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**Research/Technical Note**

# **Ammonium Di-Hydrogenocitrate and Mono-Hydrogenocitrate Synthesis by Citric Acid Neutralization with Ammonia Using Ethanol as Co-Solvent for the Crystallization – Swelling Test to Confirm Gases Emissions Capacity**

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**Abstract:** Citric acid is a  $\alpha$ -hydroxylated tricarboxylic acid present in abundance in lemon. More than one million tons of citric acid are industrially produced throughout the year. Our objective in this manuscript was to increase the value of the citric acid to ammonium citric acid salts by crystallization such as ammonium Di-hydrogenocitrate and ammonium mono-hydrogenocitrate. Studies and tests were carried out in this direction but the characteristic of our last process was the use of a co-solvent ethanol which proved more effective and more economical. At the end, we tested the capacity of the ammonium Di-hydrogenocitrate and the ammonium mono-hydrogenocitrate to swell a mixture and compared their capacities to the sodium bicarbonate. Results showed an excellent swelling capacity of the ammonium Di-hydrogenocitrate and ammonium mono-hydrogenocitrate to produce a uniformly very not much porous product's texture.

**Keywords:** Citric Acid, Ammonia, Ethanol, Crystallization, Co-solvent Crystallization, Ammonium Di-hydrogenocitrate, Ammonium Mono-hydrogenocitrate, Sodium Bicarbonate, Swelling Test

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## **1. Introduction**

Citric acid which is a tricarboxylic acid was neutralized by ammonia. According to the solution's pH, we obtained either ammonium Di-hydrogenocitrate either mono-hydrogenocitrate which are citric acid salts and have their future in agricultural, food and medicinal fields like calcium citrate and sodium citrate [1]. Studies on the effectiveness of the use of ethanol as co-solvent during the crystallization were made [2] and we have used this method.

Immediately, ammonium salts were formed. They were treated then we tested their capacity to swell a mixture by following a cooking procedure. Uniformly very not much porous texture was obtained which confirmed not only ammonia and carbon dioxide gases emissions but also water and molecules formations by esterification between citric acids and starches molecules.

## 2. Citric Acid

### 2.1. Citric Acid Generalities

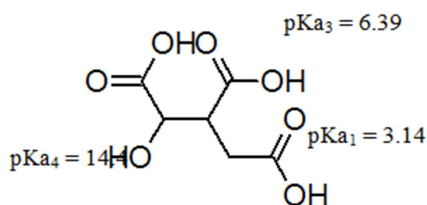


Figure 1. 3-hydroxypropane-1, 2, 3-tricarboxylic acid (Citric Acid).

Citric acid  $C_6H_8O_7$  is a tricarboxylic acid  $\alpha$ -hydrolyzed. It contains three acids with  $pK_a$  such as  $pK_{a1} = 3.14$ ,  $pK_{a2} = 4.77$  and  $pK_{a3} = 6.39$  and an  $\alpha$ -alcohol function with  $pK_a =$

14.4 [3, 4, 5, 6] "Figure 1". By its reactivity, the citric acid was the object of several studies and was used in several fields like the cosmetics, the food one, the chemistry and others [7].

We noticed that the acid form is AH with  $pK_a(AH)$ . It was shown that if the  $pH \leq [pK_a(AH) - 2]$ , the quantity of basic  $A^-$  associated to the acid/base couple  $AH/A^-$  is negligible in comparison with the AH quantity. And if the  $pH \geq [pK_a(AH) + 2]$ , the quantity of acid AH associated to the acid/base couple  $AH/A^-$  is negligible in comparison with the  $A^-$  quantity [8]. For  $[pK_a(AH) - 2] \leq pH \leq [pK_a(AH) + 2]$ , the basic  $A^-$  and the acid AH forms coexist but if  $[pK_a(AH) - 2] \leq pH \leq pK_a(AH)$  the acid form AH dominates and if  $pK_a(AH) \leq pH \leq [pK_a(AH) + 2]$  the basic form  $A^-$  dominates [8]. Consequently, for the citric acid we noted in the following Table 1 the acids and basics forms according to the  $pK_a$  and  $pH$ :

Table 1. Dominant Forms of "Citric Acid" According to the pH.

pH	Acid/base couple	$pK_a$	Acid/Base reactions	Dominant forms	Dominant molecule/Ions
$pH \leq 3.14$	$AH_3/AH_2^-$	3.14	$AH_3 \rightleftharpoons AH_2^- + H^+$	$AH_3$	Citric Acid
$3.14 \leq pH \leq 4.77$	$AH_2^-/AH^{2-}$	4.77	$AH_2^- \rightleftharpoons AH^{2-} + H^+$	$AH_2^-$	Di-Hydrogenocitrate
$4.77 \leq pH \leq 6.39$	$AH^{2-}/A^{3-}$	6.39	$AH^{2-} \rightleftharpoons A^{3-} + H^+$	$AH^{2-}$	Mono-Hydrogenocitrate
$6.39 \leq pH$	$AH^{2-}/A^{3-}$	6.39	$AH^{2-} \rightleftharpoons A^{3-} + H^+$	$A^{3-}$	Citrate

