motin,<sup>52</sup> ( $\blacksquare$ ) Goldsack and Franchetto.<sup>53</sup>

value for the liquid specific heat 3249 (J·kg<sup>-1</sup>·K<sup>-1</sup>) but 1827 (J·kg<sup>-1</sup>·K<sup>-1</sup>) for the solid specific heat. In Table 4 the values found in the literature for the specific heat capacity and the thermal conductivity are gathered.

The effective thermal conductivity was calculated by Pepin et al.<sup>28</sup> and values for the ammonium chloride solution, 0.54 (W·m<sup>-1</sup>·K<sup>-1</sup>) and pure ammonium chloride solid, 2.22 (W·m<sup>-1</sup>·K<sup>-1</sup>), are found. Ramani and Beckermann<sup>30</sup> used also two values: one for the thermal conductivity of the liquid phase of 0.468 (W·m<sup>-1</sup>·K<sup>-1</sup>) and one for the solid phase of 2.7 (W·m<sup>-1</sup>·K<sup>-1</sup>). Beckermann and Viskanta<sup>32</sup> used a thermal conductivity ratio  $k^* = k_s/k_1$  (between the solid and liquid) of 4.68 (W·m<sup>-1</sup>·K<sup>-1</sup>). Zabaras and Samanta<sup>45</sup> and Sanyal et al.<sup>46</sup> used 0.393 (W·m<sup>-1</sup>·K<sup>-1</sup>) for solid ammonium chloride thermal conductivity, and 0.468 (W·m<sup>-1</sup>·K<sup>-1</sup>) for liquid ammonium chloride thermal conductivity.

## 5. VISCOSITY

Einstein in 1911 derived from the principle of hydrodynamics a linear equation between viscosity of aqueous solution and solute concentration. Finkelstein in 1930 extended this assessment and concluded that viscosity should increase proportionally to the concentration. However, for salts the deviation from linear law becomes evident and even more pronounced at low concentration.

Jones and Talley<sup>47</sup> measured the relative viscosity (the viscosity of solution with respect to the solvent) at 298.15 K for different diluted salts. They used a new method for the automatic measurement of the flow-time in a new Oswald-type quartz viscometer. Their results proved that even salts which decrease the viscosity of water at moderate concentration will increase it at sufficiently low concentration (0.05 mol·L<sup>-1</sup>). The results for the corresponding viscosity values extracted from his measurements for ammonium chloride are shown in Figure 8.

Das<sup>48</sup> in 1954, using two Oswald viscometers, performed measurements of relative viscosity for diluted solution of

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ammonium chloride at 308.15 K. He compared the experimental results with calculation obtained using Jones and Dole's equation.<sup>48</sup> Figure 9 presents the corresponding viscosity values extracted from his measurements and the computed values.

Comparison between viscosity for concentrated aqueous solutions, extracted from conductance measurements performed at 298.15 K by Sahu and Behera,<sup>49</sup> M della Monica,<sup>50</sup> and Getman<sup>51</sup> and calculations using a modified Einstein limiting equation for aqueous solutions of 1:1 electrolytes<sup>49</sup> is shown in Figure 10.

Absolute viscosity measurements for ammonium chloride solution were performed at different temperatures but only for low concentrations by Motin.<sup>52</sup> Goldsack and Franchetto<sup>53</sup> present measurements of absolute viscosity for a larger scale of concentrations and a large scale of temperatures (283.15 to 333.15 K). Comparison of their results<sup>52,53</sup> at 313.15 and 323.15 K is shown in Figure 11.

Good agreement between the viscosity values measured by Getman<sup>51</sup> in 1908 and Goldsack and Franchetto<sup>53</sup> in 1978 can be seen in Figure 12.



**Figure 12.** Viscosity–concentration curves, measurements at 283.15 K, 303.15 K, and 323.15 K (plain symbols ( $\triangle, \bullet, \blacksquare$ ) Getman<sup>51</sup> and empty symbols ( $\triangle, \circ, \Box$ ) Goldsack and Franchetto<sup>53</sup>).

The variation of the relative viscosity of supersaturated solutions of ammonium chloride with temperature was measured by Chatterji and Gopal,<sup>54</sup> and their results are shown in Figure 13.

