



ORIGINAL ARTICLE

Relationships between structures of surfactants and their anti-hygroscopicity performance of ammonium nitrate particles

Baha I. Elzaki^{a,b,*}, Zhang Yue Jun^b

^a School of Chemical Engineering, Nanjing University of Science and Technology, Nanjing 210094, Jiangsu, China

^b Department of Chemical Engineering, College of Engineering, Karary University, Omdurman 12304, Sudan

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Abstract The coating processing condition was used for the research of coating ammonium nitrate particles by means of the surfactants as coating materials which have the same polar heads with different non-polar straight hydrocarbon tails or the same non-polar straight hydrocarbon tails with different polar heads, in order to investigate the relationships between structures of surfactants and their anti-hygroscopicity used in ammonium nitrate particles coated. Furthermore, the relationships and possibly mechanism were analyzed and discussed based on both the experimental results and the selected coating processing, basic property of materials and behaviors of material in coating processes. The experimental results indicated that, the anti-hygroscopicity performance of C₁₆-alcohol and C₁₈-acid were best ones within the all groups of selected surfactants with polar heads. The best declines of hygroscopicity of ammonium nitrate particles coated were 29.26% for C₁₆-alcohol and 24.0% for C₁₈-acid. And for the later, the anti-hygroscopicity performance of C₁₈-acid and C₂₀-acid were best ones within the all groups of selected surfactants with longer tails, and that of C₁₆-alcohol and C₁₄-amine were best ones with shorter tails, their best declines were 24.0%, 20.39%, 29.26% and 18.6%, respectively. The mechanism analysis results indicated that the decline of hygroscopicity were influenced by both the coating processing condition and the material properties, such as the polarity, hygroscopicity, solubility in solvents and especially the surfactivity of the used surfactants, and the later, i.e. the material properties would play an important role when the processing condition and solvent used in coating ammonium nitrate particles were fixed. Therefore, the property of coating materials which are depending on their structures and the behaviours of coating material molecules in coating processes dominated commonly and ultimately anti-hygroscopicity of coated ammonium nitrate particles, under a selected coating pro-

* Corresponding author at: School of Chemical Engineering, Nanjing University of Science and Technology, Nanjing 210094, Jiangsu, China
E-mail address: bahaelzaki@njjust.edu.cn (B.I. Elzaki).

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cessing condition. This work provides new insights on understanding the relationship between structure of surfactants and anti-hygroscopicity performance to further improve the anti-hygroscopicity performance of ammonium nitrate particles.

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1. Introduction

Ammonium nitrate (NH_4NO_3) is presently used as a source of ammonia, essentially to plant growth in the form of nitrogen fertilizer (Sitkiewicz-Wołodko et al., 2019; Zarebska et al., 2015). It is also as a major component in the most industrial explosives, such as amatol and ammonium nitrate fuel oil (ANFO). Especially, as an oxidant component, it can be used in rocket propellants of low smoking, but the hygroscopicity of ammonium nitrate particles has largely limit its application (Kohga and Handa, 2016; Kohga et al., 2019; Vargeese et al., 2014). Therefore AN particles will become a possible replacement after treatment its drawbacks such as hygroscopicity (Elzaki and Zhang, 2020). Ammonium nitrate particles are known to have five polymorphic forms at ordinary pressure, however, phase transitions between them are very complicated in the presence of a small amount of moisture or certain surface active agents (Vyazanova et al., 2017). The phase transition in pure AN particles can also occur at different temperatures as demonstrated in Fig. 1.2 (Maheshwari and Dhathathreyan, 2004; Zeng and Bernstein, 2019) Three of these phases (commonly referred to as phases VII, V, and IV) occur in the temperature range from -50 to 32 °C with the transition points (VI to VII) at approximately -50 °C and temperature from phase IV to V at -18 °C. The highest temperature phase (phase I) is analogous to the plastic phase observed in many molecular crystals because large reorientations of both NH_4^+ and NO_3^- ions occur (Asgari et al., 2018; Kaniewski et al., 2019).

A surfactant is an amphipathic molecule that consists of a non-polar hydrophobic tail, usually a straight or branched hydrocarbon or fluorocarbon chain containing 8–18 carbon atoms or more, which is attached to a polar or ionic head (hydrophilic) (Adamson and Gast, 1967; Tagavifar et al., 2018). Therefore, the hydrophilic portion can be nonionic, ionic or zwitterionic, and accompanied by counter ions in the last two cases (Luo and Nguyen, 2017; Nam et al., 2014). The hydrocarbon chain interacts weakly with the water molecules in an aqueous environment, whereas the polar or ionic head interacts strongly with water molecules by dipole or ion–dipole interactions. It is this strong interaction of hydrocarbon chain with the water molecules which renders the surfactant soluble in water (Krawczyk, 2018; Shinoda et al., 2016; Striolo, 2019).

There have been a lot of researches done on the surface modification of AN particles, and there are many types of researches on the anti-hygroscopic of AN particle. For example, adding an inorganic salt to the AN particle improves its anti-agglomeration by changing its lattice structure. Moreover, adding an inert powder or a waterproofing material can form an isolation layer between the AN particles, preventing particles bonding, and reducing agglomeration (Bharti and Chalia, 2016; Mannion, xxxx; Tan et al., 2015). Adding surfactants can reduce

the surface polarity of AN particles to improve anti-hygroscopic properties (Gezerman and Çorbacioğlu, 2015; Hai, 2012). In addition, the polymer materials are used to coat the surface of AN particle, so that the formation of hydrophobic film can enhance its anti-hygroscopic properties and so on (Lu and Yang, 2010; Peng and Nguyen, 2020; Wang et al., 2016). In this study, the research on comparison of surfactants with same polar heads and different chain length of tails and comparison of surfactants with the same tails and different polar heads are investigated and discussed to get the relationships between structures of surfactants and their anti-hygroscopicity performance when used for coating AN particles, in order to use this knowledge for processing improvement and for different application of coated AN particles. Based on the design idea, this paper consists of four parts: firstly, the standard experimental conditions will be selected, secondly, comparison of anti-hygroscopicity of surfactants with the same polar heads and different chain length of tails will be investigated, thirdly, comparison of anti-hygroscopicity of surfactant with the same non-polar tails and different polar heads will be investigated, fourthly, the relationships between same head of surfactant with different tails and their performance or between same tail with different heads and their performance will be discussed. And the possible mechanism will be discussed on basis of the surfactant molecular structures and property, as well as their behavior in a coating process.