### 2.2. Characteristics of Citric Acid

Citric acid is solid with monoclinic as crystal structure, white, odorless and excessively sour flavor (Table 2) [4]. Citric acid exists in hydrates forms, the monohydrate melts towards 343.15 °K and the anhydrous state melting point is 426.15°K. Citric acid is soluble in alcohol, ether, ethyl acetate and DMSO and insoluble in  $C_6H_6$ ,  $CHCl_3$ ,  $CS_2$ , and toluene. Its solubility in ethanol at 298.15°K is 62g/100g. Citric acid is very soluble in water and its solubility increases with the temperature as shown the following table (Table 3) [9].

Table 2. Citric Acid Physicochemical Properties.

Physicochemical Properties	CITRIC ACID - $C_6H_8O_7$
Appearance	Crystalline white solid
Crystal structure	Monoclinic
Molar mass	192.12 [g.mol <sup>-1</sup> ]
Density	1.665 [g.cm <sup>-3</sup> ] anhydrous 1.542[g.cm <sup>-3</sup> ] monohydrate at 291.15°K
Melting point	426.15°K anhydrous 343.15°K monohydrate
Boiling point	448.15°K
Solubility in ethanol	62g/100g
Solubility in water	59.20% at 293.15°K (Table 3)

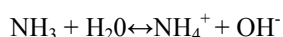
Table 3. Evolution of the Citric Acid Solubility in Water (w/w) Following to the Temperature (°K).

T°K	283.15	293.15	303.15	313.15	323.15	333.15	343.15	353.15	363.15	373.15
Solubility (% g/100mg)	54.0	59.2	64.3	68.6	70.9	73.5	76.2	78.8	81.4	84.0

## 3. Ammonia (Ammonium Hydroxide)

### 3.1. Ammonium Hydroxide Generalities

Ammonium hydroxide is a colorless aqueous solution obtained by the solubilization of ammonia in water [4, 11, 12] according to the reaction



with  $pK_a$  (Dissociation constant of the couple Acid/Base  $NH_4^+/NH_3$ ) = 9.2 [11].

We noticed again that the acid form is AH with  $pK_a(AH)$ . It

was shown that if the  $pH \leq [pK_a(AH) - 2]$ , the quantity of basic  $A^-$  associated to the acid/base couple  $AH/A^-$  is negligible in comparison with the AH quantity. And if the  $pH \geq [pK_a(AH) + 2]$ , the quantity of acid AH associated to the acid/base couple  $AH/A^-$  is negligible in comparison with the  $A^-$  quantity [8]. For  $[pK_a(AH) - 2] \leq pH \leq [pK_a(AH) + 2]$ , the basic  $A^-$  and the acid AH forms coexist but if  $[pK_a(AH) - 2] \leq pH \leq pK_a(AH)$  the acid form AH dominates and if  $pK_a(AH) \leq pH \leq [pK_a(AH) + 2]$  the basic form  $A^-$  dominates [8]. Consequently, for the ammonia we noted in the following table 4 the acids and basics forms according to the  $pK_a$  and  $pH$ :

Table 4. Dominant Forms of Ammonia in Couple Acid/Base  $NH_4^+/NH_3$  According to the pH.

pH	Acid/base couple	$pK_a$	Acid/Base reactions	Dominant forms	Dominant molecule/Ions
$pH \leq 9.2$	$NH_4^+/NH_3$	9.2	$NH_4^+ + OH^- \rightleftharpoons NH_3 + H_2O$	$NH_4^+$	Ammonia Ion
$9.2 \leq pH$	$NH_4^+/NH_3$	9.2	$NH_4^+ + OH^- \rightleftharpoons NH_3 + H_2O$	$NH_3$	Ammoniac ( $NH_3$ )

### 3.2. Characteristics of Ammonia (Ammonium Hydroxide)

The concentration of ammonia ranges up to approximately 30%. Its solution irritates eyes and suffocating odor confirms the presence of ammonium hydroxide which is relatively very volatile. The boiling point of ammonia 25% is 311.15°K [10].

Table 5. Ammonium Hydroxide Physicochemical Properties.

Physicochemical Properties	AMMONIUM HYDROXIDE – NH <sub>4</sub> OH
Appearance	Colorless liquid
Odor	Intense, pungent, suffocating odor
Molar mass	35.037 [g.mol <sup>-1</sup> ]
Density	0.90 [g.cm <sup>-3</sup> ] at 298.15°K
Melting point	215.15°K at 25%
Boiling point	311.15°K at 25%
Solubility in ethanol (95%)	Miscible
Solubility in water	Miscible

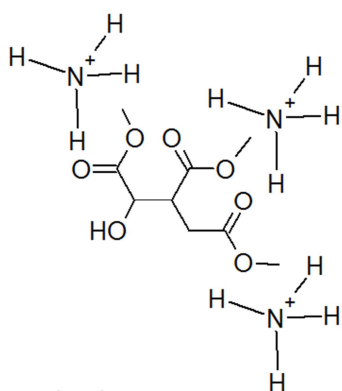


Figure 2. Ammonium Citrate.