The viscosity of the ammonium chloride solution<sup>55,56</sup> versus the concentration was measured at 393.15 K and the results are presented in Figure 14.

An analysis of all the data presented from Figure 8 to Figure 14 shows that the ammonium chloride viscosity varies with the temperature and with the concentration. Moreover it can be observed that the evolution with the concentration presents a minimum (except for diluted solutions).

Moreover a model for calculating the viscosity of aqueous solution was developed by M. Laliberte.<sup>57</sup> For ammonium chloride the model is based on several experimental data, some were presented before (Figure 8 to Figure 14), and is valid for solute concentration up to 0.324 mass fraction and temperatures in between 383.15 and 346.15 K.

Figure 15a displays the evolution of calculated ammonium chloride viscosity<sup>57</sup> for different temperatures versus the concentration. Equation 6 presents the formula used to describe the  $NH_4Cl$  viscosity:<sup>57</sup>

$$\eta_m = \eta_i^{w_i} \cdot \eta_w^{w_w} \tag{6}$$

where  $\eta_m$  is the ammonium chloride solution viscosity,  $\eta_i$  is the solute viscosity,  $\eta_w$  is the water viscosity, and  $w_i$  and  $w_w$  are solute and water mass fraction, respectively.

The viscosity of the solute and water are expressed as follows:

$$\eta_{i} = \exp\left(\frac{\nu_{1}(1-w_{i})^{\nu_{2}}+\nu_{3}}{(\nu_{4}T(^{\circ}C)+1)(\nu_{5}(1-w_{w})^{\nu_{6}}+1)}\right)$$
(7)

$$\eta_{\rm w} = \frac{T(^{\circ}{\rm C}) + 246}{(0.05594T(^{\circ}{\rm C}) + 5.2842)T(^{\circ}{\rm C}) + 137.37}$$
(8)

The factors  $\nu_1$  to  $\nu_6$  are given in Table 5.

The values measured at 283.15, 303.15, and 323.15 K, by Goldsack and Franchetto<sup>53</sup> are presented in Figure 15b, and good agreement is found with the values calculated by Laliberte.<sup>57</sup> In Figure 15c the values measured at 313.15 and 323.15 K, by Motin<sup>52</sup> are compared with Laliberte's calculation<sup>57</sup> and for concentrations up to 0.02 mass fraction (diluted solution) some deviation is observed, but for more concentrated solution good agreement can be seen.

Figures 10 and 14 show also good agreement between measured and calculated<sup>57</sup> values at 298.15 and 293.15 K. However, for a diluted solution, deviation from experimental data can be observed (Figures 8 and 9).

# 6. **DIFFUSIVITY**

6.1. Available Experimental Data. Other physical data very important in solidification are the diffusion coefficient D and the Gibbs-Thomson coefficient  $\Gamma$ . The range for these data values used in numerical simulations is large, between  $10^{-9}$ and  $10^{-10}$  for the diffusion coefficient and between  $10^{-7}$  and  $10^{-9}$  (2 orders of magnitude) for the Gibbs-Thomson coefficient (Table 1). As a first approximation, because for ammonium chloride there is not sufficient experimental data available, it is possible to assume that the ammonium chloride diffusivity is close to the  $\rm NH_3$  diffusivity. The advantage is that  $\rm NH_3$  diffusivity in water was measured  $^{58}$  for a large range of temperatures and concentrations (Figure 16). It can be observed that the diffusivity is concentration and temperature dependent, and the dependence is not linear. The Arrhenius relation, shown in eq 9 was employed to model the temperature variation of the diffusion coefficients, and it is the best correlation seen.

$$D = AT e^{-E_a/K_B T}$$
<sup>(9)</sup>

where *T* is the absolute temperature (in Kelvins), *A* is a constant pre-exponential factor,  $K_B$  is the Bolzmann constant, and  $E_a$  is the activation energy (in Joules molecule<sup>-1</sup>).

