Complexation Reaction Using Ammonium Based Chloride Compounds for Preparation of Eutectic Mixtures

Ahmad Adlie Shamsuri (Corresponding author)

Laboratory of Industrial Biotechnology, Institute of Bioscience

Universiti Putra Malaysia, 43400 UPM Serdang

Selangor Darul Ehsan, Malaysia

E-mail: adlie@putra.upm.edu.my

Dzulkefly Kuang Abdullah

Laboratory of Industrial Biotechnology, Institute of Bioscience

Universiti Putra Malaysia, 43400 UPM Serdang

Selangor Darul Ehsan, Malaysia

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Abstract

In this study, we are interested in the eutectic processing of chloride compounds and decided to focus on ammonium based compounds that can provide sufficient insight in the fundamental chemistry. 10 types of ammonium based chloride compounds namely ammonium chloride, methanaminium chloride, dimethylammonium chloride, trimethylammonium chloride, tetramethylammonium chloride, dodecyltrimethylammonium chloride, hexadecyltrimethylammonium chloride, phenyltrimethylammonium chloride, benzyltrimethylammonium chloride and (vinylbenzyl)trimethylammonium chloride were used in this study. This research led to a hypothesis that the ammonium based chloride compounds could be reacted with urea through complexation reaction giving eutectic mixtures. However, functional groups have plays an important role to influence melting points of these eutectic mixtures. This is regarded to be a motivating finding that will be important for the most future research work involving complexation reaction for the production of eutectic mixtures.

Keywords: Eutectic mixture, Ammonium based chloride compounds, Complexation reaction, Ionic liquids

1. Introduction

Eutectic mixtures which are materials consisting of components that form a low melting point mixture, provide a unique substance for developing advanced materials and usually cheaper with less time-consuming than the development of new materials. It is composed of a mixture with a melting point much lower than each of the individual components. For example, changing metal such as tin and lead into metallic eutectic is a common way to make them low melting point material usually used in soldering (Kanchanomai, et al., 2002). Other eutectic mixture is sodium chloride and water; it has a eutectic point of -21.2°C (Chen, et al., 2005) it is used to aid ice removal or to produce low temperatures ice. Eutectic mixtures are simple to prepare, the components of the eutectic can be easily mixed and converted without further purification. Most recently, eutectic mixtures were utilized to produce ionic liquids that might be used as green solvents (Hou, et al., 2008).

Since little information using common ammonium based compounds as eutectic components is known concerning the chloride compounds (except for choline chloride) related to the preparation of eutectic mixture. Therefore, we have produced some eutectic mixtures using common ammonium based chloride compounds. Previous study has shown that complexation reaction was used to produce eutectic mixture by means of ammonium based chloride compounds such as choline chloride with urea as complexing agent (Abbott, et al., 2003), although low melting point of eutectic mixture was observed in that study, but we have found that the role of functional groups in ammonium based chloride compounds for producing eutectic mixtures through complexation reaction is still not fully discovered and identified. In this study, eutectic mixtures have been prepared via complexation reaction by means of ammonium based chloride compounds with different functional groups; its physical appearance and melting point were also studied.

2. Materials and methods

2.1 Materials

Ammonium chloride, methanaminium chloride, dimethylammonium chloride, trimethylammonium chloride, tetramethylammonium chloride, dodecyltrimethylammonium chloride, hexadecyltrimethylammonium chloride, phenyltrimethylammonium chloride, benzyltrimethylammonium chloride and (vinylbenzyl)trimethylammonium chloride were supplied by Sigma Aldrich. Urea was also obtained from Sigma Aldrich. All chemicals purity ≥98.0% and were recrystallized before use.

2.2 Preparation of eutectic mixture

Preparation of eutectic mixture via complexation reaction was done according to (Abbott, et al., 2007). In this study, ammonium based chloride compounds were mixed in the flask with urea as 1:2 mole ratios, respectively. The flask was immersed in oil bath at 100°C and stirred for at least 1 hour. Then, the reaction mixture was dried for overnight at 100°C in a vacuum oven to obtain the final product and prior to the melting point measurements.

2.3 Melting point characterization

Differential scanning calorimetry (DSC) analysis was conducted on a Mettler Toledo DSC822^{e} apparatus using the STAR analysis software under a constant stream of nitrogen at flow rate of 50 mL/min. The samples were tightly sealed in aluminium pans. The samples were first heated to 100°C to eliminate the thermal history. The analyses were carried out in a temperature range of 25 to 350ºC with a heating rate of 10ºC/min to obtain the melting point, T_m which were determined from thermograms during the programmed reheating steps.

3. Results and discussion

3.1 Physical appearance

Table 1 shows the physical appearances profile of eutectic mixtures at room temperature (25ºC). All prepared eutectic mixtures are solid at ambient temperature corresponding to physical properties of its individual components. Ammonium based chloride compounds are composed of nitrogen cations and chloride ions, so, they have tendency to form eutectic mixture with complexing agent (urea) assisted by elevated temperature (Abbott, et al., 2003). It can also be seen in Table 1 all eutectic mixtures are solid possibly due to high melting points. Nonetheless, DSC thermal analysis was carried out to determine the melting points accurately.