## 4. Ammonium Citrate, Ammonium Di-hydrogenocitrate, Ammonium Mono-hydrogenocitrate

### 4.1. Ammonium Citrate (Formula and Characteristics)

The Ammonium citrate or Triammonium citrate (Figure 2) was salt obtained by acid/base reaction between citric acid (C<sub>6</sub>H<sub>8</sub>O<sub>7</sub>) as acid and ammonia (Ammonium Hydroxide - NH<sub>4</sub>OH) as base. It was shown that the respect of the couple Citric acid (acid)/Ammonia (base) solution's pH (cf. §2.1 - §3.1) (Table 1) and crystallization temperature controls led to the tri-ammonium citrate salt formation [13, 15]. We putted 150 [g] of citric acid with 234.23 [ml] of ammonium hydroxide (25%) in a baker, the solution's pH is on 9.45. According to the table 1 and the table 4, the dominant form of ions are A<sup>3-</sup> and NH<sub>4</sub><sup>+</sup>. Then, baker was carried in a 373.15 °K water bath during 60 mn to evaporate the water and to decrease the solubility of the tri-ammonium citrate formed. Then, the solution became tri-ammonium saturated and to increase the amount of this salt we brought this saturated solution to labile region which is over the metastable limit by cooling the baker on magnetic stirrer [14]. After filtration on filter paper, we obtained odorless white crystals of slightly acid tri-ammonium citrate (C<sub>6</sub>H<sub>17</sub>N<sub>3</sub>O<sub>7</sub>) [13].

### 4.2. Ammonium Di-hydrogenocitrate and Ammonium Mono-hydrogenocitrate

We synthesized the Ammonium Di-hydrogenocitrate (AH<sub>2</sub><sup>-</sup>/ NH<sub>4</sub><sup>+</sup>) and mono-hydrogenocitrate (AH<sup>2-</sup>/2NH<sub>4</sub><sup>+</sup>). We putted 250 [g] of citric acid with 39 [ml] of ammonium hydroxide (25%) in a baker, the solution's pH is on 3.55. According to the table 1 and the table 4, the dominant form of ions is AH<sub>2</sub><sup>-</sup> and NH<sub>4</sub><sup>+</sup>. Then, baker was carried in a 373.15 °K water bath during 60 mn to evaporate the water and to decrease the solubility of the Ammonium Di-hydrogenocitrate formed. Then, the solution became Ammonium Di-hydrogenocitrate saturated and to increase the amount of this salt we brought this saturated solution to labile region which is over the metastable limit by cooling the baker on magnetic stirrer [14]. After filtration on filter paper, we obtained odorless white crystals of Ammonium Di-hydrogenocitrate [Figure 3] salts which taste acid [13].

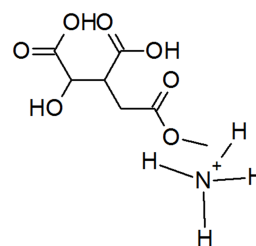


Figure 3. Ammonium Di-hydrogenocitrate.

To obtain the mono-hydrogenocitrate [Figure 4] we brought the pH of solution between 4.77 and 6.39 by putting 9.6 [g] of citric acid with 20 [ml] of ammonium hydroxide (25%) in a baker. According to the table 1 and the table 4, the dominant form of ions are AH<sup>2-</sup> and NH<sub>4</sub><sup>+</sup>. Then, baker was carried in a 373.15 °K water bath during 60 mn to evaporate the water and to decrease the solubility of the mono-hydrogenocitrate formed. Then, the solution became mono-hydrogenocitrate saturated and to increase the amount of this salt we brought this saturated solution to labile region which is over the metastable limit by cooling the baker on magnetic stirrer [14]. After filtration on filter paper, we obtained odorless white crystals of mono-hydrogenocitrate (AH<sup>2-</sup>/2 NH<sub>4</sub><sup>+</sup>) salts which taste non-acid [13].

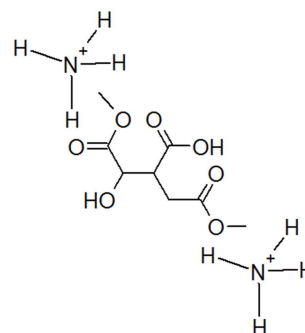


Figure 4. Ammonium Mono-hydrogenocitrate.