For ammonium chloride, measurements of differential diffusivity have been done only at 293.15 and 298.15 K. Two ammonium chloride solutions of different concentrations very nearly equal, were put in contact, and the diffusivity measured is equal to the differential diffusivity at the mean concentration. <sup>59,60</sup> Figure 17 presents these experimental results, and respectively the calculated integral diffusivity, <sup>59</sup> which cover the



Figure 13. Relative viscosity versus temperature for supersaturated solution of ammonium chloride: ( $\blacksquare$ ) 0.295 mass fraction NH<sub>4</sub>Cl, ( $\bullet$ ) 0.324 mass fraction NH<sub>4</sub>Cl.<sup>54</sup>



Figure 14. Ammonium chloride viscosity versus concentration measured ( $\blacksquare$ , Wolf,<sup>55</sup> Söhnel and Novotny<sup>56</sup>) and calculated ( $\Box$ , Laliberte<sup>57</sup>) at 293.15 K.

range of concentration from equilibrium until the bulk solution and are the relevant diffusivity in the case of solidification.

**6.2.** Calculation of Diffusivity with Einstein–Stock Relation. The ammonium chloride dissociates in water and forms an ion of  $NH_4^+$  and an ion of  $Cl^-$ . The size of the ion is very important and also the hydration of the ion (how many water molecules are around). The size of the single  $NH_4^+$  ion is similar to that of the single  $Cl^-$  ion (Table 6).

The Stokes–Einstein formula to calculate the mass diffusivity of a molecule in aqueous solution is given in eq 10.

$$D = \frac{K_{\rm B}T}{6\pi\eta r} \tag{10}$$

where  $K_{\rm B}$  is the Bolzmann constant,  $\eta$  is the water dynamic viscosity, and r is the ion radius.

Using this relation we can calculate the diffusivity of ammonia  $NH_4^+$  and chlorine  $Cl^-$ , in water. A comparison of

theoretical values obtained using eq 10 (for NH<sub>4</sub><sup>+</sup> and Cl<sup>-</sup>) and NH<sub>3</sub> experimental values, can be done, and the results are presented in Table 6. The measured diffusion coefficient<sup>61</sup> for a Cl<sup>-</sup> ion in water varies from  $1.38 \times 10^{-9}$  (m<sup>2</sup>·s<sup>-1</sup>) at 298.15 K to  $3.11 \times 10^{-9}$  (m<sup>2</sup>·s<sup>-1</sup>) at 333.15 K, being values that are very close to the corresponding calculated values with the relation given in eq 10 (Table 6). It should be kept in mind that the Stokes–Einstein equation overpredicts the diffusivity as it considers only one ion unhydrated, but in reality all ions are hydrated (up to four molecules of water can exist around an ammonia ion). Moreover the diffusion coefficient calculated at 298.15 and 333.15 K for one ion of ammonia is proximate to the measured<sup>58</sup> diffusion coefficient of 0 mol NH<sub>3</sub> at these temperatures.

The measured diffusion coefficient  $D_{Cl-}$  presents the lowest values for all three temperatures 293.15, 298.15, and 333.15 K, and the diffusion coefficient  $D_{NH_3}$  values are the highest measured at 293.15 and 298.15 K, but at 333.15 K these values are lower than the diffusion coefficient  $D_{NH_4}^+$ . The diffusion coefficients  $D_{NH_4}^+$  at 293.15 and 298.15 K are situated in between the  $D_{Cl-}$  and  $D_{NH_3}$  values. The existent measurement values are not easily compared because we do not dispose of values for different concentrations and different temperatures, for each ion (Cl<sup>-</sup>, NH<sub>4</sub><sup>+</sup>). However, we believe that the NH<sub>3</sub> diffusivity, th values of which are better known, can be used as a good approximation for the NH<sub>4</sub>Cl diffusivity, when other measurements or calculations are not available.

**6.3. Estimation of the Diffusivity and the Gibbs– Thomson Coefficient from the Experiments of Melt**<sup>40</sup>/ **Solidification.**<sup>62</sup> In this section two experiments of measurement of the capillary length of the ammonium chloride, used to extract the diffusivity and the Gibbs–Thomson coefficient, from Dougherty and Nunnally<sup>62</sup> and from Tanaka and Sano,<sup>40</sup> are reported and discussed. The approach to fit their results is presented, and comparison between these estimations is performed.