2. Materials and method

2.1. Materials

The specifications of experimental materials used in this paper for coating process such as cyclohexane and chloroform as solvents, and surfactants materials (alcohol, acid, amine and amide surfactant with different tails C_{12} – C_{22}), as coating materials, as shown in Table 1.

2.2. Method

2.2.1. Coating process procedure

Based on the exploration experiments and the selection of surfactants and coating processing conditions, it is necessary to determine the basic operating conditions for the experimental study on processing improvement through coating AN particles with surfactants to reduce the hygroscopicity (Elzaki and Zhang, 2019). AN particles with the size 70–140 mesh placed in an oven at 100 °C. The drying process AN particle carried out, to ensure that AN particle completely dry. The grinded AN particle removed after 1 h, and AN particle placed in a desiccator containing silica gel to saved and used as raw materials for the coating processing. Therefore, the experimental

Table 1 Experimental materials and specifications.

Name	Specifications %	Manufacturer
Ammonium nitrate	≥99.0	Kecheng Fine Chemical CO. Ltd, China
chloroform	≥99.0	Shanghai Ling Feng Chemical Reagent Co. LTD, China
cyclohexane	≥99.5	Kelong Chemical Reagent, Chengdu, China
C ₁₄ -alcohol	≥97.0	Aladdin Industrial Corporation, Shanghai, China
C ₁₆ -alcohol	≥98.0	Kelong Chemical Reagent, Chengdu, China
C ₁₈ -alcohol	≥99.0	Aladdin Industrial Corporation, Shanghai, China
C ₂₀ -alcohol	≥95.0	Meryer Chemical Technology Co. Ltd. Shanghai, China
C ₂₂ -alcohol	≥98.0	Meryer Chemical Technology Co. Ltd. Shanghai, China
C ₁₂ -acid	≥98.5	Kelong Chemical Reagent, Chengdu, China
C ₁₄ -acid	≥97.0	Aladdin Industrial Corporation, Shanghai, China
C ₁₆ -acid	≥99.0	Kelong Chemical Reagent, Chengdu, China
C ₁₈ -acid	≥99.0	Kelong Chemical Reagent, Chengdu, China
C ₂₀ -acid	≥99.0	Meryer Chemical Technology Co. Ltd. Shanghai, China
C ₂₂ -acid	≥85.0	Meryer Chemical Technology Co. Ltd. Shanghai, China
C ₁₂ -amine	98.0	Aladdin Industrial Corporation, Shanghai, China
C ₁₄ -amine	≥95.0	TCI (Shanghai) Development Co. Ltd. Shanghai, China
C ₁₆ -amine	90.0	Aladdin Industrial Corporation, Shanghai, China
C ₁₈ -amine	90.0	Aladdin Industrial Corporation, Shanghai, China
C ₁₂ -amide	≥96.0	Tokyo Chemical Industry Co. Ltd, Tokyo, Japan
C ₁₄ -amide	98.0	Alfa Aesar Chemical Co. Ltd, Tianjin, China
C ₁₆ -amide	≥95.0	Tokyo Chemical Industry Co. Ltd, Tokyo, Japan
C ₁₈ -amide	≥90.0	TCI (Shanghai) Development Co. Ltd. Shanghai, China
C ₂₀ -amide	≥75.0	TCI (Shanghai) Development Co. Ltd. Shanghai, China
Deionized water	–	Nanjing university of science and technology water center

procedures were used as basic operating conditions on processing improvement through coating AN particles with surfactants as the following:

- (1) Adding mixture of solvents consisting of 15 ml chloroform and 15 ml cyclohexane to 50 ml four-necked flask, then, 1.5 g of surfactant material was added, until the surfactant was completely dissolved under stirring. 6.0 g of ammonium nitrate particles were added to a surfactant solution in the four-necked flask.
- (2) The flask was placed in water bath for heating to temperature 60 °C. When the solution temperature rose to 60 °C, the coating process started and maintained for 2.0 h at this temperature, and then the temperature was gradually decreased within 8.0 h to 30 °C after stopping bath heating, through the water of in bath heating changed, and when the temperature reached to 25 °C, the coating process finished.
- (3) The coated sample was filtered in a sand core filter funnel, until to the last drop of solvents. Then coated AN particles were spreaded on a big glass dish for air-dried of 2.0 min, and the dish was placed in an oven for 1.0 h, at a certain temperature with consideration of the melting point of each used surfactant.
- (4) The hygroscopicity test was carried out under the conditions 5.0 g consideration of coated AN particles in a 60x30 weighing bottle was placed in desiccator with a saturated solution of strontium chloride (RH = 68%), at 35 °C in an oven for 24 h.

2.2.2. Evaluation of results

The evaluation indexes of the samples are mainly the decline of hygroscopicity and the mass ratio of the coating layer. In this part the measurement of moisture absorption rate and determination method of the mass ratio of coating layer will be explained as the following.

2.2.3. Measurement of moisture absorption rate.

The moisture absorption rate refers to the mass percentage of hygroscopic increment of a substance over a period of time under a constant temperature and a relative humidity conditions (Elzaki and Zhang, 2019). According to (GJB770B-, 2005) “hygroscopicity - dryer balance method” (Hu et al., 2006);, the measurement method of moisture absorption rate for 5 g ammonium nitrate particles will be used. The hygroscopicity test conditions are selected based on literature (GJB770B-, 2005): the temperature is 35 °C, the relative humidity is 68% and hygroscopicity test time is 24 h. Hygroscopicity rate formula is shown as formula (1).

$$HR = \frac{M - M_0}{M_0} \times 100\% \quad (1)$$

where: *HR*- moisture absorption rate, %

M₀- The weight of sample before absorbing moisture, g

M- The weight of the sample after absorbing moisture, g

Meanwhile, according to the above method of measurement (formula 1), the decline of the hygroscopicity of ammonium nitrate samples will be calculated by formula (2) (GJB770B-, 2005) as follows:

$$A = \frac{HR_1 - HR}{HR_1} \times 100\% \quad (2)$$

where: A - decline of hygroscopicity, %

HR_1 - absorption rate of blank AN sample, %

HR - absorption rate of coated AN sample, %

2.2.4. Measurement method of the mass ratio of coating layer

The measurement method of the mass ratio of the coating layer was improved to achieve more accuracy than the reported in previous literature (GJB770B-, 2005) as following steps:

Firstly, a filter paper of 18 cm diameter was wetted with deionized water.