To summarize we put in the following figure (Figure 5) the

Ammonium citrate, Ammonium Di-hydrogenocitrate and Ammonium mono-hydrogenocitrate crystallization procedure [13]. The output of ammonium salts was all the time over 100% because of water presence (Hydrated salts – Figure 2). To limit the water presence and to improve the quality of the ammonium salts we elaborated a new procedure using a co-solvent [14] miscible with water, ammonium hydroxide, soluble in citric acid but practically insoluble in Ammonium Di-hydrogenocitrate and Ammonium mono-hydrogenocitrate: ethanol which is not only healthy but also an environmentally responsible solvent than methanol.

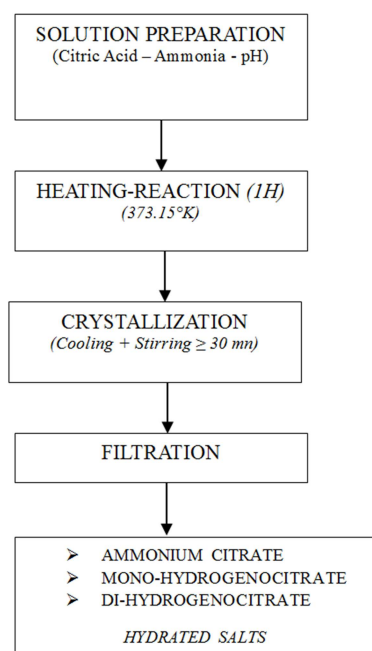


Figure 5. Ammonium Citrates Salts Crystallization Procedure.

## 5. Procedure Used for Ammonium Di-hydrogenocitrate and Mono-hydrogenocitrate Synthesis: Salts Precipitation Using the Co-solvent Ethanol

### 5.1. Equipment and Chemicals

To synthesize the Ammonium Di-hydrogenocitrate ( $\text{AH}_2^-/\text{NH}_4^+$ ) and the ammonium mono-hydrogenocitrate ( $\text{AH}^{2-}/2\text{NH}_4^+$ ) by precipitation using a co-solvent ethanol we used:

- Citric acid ( $\text{C}_6\text{H}_8\text{O}_7$ )
- Ammonium Hydroxide 25% ( $\text{NH}_4\text{OH}$ )
- Ethanol 97% ( $\text{C}_2\text{H}_5\text{OH}$ )
- Baker
- Spatula
- Precision scales
- Thermometer
- Magnetic Stirrer
- PH-meter
- Filter paper

- Funnel
- A drying oven
- Test tube

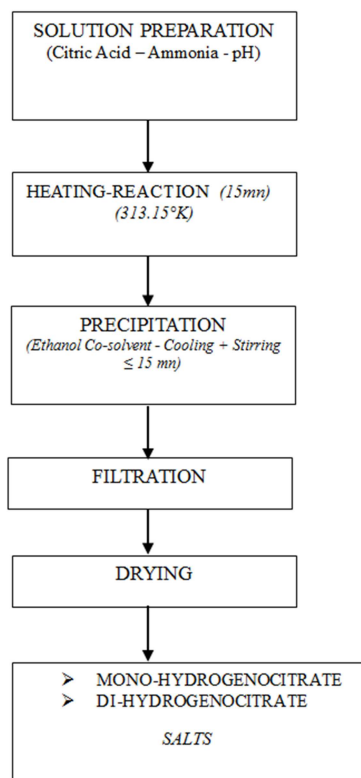
### 5.2. Procedure

We putted 62 [g] of citric acid with 9.8 [ml] of ammonium hydroxide (25%) in a baker, the solution's pH is on 3.5. According to the table 1 and the table 4, the dominant form of ions are  $\text{AH}_2^-$  and  $\text{NH}_4^+$ . Then, baker was carried in a 313.15 °K water bath during 15 mn. Critical nucleus of the new solid phase "Ammonium Di-hydrogenocitrate salt" is formed. We are on region between undersaturated regions and metastable limits. To accelerate the formation of the solid phase and to reduce its solubility in water, we cooled the baker and we used the co-solvent ethanol 97% which is not only miscible in water but also naturally cool [14, 15, 16]. It was shown that  $c^*$ , the equilibrium saturation concentration value, is empirically correlated with the concentration of the co-solvent  $x$  like  $\ln[C^*] = A+Bx+Cx^2$ . In this case, we used a quantity of ethanol which didn't bring the pH of solution more than 4.77 and stirred the solution baker. Instantaneously, the Ammonium Di-hydrogenocitrate precipitation occurs, we are on the labile region [14]. After a few minutes, we filtered the Ammonium Di-hydrogenocitrate with a filter paper and dried it in a drying oven. Knowing that the ethanol boiling point is 351.39 [°K] [17] and it's completely miscible in water with the possibility of having hydrogen bond connections with oxygens and hydrogens molecules of water and ammonium citric acid salts [18], drying with temperature higher than 358.15 [°K] is used to eliminate not only the rest of water molecules but also ethanol molecules. Then, we obtained odorless white crystals of Ammonium Di-hydrogenocitrate salts which taste acid.