Dougherty and Nunnally<sup>62</sup> performed solidification experiments with an aqueous solution of ammonium chloride (0.38



**Figure 15.** (a) Evolution of calculated NH<sub>4</sub>Cl viscosity<sup>57</sup> with the concentration at different temperatures ( $\blacklozenge$ , 283.15 K;  $\bigtriangledown$ , 288.15 K;  $\blacklozenge$ , 293.15 K;  $\blacksquare$ , 303.15 K;  $\blacktriangle$ , 313.15 K;  $\blacklozenge$ , 323.15 K. (b) Comparison of measured<sup>53</sup> ( $\blacksquare$ , 283.15 K;  $\blacklozenge$ , 303.15 K;  $\bigstar$ , 323.15 K) and calculated ( $\square$ , 283.15 K;  $\bigcirc$ , 303.15 K;  $\bigtriangleup$ , 323.15 K) viscosity.<sup>57</sup> (c) Comparison of measured<sup>52</sup> ( $\blacksquare$ , 313.15 K;  $\diamondsuit$ , 323.15 K) and calculated ( $\square$ , 313.15 K;  $\bigcirc$ , 323.15 K) viscosity.<sup>57</sup>

Table 5. Factors <sup>57</sup>	$\nu_1$ to $\nu_6$	Used for	the	Calculations of	of
NH <sub>4</sub> Cl Viscosity					

factor $\nu$	
$ u_1 $	12.396
$ u_2 $	1.5039
$ u_3$	-1.7756
$ u_4$	0.23471
$ u_5 $	-2.7591
$ u_6 $	2.8408

mass fraction NH<sub>4</sub>Cl) at a saturation temperature of 344.15 K. The solution was first heated to dissolve the ammonium chloride, then kept constant for 500 s and at last cooled down (1 K/600 s) to initiate the growth. The investigation was complete in a quasi-2D glass cell ( $40 \times 10 \times 2 \text{ mm}^3$ ). At the beginning the seed was growing spherically until instabilities appeared and dendrite started to grow. To model the initial stages of growth of a sphere, eq 11 was used:

$$\frac{\mathrm{d}R}{\mathrm{d}T} = \frac{D\chi}{R} \left( \Delta - \frac{2d_0}{R} \right) \tag{11}$$

where *D* is the diffusion coefficient for NH<sub>4</sub>Cl in aqueous solution,  $\chi$  is a geometric factor ( $\chi = 1$  for a growth in all direction), *R* is the radius of the spherical seed,  $\Delta$  is the dimensionless supersaturation, and  $d_0$  is the capillary length, and the estimated value for *D*, extrapolated from experiments,<sup>60,63</sup> was  $2.5 \times 10^{-9}$  (m<sup>2</sup>·s<sup>-1</sup>). Somehow Dougherty and Nunnally considered for their transient growth dendrite an effective diffusion constant equal to 0.71D ( $\chi = 0.71$ ), because the crystal rests on the bottom plate of the cell. The supersaturation was approximated via eq 12:

$$\Delta = \frac{d\Delta}{dT}(T_{eq} - T) = C_T \Delta T$$
(12)

where  $C_T$  is estimated to be constant (0.005/K) from the fit of eq 12. The value used for  $d_0$  to fit eq 11 was  $3 \times 10^{-10}$  (m). The capillary length can be express with eq 13:



Figure 16. NH<sub>3</sub> measured diffusivity<sup>58</sup> versus temperature at different mol concentrations: ( $\blacksquare$ ) 0.0 mole fraction, ( $\bigcirc$ ) 0.053 mole fraction, ( $\blacktriangle$ ) 0.105 mole fraction, ( $\square$ ) 0.157 mole fraction, ( $\bigcirc$ ) 0.209 mole fraction, ( $\triangle$ ) 0.312 mole fraction). The strait lines correspond to the fit with the Arrhenius law.



Figure 17. Measured differential diffusivity (O, 293.15 K; 🗆, 298.15 K) and calculated integral diffusivity (•, 293.15 K; •, 298.15 K). 59,60

$$d_0 = \frac{\Gamma}{C_{\rm s} - C_{\rm eq}} \tag{13}$$

and consequently the value for The Gibbs–Thomson coefficient can be extracted,  $\Gamma = 1.86 \times 10^{-10}$  (K·m).