Secondly, the filter paper was placed into an oven for 1 h at the temperature 100 °C, then the filter paper was weighed (W_B).

Thirdly, the sample of the coated AN particles after testing hygroscopicity was dissolved in deionized water for removing AN particles, and the water was filtered through a tapered funnel with the filter paper, and the filter paper with surfactant (residues) was washed several times with deionized water, and then placed in an oven at 100 °C for 1 h.

Finally, the filter paper containing residues was weighed again (W_A).

The mass ratio of the coating layer calculated by formula (3) is as following:

$$W = \frac{M_1}{M_0} \times 100 \quad (3)$$

where: W - mass ratio of coating layer to AN particles, %

M_0 - Blank AN particles, g

M_1 - The weight of coating layer ($W_A - W_B$), g

3. Results

3.1. Comparison of surfactants with the same polar heads

3.1.1. Comparison of surfactants with alcohol polar heads

The experiments were conducted by using alcohol surfactants according to coating process procedure, the coating process conditions were unchanged to study the relationship between

surfactants with both same alcohol heads and different tails and their anti-hygroscopicity performance. The decline of the hygroscopicity was used as evaluation index for the anti-hygroscopicity performance of coated AN particles. The hygroscopicity testing conditions same as before were that a temperature was 35 °C, a relative humidity was 68% and hygroscopicity test time was 24 h. Under these conditions, the results obtained from hygroscopicity test are shown in Fig. 1, for AN particles coated by alcohol surfactants (C₁₄-C₂₂).

As showed in Fig. 1, C₁₄-alcohol, C₁₆-alcohol, C₁₈-alcohol, C₂₀-alcohol, and C₂₂-alcohol were used as coating materials. The data from hygroscopicity tests indicated that the best results of AN particles coated by C₁₆-alcohol was recorded when the moisture absorption rate was decreased, the mass ratio of coating layer of 1.35%, and highest decline of hygroscopicity was 29.26%. C₁₈-alcohol and C₂₀-alcohol were found to be the second and third superior results, respectively, while C₂₂-alcohol and C₁₄-alcohol followed the order in sequence.

3.1.2. Comparison of surfactants with acid polar heads

The experiments were conducted by using acid surfactants, in order to investigate the relationship of surfactants with both same polar acid heads and different tails and their anti-hygroscopicity performance. The experiments were carried on according to coating process procedure, the coating process conditions and hygroscopicity testing conditions were unchanged. The results obtained from hygroscopicity test are shown in Fig. 2, for AN particles coated by acids surfactants (C₁₂-C₂₂). The decline of hygroscopicity was used as evaluation index for the anti-hygroscopicity performance of coated AN particles.

As showed in Fig. 2, C₁₂-acid, C₁₄-acid, C₁₆-acid, C₁₈-acid, C₂₀-acid and C₂₂-acid were used as coating materials. The data from hygroscopicity tests indicated that the best results of AN particles coated by C₁₈-acid was recorded when the moisture absorption rate was decreased, the mass ratio of coating layer was 0.67%, and highest decline of hygroscopicity was 18.0%. C₂₀-acid and C₁₆-acid were found to be the second and third superior results, respectively, while C₂₂-acid, C₁₄-acid, and C₁₂-acid followed the order in sequence.

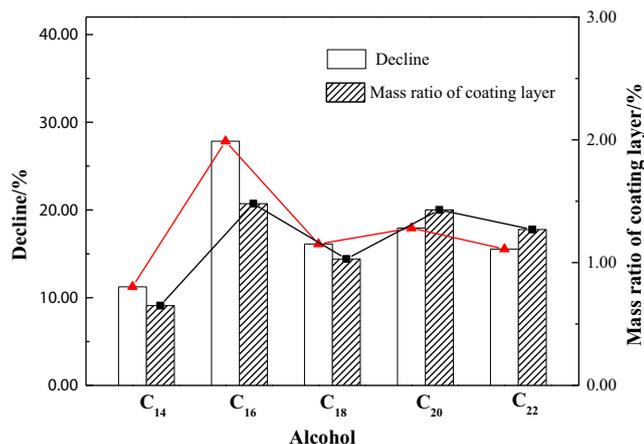


Fig. 1 Comparison of surfactants with the same polar heads (alcohol).

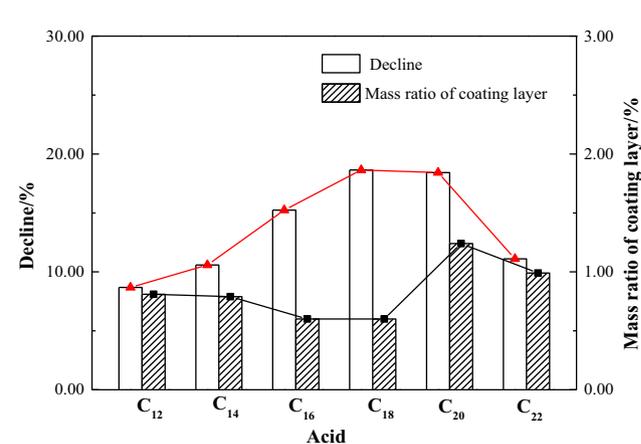


Fig. 2 Comparison of surfactants with the same polar heads (acid).

3.1.3. Comparison of surfactants with amine polar heads

The experiments were conducted by using amine surfactants, in order to investigate the relationship of surfactants with both same polar amine heads and different tails and their anti-hygroscopicity performance. The experiments were carried on according to coating process procedure, the coating process conditions and hygroscopicity testing conditions same as before were unchanged. The results obtained from hygroscopicity test are shown in table and Fig. 3, for AN particles coated by amine surfactants (C_{12} , C_{14} , C_{16} and C_{18}). The decline of hygroscopicity was used as evaluation index for the anti-hygroscopicity performance of coated AN particles.

As showed in Fig. 3, C_{12} -amine, C_{14} -amine, C_{16} -amine, and C_{18} -amine were used as coating materials. The data from hygroscopicity tests indicated that the best results of AN particles coated by C_{18} -amine was recorded when the moisture absorption rate was decreased, the mass ratio of coating layer of 1.06%, and highest decline of hygroscopicity was 23.28%. C_{14} -amine, C_{12} -amine and C_{16} -amine were found to be the second, third, and fourth superior results, respectively.