To obtain the mono-hydrogenocitrate we brought the pH of solution at 5.5 (between 4.77 and 6.39 – cf. Table 1) by putting 62 [g] of citric acid with 15.8 [ml] of ammonium hydroxide (25%) in a baker. According to the table 1 and the table 4, the dominant form of ions are  $\text{AH}^{2-}$  and  $\text{NH}_4^+$ . Then, baker was carried in a 313.15 °K water bath during 15 mn. Critical nucleus of the new solid phase "Ammonium mono-hydrogenocitrate salt" is formed. We are on region between undersaturated regions and metastable limits. To accelerate the formation of the solid phase and to reduce its solubility in water, we cooled the baker and we used the co-solvent ethanol 97% which is not only miscible in water but also naturally cool [14, 15, 16]. In this case, we used a quantity of ethanol which didn't bring the pH of solution more than 6.5 and stirred the solution baker. Instantaneously, the Ammonium Di-hydrogenocitrate precipitation occurs, we are on the labile region [14]. After a few minutes, we filtered the Ammonium mono-hydrogenocitrate with a filter paper and dried it in a drying oven. Knowing that the ethanol boiling point is 351.39 [°K] [17] and it's completely miscible in water with the possibility of having hydrogen bond connections with oxygens and hydrogens molecules of water and ammonium citric acid salts [18], drying with temperature higher than 358.15 [°K] is used to eliminate not only the rest of water

molecules but also ethanol molecules. Then we obtained odorless white crystals of Ammonium mono-hydrogenocitrate salts which taste non-acid.

To summarize we put in the following figure (Figure 6) the Ammonium Di-hydrogenocitrate and Ammonium mono-hydrogenocitrate precipitation procedure using a co-solvent ethanol.



**Figure 6.** Ammonium Di-hydrogenocitrate and Ammonium MONO-hydrogenocitrate Precipitation Procedure Using a Co-solvent Ethanol.

## 6. Results

### 6.1. Ammonium Di-hydrogenocitrate and Ammonium Mono-hydrogenocitrate Yields Using Co-solvent Ethanol Precipitation Procedure

Compared with the crystallization procedure (figure 2), the precipitation procedure using a co-solvent ethanol was not

only rapid but also energetically profitable. In the following table, we show the yields of Ammonium Di-hydrogenocitrate and ammonium mono-hydrogenocitrate obtained by the precipitation procedure.

### 6.2. Ethanol Solubility of the Ammonium Di-hydrogenocitrate and the Ammonium Mono-hydrogenocitrate Obtained by Co-solvent Ethanol Precipitation Procedure

Bibliography informs us that the ammonium mono-hydrogenocitrate is very slightly soluble in ethanol [19]. To confirm this solubility to our ammonium mono-hydrogenocitrate (Table 6), we used the oversaturated method. In this case, solid in excess of the amount required for saturation is added to the solvent and agitated until apparent equilibrium is reached [14]. At ambient temperature, we took 2 [g] of ammonium mono-hydrogenocitrate into 2 [ml] of ethanol (97%) using a test tube. After prolonged agitated contact, the weight of the rest of ammonium mono-hydrogenocitrate was 1.950 [g]. That is to say, only 0.05 [g] of ammonium mono-hydrogenocitrate was soluble in ethanol (97%) and considering that the solubility of the ammonium mono-hydrogenocitrate in water is 1mg/1mg [19], this solubility is exactly 0.0485 [g] in ethanol (100%); it correspond to 2.425% of the initial weight and confirm that the ammonium mono-hydrogenocitrate is very slightly soluble in ethanol.

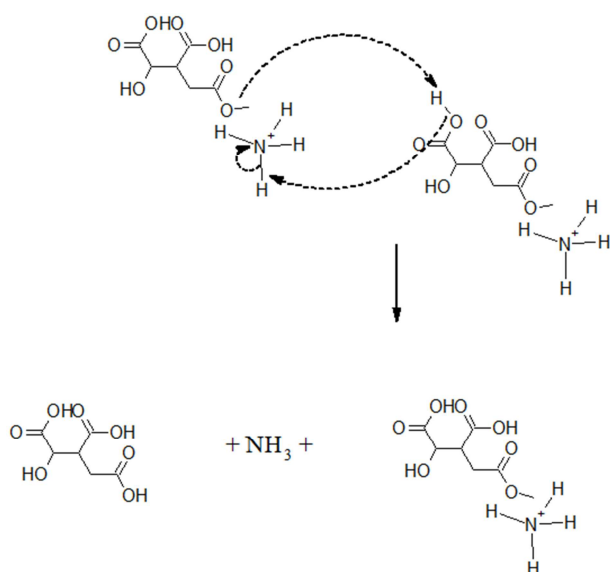
We used the same method to determine the solubility of the ammonium Di-hydrogenocitrate in ethanol. At ambient temperature, we took 2 [g] of ammonium Di-hydrogenocitrate into 2 [ml] of ethanol (97%) using a test tube. After prolonged agitated contact, the weight of the rest of ammonium mono-hydrogenocitrate was 1.935 [g]. That is to say, only 0.065 [g] of ammonium mono-hydrogenocitrate was soluble in ethanol (97%); it correspond to 3.25% of the initial weight and confirm that also the ammonium Di-hydrogenocitrate is very slightly soluble in ethanol. But, after comparison we saw that, the ammonium Di-hydrogenocitrate was more soluble in ethanol (97%) than the ammonium mono-hydrogenocitrate at ambient temperature.