Tanaka and Sano<sup>40</sup> performed practically the opposite experiment than Dougherty and Nunnally,<sup>62</sup> the dissolution of an ammonium chloride crystal of initial diameter  $R = 53.2 \times 10^{-6}$  (m) (0.33 mass fraction NH<sub>4</sub>Cl, saturation temperature 321.15 K) in a glass cell ( $26 \times 50 \text{ mm}^2$ ) with a thickness of 0.5 mm on one side and 1 mm at the other side. From eq 11 we can notice that the larger is the radius of the crystal, the lower is the growth rate, thus the smaller is the crystal, the more precise are the measurements. The value for the diffusion coefficient,

2.6 × 10<sup>-9</sup> (m<sup>2</sup>·s<sup>-1</sup>), was extrapolated from literature values,<sup>64</sup> but like Dougherty, Tanaka used a geometric factor of 0.71 to reduce it, because they believe a constraint growth will take place, as the crystal rested on the bottom of the cell. To fit eq 11 Tanaka used  $d_0 = 1.59 \times 10^{-9}$  (m) and subsequently using eq 13,  $\Gamma$  was calculated to be equal to 1.06 × 10<sup>-9</sup> (K·m).

To model the growth/dissolution measured by Dougherty and Tanaka in their experiments, eq 11 was modified by taking into account the density difference between the liquid and solid phase and calculating the supersaturation differently. Equation 14 shows this new relation:

Table 6. Comparison between Different Diffusion	Coefficients	$(D_{\text{Cl}-}, D_{\text{NH}_4+}, D_{\text{NH}_5+})$	$, D_{\rm NH_4Cl})$	Calculated with	Stokes-Einstein
Relation <sup><i>a</i></sup> (eq 10) and Experimental Measurement	$5^{58-61}$				

	<i>T</i> = 293.15 K	T = 298.15  K	T = 333.15  K
$r_{\rm Cl-}$ (m)	$1.64 \cdot 10^{-10}$	$1.64 \cdot 10^{-10}$	$1.64 \cdot 10^{-10}$
$r_{\rm NH_{4^+}}$ (m)	$1.48 \cdot 10^{-10}$	$1.48 \cdot 10^{-10}$	$1.48 \cdot 10^{-10}$
$\eta_{\rm H2O}~({ m Pa} ightarrow { m s})$		$0.89 \cdot 10^{-3}$	$0.46 \cdot 10^{-3}$
$D_{\text{Cl-}}$ (calculated) (m <sup>2</sup> ·s <sup>-1</sup> )	$1.306 \cdot 10^{-9}$	$1.495 \cdot 10^{-9}$	$3.19 \cdot 10^{-9}$
$D_{\text{Cl-}} (\text{measurement})^{61} (\text{m}^2 \cdot \text{s}^{-1})$		$1.38 \cdot 10^{-9}$	$3.11 \cdot 10^{-9}$
$D_{\rm NH_{4^+}}$ (calculated) (m <sup>2</sup> ·s <sup>-1</sup> )	$0.9 \cdot 10^{-9}$	$1.657 \cdot 10^{-9}$	$3.53 \cdot 10^{-9}$
$D_{ m NH_3}~( m measurement)^{58}~( m m^2 \cdot s^{-1})$	$1.5 \cdot 10^{-9}$	$1.70 \cdot 10^{-9}$	$3.39 \cdot 10^{-9}$
$D_{ m NH_4Cl} \ ( m measurement)^{59} \ ( m m^2 \cdot  m s^{-1})$	$1.54 \cdot 10^{-9}$		
$D_{ m NH_4Cl} \ ( m measurement)^{60} \ ( m m^2 \cdot  m s^{-1})$		$1.84 \cdot 10^{-9}$	

 $a_{r_{Cl-}}^{a}r_{NH_{4}+}$  represent the radius of the chloride ion and the ammonium ion respectively;  $\eta_{H,O}$  is the water viscosity.