3.1.4. Comparison of surfactants with amide polar heads

The experiments were conducted by using amide surfactants, in order to investigate the relationship of surfactants with both same polar amide heads and different tails and their anti-hygroscopicity performance. The experiments were carried on according to coating process procedure, the coating process conditions and hygroscopicity testing conditions same as before were unchanged. The results obtained from hygroscopicity test are shown in Fig. 4 shown, for AN particles coated by amide surfactants (C_{12} , C_{14} , C_{16} , C_{18} and C_{22}). The decline of hygroscopicity was used as evaluation index for the anti-hygroscopicity performance of coated AN particles.

As showed in Fig. 4, C_{12} -amide, C_{14} -amide, C_{16} -amide, C_{18} -amide and C_{20} -amide were used as coating materials. The data from hygroscopicity tests indicated that the best results of AN particles coated by C_{12} -amide was recorded when the moisture absorption rate was decreased, the mass ratio of coating layer of 17.0%, and highest decline of hygroscopicity was 18.0%. C_{18} -amide and C_{14} -amide were found to be the second and third superior results, respectively, while C_{20} -amide and C_{16} -amide followed the order in sequence.

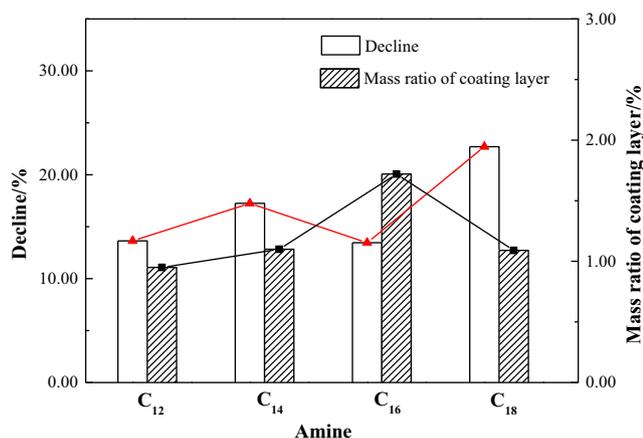


Fig. 3 Comparison of surfactants with the same polar heads (amine).

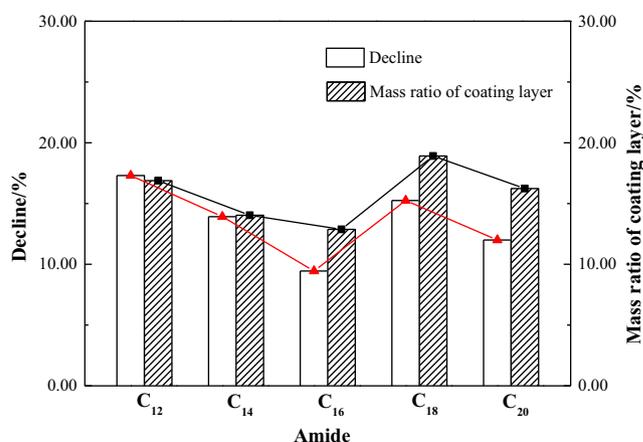


Fig. 4 Comparison of surfactants with the same polar heads (amide).

3.2. Comparison of surfactants with the same non-polar tails

3.2.1. Comparison of surfactants with non-polar C_{14} -tails

The experiments were conducted by using surfactants with same non-polar tails, in order to investigate the relationship of surfactants with both same non-polar C_{14} -tail and different polar heads and their anti-hygroscopicity performance. The experiments were carried on according to coating process procedure, the coating process conditions and hygroscopicity testing conditions same as before were unchanged. The decline of the hygroscopicity was used as evaluation index for the anti-hygroscopicity performance of coated AN particles. The results of the decline of hygroscopicity and the mass ratio of the coating layer were shown in Fig. 5.

As showed in Fig. 5, C_{14} -alcohol, C_{14} -acid, C_{14} -amine and C_{14} -amide were used as coating materials. The data from hygroscopicity tests indicated that the best results of AN particles coated by C_{14} -amine was recorded when the moisture absorption rate was decreased, the mass ratio of coating layer of 1.22%, and highest decline of hygroscopicity was 18.64%. C_{14} -amide, C_{14} -alcohol, and C_{14} -acid were found to be the second, third and fourth superior results, respectively.

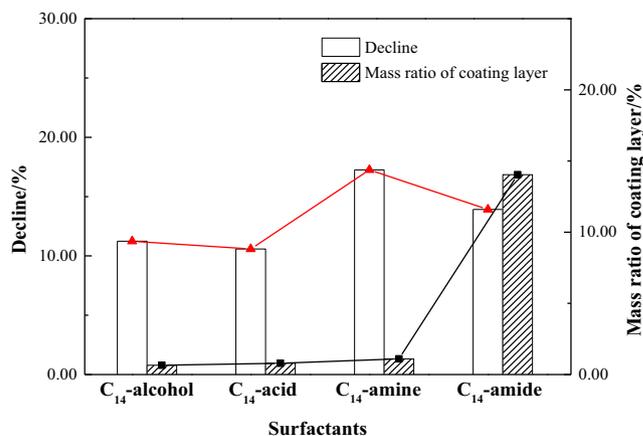


Fig. 5 Comparison of surfactants with C_{14} -tails.

3.2.2. Comparison of surfactants with non-polar C_{16} -tails

The experiments were conducted by using surfactants with same non-polar C_{16} -tails, in order to investigate the relationship of surfactants with both same non-polar tails and different heads and their anti-hygroscopicity performance. The experiments were carried on according to coating process procedure, the coating process conditions and hygroscopicity testing conditions same as before were unchanged. The decline of the hygroscopicity was used as evaluation index for the anti-hygroscopicity performance of coated AN particles. The results of the decline of hygroscopicity and the mass ratio of coating layer were shown in Fig. 6.

As showed in Fig. 6 above, C_{16} -alcohol, C_{16} -acid, C_{16} -amine and C_{16} -amide were used as coating materials. The data from hygroscopicity tests indicated that the best results of AN particles coated by C_{16} -alcohol was recorded when the moisture absorption rate was decreased, the mass ratio of coating layer was 1.35%, and highest decline of hygroscopicity was 29.26%. C_{16} -acid, C_{16} -amine, and C_{16} -amide were found to be the second, third and fourth superior results, respectively.