**Table 6.** Ammonium Di-hydrogenocitrate and Ammonium Mono-hydrogenocitrate Yields Using Co-solvent Ethanol Precipitation Procedure.

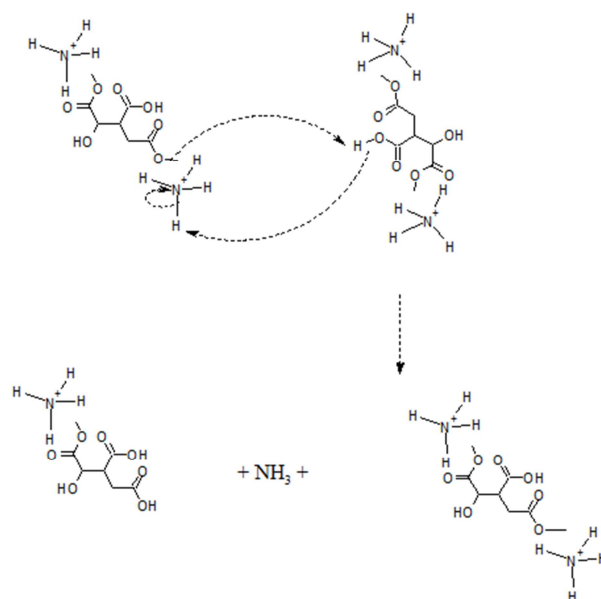
	Ammonium Di-hydrogenocitrate ( $\text{AH}_2^- / \text{NH}_4^+$ )	Ammonium mono-hydrogenocitrate ( $\text{AH}^{2-} / 2 \text{NH}_4^+$ )
Citric acid ( $\text{C}_6\text{H}_8\text{O}_7$ ) [g]	62 [g]	62 [g]
Ammonium Hydroxide 25% ( $\text{NH}_4\text{OH}$ ) [ml]	9.8 [ml]	15.8 [ml]
+ Ethanol 97% ( $\text{C}_2\text{H}_5\text{OH}$ ) (Co-solvent)	25 [ml] (pH < 4.77)	25 [ml] (pH < 6.5)
Solution pH	pH $\approx$ 3.5 (< 4.77)	pH $\approx$ 5.5 (< 6.5)
Yields (%)	77.42 [%]	82.26 [%]
	Ammonium Di-hydrogenocitrate ( $\text{AH}_2^- / \text{NH}_4^+$ )	Ammonium mono-hydrogenocitrate ( $\text{AH}^{2-} / 2 \text{NH}_4^+$ )
Citric acid ( $\text{C}_6\text{H}_8\text{O}_7$ ) [g]	62 [g]	62 [g]
Ammonium Hydroxide 25% ( $\text{NH}_4\text{OH}$ ) [ml]	9.8 [ml]	15.8 [ml]
+ Ethanol 97% ( $\text{C}_2\text{H}_5\text{OH}$ ) (Co-solvent)	25 [ml] (pH < 4.77)	25 [ml] (pH < 6.5)
Solution pH	pH $\approx$ 3.5 (< 4.77)	pH $\approx$ 5.5 (< 6.5)
Yields (%)	77.42 [%]	82.26 [%]

## 7. Swelling Tests of the Ammonium Di-hydrogenocitrate and Mono-hydrogenocitrate Salts

The objective of this part was to test the capacity of the Ammonium Di-hydrogenocitrate and the Ammonium mono-hydrogenocitrate to swell a mixture. As we see, these salts contains ammonium function (from  $-ONH_4$ ) (Figure 3 - Figure 4) which can generate the ammonia ( $NH_3$ ) (Table 4 – Table 5) and acids functions (from the citric acid function) which catalyzed the ammonia reactions formation (Figure 7 – Figure 8) [20]. In addition, we noticed that according to the Van't Hoff equation the pKa value was influenced by the temperature [21]. In the end, we compared these salts and the sodium bicarbonate baking powder (rising powder) capacity to swell a mixture.