$$\frac{\mathrm{d}R}{\mathrm{d}T} = \frac{\rho_1}{\rho_{\rm s}} \frac{D\chi}{R} \left( \Omega - \frac{2d_0}{R} \right) \tag{14}$$

with the supersaturation  $\Omega = \frac{C_l - C_{eq} - \frac{2\Gamma}{R}}{C_s - C_{eq} - \frac{2\Gamma}{R}}$  and  $\chi = 1$  (because its value is not known when the growth is restraint). The ratio  $\frac{\rho_l}{\rho_s} = \frac{1078}{1527}$  gives exactly 0.7059, which is almost the value of the geometric factor that Dougherty and Tanaka used to reduce the diffusion coefficient extrapolated from literature values. To fit the experimental results from Dougherty (Figure 18a) and Tanaka (Figure 18b) a value of  $d_0 = 0.5 \times 10^{-9}$  (m) was used, and the extracted diffusion coefficients are  $4.5 \times 10^{-9}$  (m<sup>2</sup>·s<sup>-1</sup>) (instead of 2.5  $\times 10^{-9}$  and



Figure 18. Experimental results (dots) for the seed radius: (a) Dougherty and Nunally;<sup>62</sup> (b) Tanaka and Sano<sup>40</sup> and fitted line using our approach (eq 14).

 $2.6 \times 10^{-9} \text{ (m}^2 \cdot \text{s}^{-1})$ ). In the case of the Tanaka experiment, only the last values (from  $R = 19.74 \times 10^{-6} \text{ (m)}$ ) were used for fitting, since the rate of dissolution increased with decreasing the radius and thus the measurements are more precise. The diffusivity values found by ourselves in order to fit the experimental results of Dougherty and Tanaka are obviously larger than their values, thus we believe the geometrical factor  $\chi$  should have a value lower than 1.

The  $\Gamma$  values found by our approach (eq 14) are  $3.1 \times 10^{-10}$  (K·m) (~1.6 times the value found by Dougherty  $1.86 \times 10^{-10}$  (K·m)) and correspondingly  $3.75 \times 10^{-10}$  (K·m) (~2.8 times lower than the value of Tanaka  $1.06 \times 10^{-9}$  (K·m)).

In Figure 19 we plotted together with the NH<sub>3</sub> diffusivity values the only experimental values available for the ammonium



**Figure 19.** Diffusivity values extrapolated from measurements<sup>59,60</sup> (dots and line) for ammonium chloride concentration larger than 0.20 mass fraction NH<sub>4</sub>Cl, compared with NH<sub>3</sub> measurements at 0.157 NH<sub>3</sub> mol fraction<sup>58</sup> (filled squares), measurements from Dougherty and Nunally,<sup>62</sup> and Tanaka and Sano<sup>40</sup> (empty squares), and calculated values using eq 14 (triangles).

chloride (from Figure 17). In Figure 17 it can be observed that the diffusivity is almost constant after 0.20 mass fraction NH<sub>4</sub>Cl, thus we consider for all concentrations larger than 0.20 mass fraction NH<sub>4</sub>Cl an average value  $(1.99 \times 10^{-9} \text{ (m}^2 \cdot \text{s}^{-1}) \text{ at}$ 293.15 K and 2.26 ×  $10^{-9} \text{ (m}^2 \cdot \text{s}^{-1})$  at 298.15 K), which are plotted on Figure 19. Using these two values we extrapolated the diffusivity using the Arrhenius relation (eq 9 with A = 4.87and  $E_a = 1926.89$  (J·molecule<sup>-1</sup>)) to the two temperatures of interest 321.15 and 344.15 K, corresponding to Tanaka and Dougherty experiments. Their diffusivity values are not fitting this plot, they correspond closely to the diffusivity measured at 298.15 K, but they are far from the values corresponding to 321.15 and 344.15 K. The diffusivity values calculated with our approach (eq 14) to fit these two experiments are not on this extrapolated curve. There exists a factor of 0.73 and respectively 0.77 between our values and the extrapolated plot, which should correspond to the geometrical factor  $\chi$ . These factors are very close to the reduction factor 0.71 used by Tanaka and Dougherty in order to reduce the growth due to the flat bottom.

As a conclusion, ammonium chloride properties are very well-known including phase diagram, density, heat capacity, and viscosity. Concerning the thermal conductivity, the diffusivity, and the Gibbs—Thomson coefficient, little data are available.

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### Notes

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# NOTE ADDED AFTER ASAP PUBLICATION

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