3.2.3. Comparison of surfactants with non-polar C_{18} -tails

The experiments were conducted by using surfactants with same non-polar tails, in order to investigate the relationship of surfactants with both same non-polar C_{18} -tails and different polar heads and their anti-hygroscopicity performance. The experiments were carried on according to coating process procedure, the coating process conditions and hygroscopicity testing conditions same as before were unchanged. The decline of the hygroscopicity was used as evaluation index for the anti-hygroscopicity performance of coated AN particles. The results of the decline of hygroscopicity and the mass ratio of coating layer were shown in Fig. 7.

As showed in Fig. 7, C_{18} -alcohol, C_{18} -acid, C_{18} -amine and C_{18} -amide were used as coating materials. The data from hygroscopicity tests indicated that the best results of ammonium nitrate particles coated by C_{18} -acid was recorded when the moisture absorption rate was decreased, the mass ratio of coating layer was 0.67%, and highest decline of hygroscopicity was 24.0%. C_{18} -amine, C_{18} -alcohol, and C_{18} -amide were

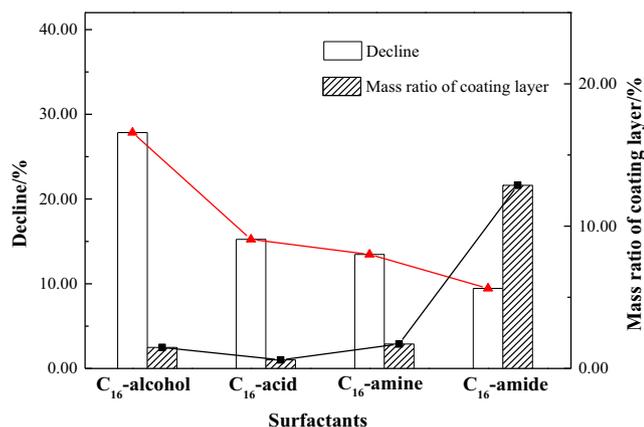


Fig. 6 Comparison of surfactants with C_{16} -tails.

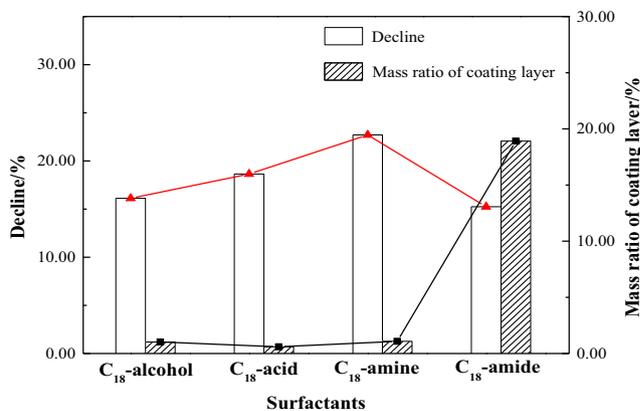


Fig. 7 Comparison of surfactants with C_{18} -tails.

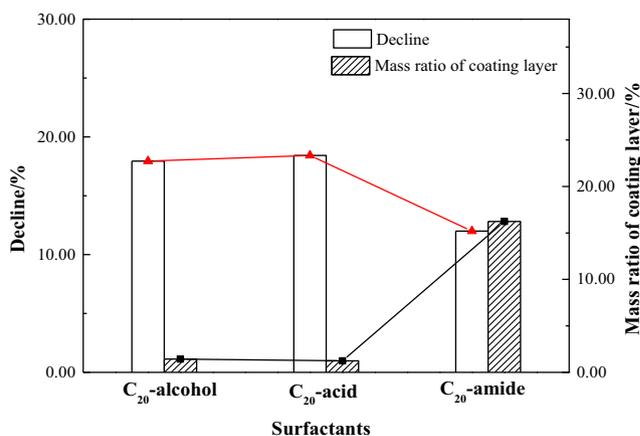


Fig. 8 Comparison of surfactants with C_{20} -tails.

found to be the second, third and fourth superior results, respectively.

3.2.4. Comparison of surfactants with non-polar C_{20} -tails

The experiments were conducted by using surfactants with non-polar C_{20} -tails, in order to investigate the relationship of surfactants with both same non-polar C_{20} -tails and different polar heads and their anti-hygroscopicity performance. The experiments were carried on according to coating process procedure, the coating process conditions and hygroscopicity testing conditions same as before were unchanged. The decline of the hygroscopicity was used as evaluation index for the anti-hygroscopicity performance of coated AN particles. The results of the decline of hygroscopicity and the mass ratio of coating layer were shown in Fig. 8.

As showed in Fig. 8, C_{20} -alcohol, C_{20} -acid and C_{20} -amide were used as coating materials. The data from hygroscopicity tests indicated that the best results of AN particles coated by C_{20} -acid was recorded when the moisture absorption rate was decreased, the mass ratio of coating layer was 1.03%, and highest decline of hygroscopicity was 20.39%. C_{20} -alcohol and C_{20} -amide were found to be the second and third superior results, respectively.

4. Discussion

4.1. A general description of coating process features

4.1.1. Coating process features of using surfactants

From the views in literatures (Ye, 2007); there have been various anti-hygroscopicity treatments for the AN particles. The most conventional way to achieve this is to reduce the surface polarity, which then hampers the hygroscopicity of the material. The related surface modification can be realized by physical and chemical coating, as well as through encapsulation (Elzaki and Zhang, 2016; Nagayama et al., 2015). This chapter rests on coating the surface by surfactants, essentially belongs to a physical coating. The procedure for coating the surface of particles by surfactants, including the step of inclusion of the coating materials (amphiphilic surfactants), diluting the surfactant and then adding the dry ammonium nitrate particle with the particle diameter in a specific range, finally keeping the particle suspended (Zhang et al., 2008). Through stages of heating to, maintaining at and cooling down the temperature, the polar parts of the surfactants in the solution can be adsorbed in the surface of the AN particles, whereas the non-polar parts get dispersed (Santra and Adams, 2001). With that, the resultant hydrophobic layer on surface can keep the anti-hygroscopicity of the AN particles.