**Figure 7.** Ammonia and Citric Acid Formed by Ammonium Di-hydrogenocitrate Transformation.



**Figure 8.** Ammonia and Ammonium Mono-hydrogenocitrate Formed by Ammonium Mono-hydrogenocitrate Transformation.

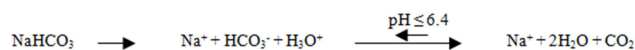
With water, we noticed that the ammonia can formed  $NH_4OH$  according to the pH and the temperature (Table 4 – Table 5) [21].

### 7.1. Sodium Bicarbonate and Ammonium Bicarbonate Baking Powder Swelling Characteristics

Baking powders are white powders used to swell biscuits and pastry during cooking. According to their natures, they produced carbon dioxide (Sodium bicarbonate – Figure 9) and or ammonia (Ammonium bicarbonate – Figure 10) with water. The paste swelled and developed. Then, cavities and pores was been left by these gases and steams emission (Table 7) - [22].

**Table 7.** Dominant Forms of  $CO_2$  in Couple Acid/Base  $H_2O$ ,  $CO_2/HCO_3^-$  According to the pH. [11].

pH	Acid/base couple	pKa	Acid/Base reactions	Dominant forms
$pH \leq 6.4$	$H_2O$ , $CO_2/HCO_3^-$	6.4	$H_2O + CO_2 + H_2O \rightleftharpoons HCO_3^- + H^+ + H_2O$	$H_2O$ , $CO_2$
$6.4 \leq pH$	$H_2O$ , $CO_2/HCO_3^-$	6.4	$H_2O + CO_2 + H_2O \rightleftharpoons HCO_3^- + H^+ + H_2O$	$HCO_3^-$



**Figure 9.** Decomposition Reaction of the Sodium Bicarbonate.



**Figure 10.** Decomposition Reaction of the Ammonium Bicarbonate.

According to the figure 7, figure 8 and figure 9 we showed in the following table 8 the theoretical swelling capacity of the ammonium Di-hydrogenocitrate, the ammonium mono-hydrogenocitrate and the sodium bicarbonate by respectively  $NH_3$  and  $CO_2$  gas emission with water.

**Table 8.** Theoretical Swelling Capacity of Salts.

SALTS	SALTS Quantity		$NH_3$ gas emission		$CO_2$ gas emission		Water	
	Mass [g]	Moles	Mass [g]	Moles	Mass [g]	Moles	Mass [g]	Moles
$(AH_2^-/NH_4^+)$	1	$4.782 \times 10^{-3}$	$8.13 \times 10^{-2}$	$4.782 \times 10^{-3}$	-	-	-	-
$(AH_2^-/2 NH_4^+)$	1	$4.422 \times 10^{-3}$	$15.04 \times 10^{-2}$	$8.845 \times 10^{-3}$	-	-	-	-
$NaHCO_3$	1	$11.905 \times 10^{-3}$	-	-	$52.8 \times 10^{-2}$	$11.905 \times 10^{-3}$	$43.2 \times 10^{-2}$	$23.81 \times 10^{-3}$

We noticed that at the same quantity 1 [g], the  $\text{NaHCO}_3$  salt should have 2.5 times and 1.4 times capacity to swell than respectively the ammonium Di-hydrogenocitrate and the ammonium mono-hydrogenocitrate salts considering only the  $\text{NH}_3$  and  $\text{CO}_2$  gas emission. However, it was shown that

water was not only the solvent which is the responsible of the ingredients repartition but its evaporation was also responsible of the porous formation [22]. Consequently, the ammonium Di-hydrogenocitrate and the ammonium mono-hydrogenocitrate should have respectively less 7.5 times and 4.1 times capacity to swell than the sodium carbonate. Discussions and explanations about the swelling salts capacities will be broached at the paragraph 7.3.

## 7.2. Cooking Procedure

During the swelling capacity tests of ammonium Di-hydrogenocitrate and ammonium mono-hydrogenocitrate in comparison with sodium bicarbonate [23]. We adopted the following cooking procedure: we preheated the oven at 423.15 [°K] and prepared the mixture in the cake pan. When

the 423.15°C was stable we putted the mixture in the oven. We progressively increased the temperature at 473.15°C. The cooking at 473.15°C lasted 30 [mn] after which we took out the product obtained.

## 7.3. Tests Results and Comparisons, Discussions

About the swelling tests, we prepared cake pastries using respectively 3 [g] of ammonium Di-hydrogenocitrate, ammonium mono-hydrogenocitrate and sodium carbonate. Then, we adopted the cooking procedure previously described [23]. We noticed that flour is the pastry principal ingredient which is compound with starch (70%), water (16%), Gluten (11%), Sugar (2%) and fatty substance (1%) [4]. We noticed also that the pastry height in the cake pan before cooking was all the time equal to 15 [mm] and for each salts we read not only the pastry height after the cooking procedure but also its taste and texture to assess each salts swelling capacity. We showed in the following table (Table 9) the tests results and comparisons for all salts [23].

Table 9. Results of Swelling Capacity Salts Tests.