4.1.2. Various influence factors on anti-hygroscopicity

In terms of the surface of AN particles that is coated by the above surfactants, and from the procedure and principle to reduce the hygroscopicity, it is not difficult to know, there are multiple factors that impact on the anti-hygroscopicity of the AN particles coated. Concerning the process to absorb the coating material on the surface of AN particles, this process involves three comprehensive interface function between the coating material and AN particles, the coating material and the solvent, and the solvent and the AN particles (Ye, 2007). In other words, the factors that influence the anti-hygroscopicity of the particles after coating are not only the process conditions, i.e., the sequence of coating procedure, the time, the temperature, the amount of coating materials on the surface and materials in center, and the property of solvent and its amount, but also the basic properties for the coating materials, i.e. the surfactants (Tadros, 2006). Under the optimized and fixed condition of the coating technique, including fixing the condition of the solvent, the only factor that impacts on the anti-hygroscopicity of the coated products, is the property of the molecular structures of the surfactants used as the coating materials and their behavior features in coating process. With that, the investigation of the changes on the molecular structure of the coating material and its impact on the anti-hygroscopicity of the coated products are surely of large signification, in order to instruct the further study to optimize the coating technique in the advanced level.

4.2. The several essential properties of coating material surfactants

By coating of the surfactants, the surface of AN particles is modified in terms of its anti-hygroscopicity. During this process, the polar heads of the surfactant will be adsorbed on

the surface of the AN particles, whereas the non-polar ends are kept away (Zhou et al., 2005). This accounts for the construction of the anti-hygroscopicity layer.

4.2.1. The effects of polarities

In the adsorption way of the surfactant on the surface of the ammonium nitrate particle, the adsorption affinity, or the difference of it, results from the polarity of the polar heads of the surfactants. Since no literature has reported about the polarity of these four kinds of the surfactants used in this paper yet, this can be inferred from the following method. Firstly, one can refer to the solvent manual, with some estimation (Hou and Zhang, 2016). From the solvent manual, it could be known, that the increasing order of dipole moments of four mother compounds of the four kinds of surfactants can meanwhile be indicated the increasing sequence of their polarities. The polarity estimation of the four kinds of the surfactants such as Methane (CH_3NH_2), Methanol (CH_3OH), Methane acid (CHOOH), and Methane amide (CHONH_2) were 3.60×10^{-30} , 5.55×10^{-30} , 6.07×10^{-30} , and 11.24×10^{-30} , respectively. And even more, it can be imaged, upon the elongation of the non-polar tail, the ranking of the polarity of the four kinds of the surfactants is: $\text{R-CONH}_2 > \text{R-COOH} > \text{R-OH} > \text{R-NH}_2$, while R is a same structure and length. In case the polar groups or heads of the above surfactants can be adsorbed on the surface of the ammonium nitrate particle, the anti-hygroscopicity of the four kinds of surfactants might be similarly ranked as $\text{R-CONH}_2 > \text{R-COOH} > \text{R-OH} > \text{R-NH}_2$, given the same length of the carbon chain.

4.2.2. The effects of hygroscopicity

The above analysis suggests that, because of their polarity, the surfactants belonging to alcohol, acids, amines and amides can be adsorbed on the surface of AN particles and form the coating membrane or layer. However, the question that must not be disregarded is the hygroscopicity of the coating membrane itself. The current research results reported on the moisture absorption rate under various conditions refer to the Table 3 (Hou and Zhang, 2016).

From Table 2, the saturated moisture absorption rate appears to be below 0.01% for C_{16-22} -alcohol, C_{12-22} -acids and amides under the relative humidity 68%, temperature 35°C and after measuring for 72 h. These surfactants satisfy the basic requirement for the coating material to be anti-hygroscopicity. However, with that, it is implied that the ranking of the surfactant polarity up on polar ends or heads is opposite towards that of their hygroscopicity up on the testing results in Table 2. That may be attributed to the strongest capability to create the hydrogen bond of the amines among the four surfactants, which is followed by the alcohol, acids, and acid amides. Therefore, there are polar and hydrogen bond interaction between the surfactant polar ends or heads and the water molecules, which gives rise to the high hygroscopicity of the partial surfactants of shorter carbon chains, and thus disable its application under the condition of the above coating and measurement.

4.2.3. The effects of solubility

Apart from the hygroscopicity from the polar ends or heads of the surfactants, their solubility in the suspended solution accounts for an important factor in the coating processing. It

Table 2 Hygroscopicity of the surfactants used under some conditions.

Material Names	Conditions					
	25°C RH 52%		35°C RH 68%		35°C RH 92%	
	Hygroscopicity/%	Test time/h	Hygroscopicity/%	Test time/h	Hygroscopicity/%	Test time/h
C ₁₄ -alcohol	< 0.01	0 ~ 12	1.63	12 ~ 24	2.60	48 ~ 60
C ₁₆₋₂₂ -alcohol	< 0.01	0 ~ 12	< 0.01	0 ~ 12	< 0.01	0 ~ 12
C ₁₂₋₂₂ -acid	< 0.01	0 ~ 12	< 0.01	0 ~ 12	< 0.01	0 ~ 12
C ₁₂ -amine	5.09	24 ~ 36	7.15	24 ~ 36	7.75	36 ~ 48
C ₁₄ -amine	0.60	24 ~ 36	5.92	24 ~ 36	6.68	36 ~ 48
C ₁₆ -amine	0.20	12 ~ 24	5.49	12 ~ 24	6.59	24 ~ 36
C ₁₈ -amine	< 0.01	0 ~ 12	2.19	24 ~ 36	6.85	24 ~ 36
C ₁₂ -amide	< 0.01	0 ~ 12	< 0.01	0 ~ 12	2.45	0 ~ 12
C ₁₆₋₂₂ -amide	< 0.01	0 ~ 12	< 0.01	0 ~ 12	< 0.01	0 ~ 12

is not deniable that, however, the ammonium nitrate particle is required to be not dissolvable in the solution, whereas the solubility will be granted to some extent for the surfactant used. The mixed solvent with the chloroform and the cyclohexane used in this paper is a polar organic solvent. On one side, it will cause a waste of the surfactant with a high solubility in the solution, resulting to the incomplete coat of the surfactant on the AN particles and thus degrade its efficacy. On the other side, too small solubility in the solution will disable the homogeneous structure of the coating membrane or layer, including the membrane or layer over-large or insufficient in amount, or inhomogeneous layer. Both occasions can obviously harm the efficacy of the anti-hygroscopicity membrane or layer on the

surface of AN particles. There has been literature measuring the solubility of the four kinds of the surfactants in the organic solution as shown in Fig. 9 (Hou and Zhang, 2016).

From the Fig. 9, it is shown that such as surfactants belong to the C₁₄-alcohol and C₁₂₋₁₄-acids, their solubility in the solution related to the research in this paper is too large which belong to the former case. Yet, the C₁₄₋₁₈-amines and C₁₂₋₂₂-acids and C₁₂₋₂₂-amides, they have an over too small solubility which belong to the latter case. Thus, at 20 °C, among the solvents related to this study, only the surfactants of C₁₆₋₁₈-alcohols, C₁₆₋₁₈-acids and C₁₄-amine have the eligible solubility. However, C₁₄-amine is out of the selection due to its hygroscopicity nature.

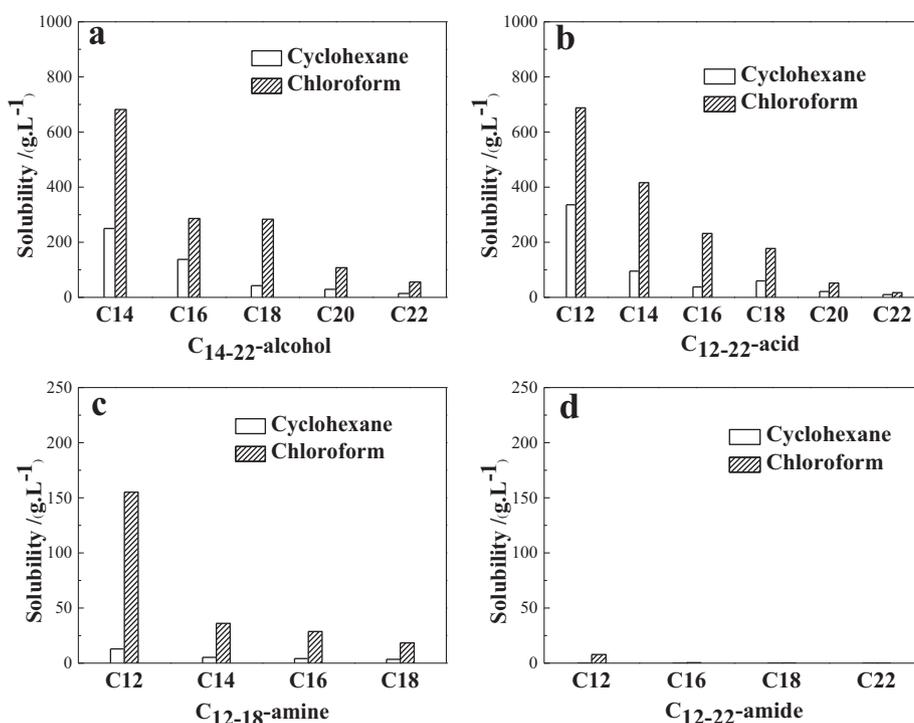


Fig. 9 Solubility of surfactants in the cyclohexane and chloroform a. alcohol surfactants: R-OH; b. acid surfactants: R-COOH; c. amine surfactants: R-NH₂; d. amide surfactants: R-CONH₂.

4.2.4. The effects of surfactants

Based on the principle of coating process by using surfactants, the surfactants should be precipitated from a solvent in which they are dissolved before reaching the surface of AN particles. However, the distribution situation of surfactant molecules in the solvent or solution depends on its concentration under a certain temperature. As that concentration increases, the dissolved surfactants firstly adsorb on the solution surface and are in equilibrium with their molecules in the solution, at that time, when the AN particles suspends in the solution, the adsorption amount of surfactants on it is in the competition of the surface absorption the coating layer is unsatisfied. Moreover, as a surfactant concentration is steeply increased, the surfactants get saturated in the solution surface, and begin to form the large amount of micelle due to the hydrophobic tail nature, i.e. closed to Critical Micelle Concentration (CMC). At that time, if there are AN particles existed and suspended in the solution, then there will be sufficient number of the surfactants getting adsorbed, and the ordered coating membrane can be achieved via the dynamic equilibrium of surfactant concentration between the surface of solution, solution bodies and the interface of solution with AN particles, beside original equilibrium between surface of solution and formed micelles. If surfactant concentration is further increased too high, there the possible unexpected structural changes on the coating membrane or layer will happen upon massive micelles in the solution, which is unfavorable for enhance the anti-hygroscopicity of the AN particles. The results of CMC mentioned for C₁₆₋₁₈-alcohol, C₁₆₋₁₈-acids are as shown in Table 4 (Chai et al., 2009).

From the above Table 4, and taking the examples of the relationships between the concentration of surfactants as C₁₆-alcohol and C₁₆₋₁₈-acids and their surface tension in chloroform and cyclohexane, it is easily to find the forming of the critical micelle concentration of the C₁₆ alcohol and C₁₆₋₁₈ acids in chloroform corresponds to the concentration of 80.00, 80.00 and 90.00 g/L at 20 °C, while in the cyclohexane that corresponds to 9.00, 15.00 and 15.00 g/L. Therefore, the desired amount of the surfactants during the coating processing design of the anti-hygroscopicity modification of the AN particles can refer to the critical micelle concentration measured in the relevant solvent above.

4.3. Mechanism analysis of coating performance of using C₁₆₋₁₈ alcohol and acid

4.3.1. The main results of the relationships between the structures and performance

Through the experimentally investigation of the relationships between the molecular structure of surfactants and

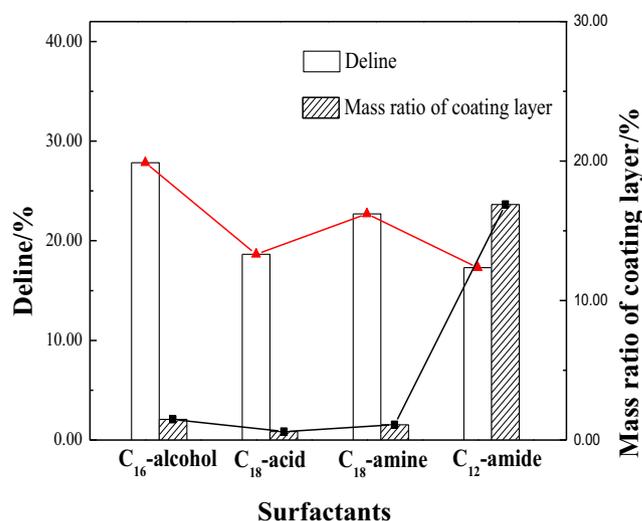


Fig. 10 Better performance of surfactants.