	Without salt	$(\text{AH}_2/\text{NH}_4^+)$ 100%	$(\text{AH}^{2-}/2 \text{NH}_4^+)$ 100%	$\text{NaHCO}_3$ 100%	$(\text{AH}_2/\text{NH}_4^+)$ 75% $\text{NaHCO}_3$ 25%	$(\text{AH}_2/\text{NH}_4^+)$ 50% $\text{NaHCO}_3$ 50%	$(\text{AH}^{2-}/2 \text{NH}_4^+)$ 50% $\text{NaHCO}_3$ 50%
Mixture height [mm]	15	15	15	15	15	15	15
Cake height [mm]	18	22	23	35	29	32	33
Height increase (HI) in comparison with Without salt [mm]	0	4	5	17	11	14	15
$\text{NaHCO}_3$ (HI) / Ammonium salts (HI)	-	4.25	3.4	1	1.55	1.21	1.13
Taste	Neutral	Acid	Acid	Neutral	Lightly Acid	Very Lightly Acid	Very Lightly Acid
Texture	Very compact	Uniformly Very Not much porous	Uniformly Very Not much porous	Porous	Uniformly Not much porous	Uniformly Not much porous	Uniformly Not much porous

According to the results in the table 9, the ammonium Di-hydrogenocitrate had 4.25 times less capacity to swell than the sodium carbonate but theoretically we was in a hurry for 7.5 times (cf. § 7.1). It was the same for the ammonium mono-hydrogenocitrate which had 3.4 times less capacity to swell than the sodium carbonate but theoretically we was in a hurry for 4.1 times (cf. § 7.1). These results was due to the water molecules and carbon dioxide  $\text{CO}_2$  formations from the ammonium Di-hydrogenocitrate and the ammonium mono-hydrogenocitrate. Water molecules formed are solvent and responsible of the ingredients repartition until the ammonium salts evaporation to form porous particularly uniform (Table 9). For these ammonium Di-hydrogenocitrate and the ammonium mono-hydrogenocitrate, water and carbon dioxide molecules were formed either by their dehydration and decarboxylation like a citric acid [13-24-26], either by the dehydration and decarboxylation of citric acid molecules formed (figure 7) and either by the esterification reaction [24] between the acid of the citric acid formed and the starch's alcohol functions [27-28] according to the figure

11. That explained the uniformly very not much porous of the ammonium Di-hydrogenocitrate and mono-hydrogenocitrate salts samples texture (table 9).

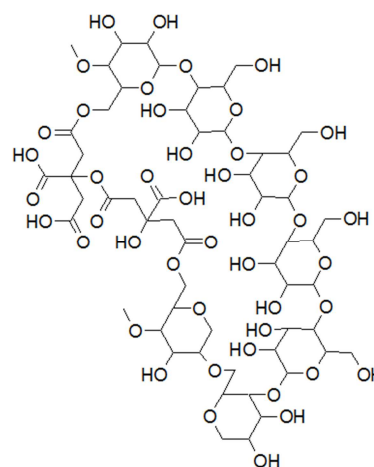
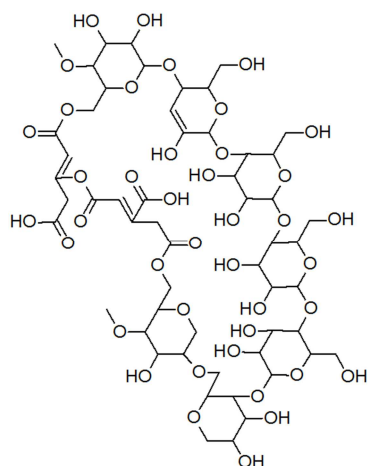


Figure 11. Esterification reactions Between Citric Acids and Starches Molecules.



**Figure 12.** Dehydration and decarboxylation of alcohol and acid functions of the figure 11 molecule to obtain alkenes.

## 8. Conclusion

The crystallization of the ammonium Di-hydrogenocitrate and the ammonium mono-hydrogenocitrate obtained by the ammonia and the citric acid reaction using an ethanol as co-solvent while respecting the pH rule was not only easier but also energetically economical. The swelling test capacity of these salts by following a cooking procedure informed us the gases emissions like ammonia, carbon dioxide, water vapor and consequently the real formation of water molecules by esterification between citric acids and starches molecules. The molecules formed by this esterification reaction like the one showed by the figure 11 was interesting because in certain conditions like the cooking procedure that we adopted on the paragraph §7.2, they are potential source of water molecules and carbon dioxide by dehydration and decarboxylation reactions (figure 12). Being given that the ammonium Di-hydrogenocitrate and the ammonium mono-hydrogenocitrate contains azote and citric acid which plays a significant role in biochemistry as metabolite of the Krebs' cycle, a major metabolic way at all the aerobic organism, it's possible in certain conditions to use these salts as fertilizer supplements.

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