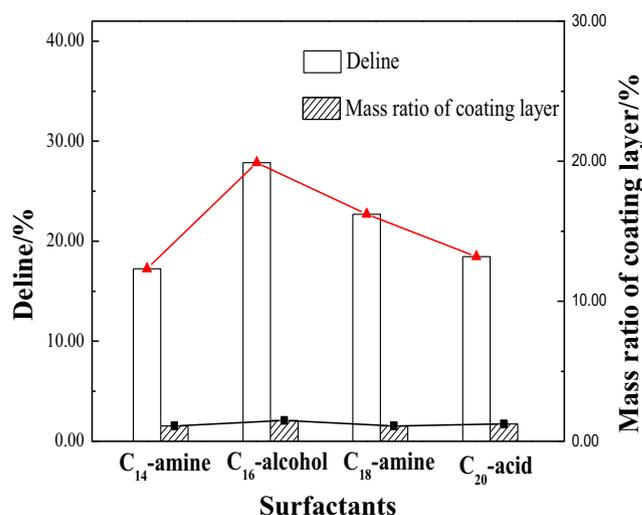


Fig. 11 Better performance of surfactants from the same kind of heads from the same kind of tails.

their anti-hygroscopicity property to AN particles coated, the comparable results in anti-hygroscopicity performance of surfactants both with the same polar heads and different non polar tails and with same non polar tails and different polar heads could be obtained and the best ones of them in performance are shown in Figs. 10 and 11.

Table 4 CMC of C₁₆₋₁₈-alcohol and C₁₆₋₁₈-acid in chloroform and cyclohexane.

Temp./°C	Chloroform, CMC g/L				Cyclohexane, CMC g/L			
	C ₁₆ -alcohol	C ₁₈ -alcohol	C ₁₆ -acid	C ₁₈ -acid	C ₁₆ -alcohol	C ₁₈ -alcohol	C ₁₆ -acid	C ₁₈ -acid
20	80	5	90	90	9	4	10	10
25	70	5	60	60	9	2	10	10
30	70	5	70	50	9	2	8	8

4.3.2. The behavior analysis of surfactant molecules in coating processing

From the basic property of the surfactant molecules and their anti-hygroscopicity modification principle on the surface of AN particles, it is not difficult to discuss their behaviors in the process of coating the AN particles under fixed processing conditions, and furthermore, some mechanism explanation could be acquired.

Firstly, in the aspect of the polarity and the binding affinity with the surface of AN particles for the surfactants, the ranking in terms of the anti-hygroscopicity for the molecules with the same carbon chain length is: R-CONH₂ > R-COOH > R-OH > R-NH₂.

Secondly, for C₁₈-amines, C₁₆₋₂₂-alcohols, C₁₂₋₂₂-acids, and C₁₂-amides, their moisture absorption rates are all below 0.01%, corresponding to the basic requirement of the anti-hygroscopicity for uses as coating materials. However, from here, it can be found that the ranking of the polarity of the surfactants depending on the polar ends or heads is opposite to that of the moisture absorption rate. One of the essential reasons could be due to the tendency ranking to create the hydrogen bonding which starts with amines and is followed by the alcohols, acids and acid amides. Thus, even more, the moisture absorption rate for these first two surfactants when with less carbon in the molecular chain, is relatively higher because of their polar and hydrogen-bonding interactions between the polar groups of the surfactants and the water molecules, so that they are improper used. Furthermore, the solvents under this study are the chloroform and cyclohexane. The surfactants with mediate level of the solubility are the C₁₆₋₁₈-alcohols and C₁₆₋₁₈-acids and C₁₂-amines. But, obviously C₁₂-amine cannot be used for a coating material in the view of its hygroscopicity property.

Finally, even for the C₁₆₋₁₈-alcohols and C₁₆₋₁₈-acids surfactants with eligible anti-hygroscopicity property and solubility, the enough adsorption on the surface of the AN particles is triggered, in the case of the surfactant concentration reaches or around the value of CMC in the massive amount. Meanwhile, it might be possible to tune the dynamic equilibrium of surfactant concentration on the surface, in the interface and solution body, i.e., to control the processing condition, in order to acquire the ordered and adjustable coating membrane or layer. It is easily to see, that from the discussions above, on the one hand, at 20 °C, the concentration for the C₁₆-alcohol and C₁₈-acids to reach their CMC values in chloroform are 80.00 g/L and 90.00 g/L and in cyclohexane are 15.00 g/L and 15.00 g/L in the cyclohexane, respectively. Concerning the coating process in this paper, the selectable adding amount or concentration of the surfactant is in the range of 15.00–90.00 g/l, because of using the mixed solvent of 30 ml comprising chloroform and cyclohexane in the volume ratio 1:1. On the other hand, the amount for C₁₆-alcohol and C₁₈-acids for the coating process is only 2 g, which corresponds to the concentration 66.67 g/L. This serves for a justification of the adding amount of C₁₆-alcohol and C₁₈-acid which is within a reasonable range. Thus, it is not difficult for researcher to understand the real mechanism that C₁₆-alcohol and C₁₈-acids can achieve a best level to gain the anti-hygroscopicity property, by a series of optimization of coating processing investigation.

5. Conclusion

In this study, the relationships between structures of surfactants and their anti-hygroscopicity performance in coated AN particles were experimentally investigated by using a fixed coating process condition, based on which some mechanism was conducted by means of analysis of properties of surfactant molecular structures and their possible behaviors in coating processing. The summary of this study as follows:

- (1) The comparison of surfactants with the same polar heads showed that: C₁₆-alcohol displayed best performance in decline of hygroscopicity of AN particles coated. The decline of hygroscopicity of C₁₆-alcohol was 29.26%. C₁₈-acid was recorded the decline of hygroscopicity 24.0%. Furthermore, C₁₈-amine and C₁₂-amide were followed the order in sequence.
- (2) The comparison of surfactants with same non-polar tails showed that: In the long non-polar tails of surfactants (C₁₈ and C₂₀), the anti-hygroscopicity performance results showed that the best anti-hygroscopicity performances were C₁₈-acid and C₂₀-acid, and in the short non-polar tails of surfactants (C₁₆ and C₁₄) the anti-hygroscopicity performance results showed that the best anti-hygroscopicity performances were C₁₆-alcohol and C₁₄-amine.
- (3) It was shown that under the fixed processing condition including the solvent which is from processing optimization results in this study, C₁₆-alcohol and C₁₆₋₁₈-acids were the best choices of surfactants, based on analysis and discussion of both the practical coating processes and the effects of the relationship between the molecular structures of surfactants used and their properties including polarity, solubility, hygroscopicity and CMC values.

Declaration of Competing Interest

The authors declare that there is no conflict of interests regarding the publication of this paper

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