3.2 DSC characterization

Table 2 shows the melting points of pristine eutectic components were supplied by Sigma Aldrich MSDS, which obviously high. DSC is a well known as technique which gives an exhaustive overview the relevant thermal analysis (Ford & Timmins, 1989). The calorimetric data was obtained by heating the eutectic mixtures; all melting points corresponding with the peaks of DSC traces were listed in Table 3. Each melting point of DSC traces means a crystalline melting point of the eutectic mixtures. From this result, it can be observed that the melting points of eutectic mixtures are different from its pristine eutectic components. In other words, melting points of eutectic mixtures are significantly lower than its individual components. Therefore, in this study all eutectic mixtures were indicating absolute eutectic behaviour due to the reduction in melting points. In Table 3 it seems that the complexation reaction has been taking place which chloride ions complexed with urea. The reasons why they have low melting points are basically the endothermic shifted to the lower temperature after complexing agent was given to the ammonium based chloride compounds. Mostly the chloride ions could be reacted with urea through complexation reaction assisted by high temperature condition. The complexation reaction of chloride ions with urea is actually driven by hydrogen bonding between them (Abbott, et al., 2003).

Although hydrogen bonding is fully known as strong bond between the hydrogen atom with the organic constituents such as nitrogen, oxygen, and fluorine (Brady, et al., 2000), essentially, hydrogen bonding also could be formed between the hydrogen atoms with the electronegative constituent such as chloride ions. In this case, the hydrogen atoms of complexing agent are attached to the chloride ions from ammonium based chloride compounds that relatively electronegative to form chloride ions complex. Since eutectic mixtures consist of nitrogen cations and complex anions so, when higher temperature was applied, these structures possible dissociated cations from anion relations owing to the larger size ratios thus, offered weak interactions, as a result increased degrees of freedom and amounts motion of nitrogen cations and complex anions. Apart from that, the reason we have chosen 1:2 mole ratio is when chloride compound or complexing agent are more or less than that composition the tendency to form complex anions are low (Abbott, et al., 2003). Formation of hydrogen bonding between eutectic components in the eutectic mixtures has been shown in Figure 1.

In the pristine ammonium based chloride compounds phase, the interactions between cations and anions are generally stronger, which are normally held together by strong ionic bond. As a result, compounds in these structures tend to have higher melting points compared to the nitrogen cations and complex anions of the eutectic mixtures. The highest melting point is can be observed for eutectic mixture of ammonium chloride and urea which contained fully hydrogen atoms. Hence, nitrogen cations with the hydrogen atoms in the all side group causing the melting point slightly decreased to a value below its origin. Eutectic mixtures with ammonium based chloride compounds that consisted of methyl branches such as methanaminium chloride, dimethylammonium chloride, trimethylammonium chloride and tetramethylammonium chloride have significant results related to the melting point reduction compared with ammonium chloride. A completely unexpected observation can be seen for eutectic components of dodecyltrimethylammonium chloride and hexadecyltrimethylammonium chloride give important results, due to their melting points far away from individual components eventhough they have longest alkyl chains contrasted to tetramethylammonium chloride. While, with phenyl and benzyl functional group as can be seen on eutectic mixture of phenyltrimethylammonium chloride and benzyltrimethylammonium chloride with urea, respectively were demonstrating higher melting point than (vinylbenzyl)trimethylammonium chloride.

The melting points of these eutectic mixtures are dependent upon the interaction lattice energies of the ammonium based chloride compounds with complexing agent and the entropy changes arising from forming eutectics, therefore the reduction of melting point are measure of the entropy change (Abbott, et al., 2004). However, first it is important to relate the structure of the ammonium based chloride compounds to the melting points of the eutectic mixtures. The DSC results clearly show to relate to the differences of chemical structure between each eutectic mixture. In other words, the highest of the melting point may suggest the existence of inappropriate character of the functional groups in the nitrogen cations (Abbott, et al., 2001) in term of reducing the melting point. The appropriate functional groups of ammonium based chloride compounds will create the suitable eutectic components for preparation of low melting points eutectic mixtures.

In addition, melting points of eutectic mixtures also decrease with the larger more asymmetric nitrogen cations (Buzzeo, et al., 2004), which the highest melting points are observed with the more symmetric nitrogen cations. This may be a reason for the highest melting points of eutectic components such as ammonium chloride and tetramethylammonium chloride also the lowest melting points of dimethylammonium chloride and hexadecyltrimethylammonium chloride. On the other hand, in comparison with phenyl and benzyl functional group, the lower melting point is observed for (vinylbenzyl)trimethylammonium chloride, possibly due to the larger size of nitrogen cations providing greater asymmetry. Based on this study, the order of melting point reduction for varying functional groups for the ammonium based chloride compounds has been shown in Figure 2.

4. Conclusions

This study was indicated that eutectic mixtures were successfully produced by using ammonium based chloride compounds and complexing agent specifically urea. Based on these results, it is clear that ammonium based chloride compounds can undergo reactions with the urea through complexation reaction. The most important and intriguing discovery from this research is the fact that the functional groups of ammonium based chloride compounds are necessarily have play an important role to influence the melting point. The order of melting point reduction for varying functional groups is hydrogen > alkyl > phenyl > benzyl > vinylbenzyl > fatty alkyl. Eutectic components should be having appropriate functional group that will not influence functionality of nitrogen cations so that can reduce melting points of eutectic mixtures to the lowest points. This information is regarded as the motivating finding that will be the most important for future studies involving complexation reaction therefore, could be useful for fundamental chemistry especially if wanted to generate low melting points of eutectic mixtures for developing advanced materials such as ionic liquids.

References

Abbott, A. P., Capper, G., Davies, D. L., Munro, H. L., Rasheed, R. K., & Tambyrajah, V. (2001). Preparation of novel, moisture-stable, Lewis-acidic ionic liquids containing quaternary ammonium salts with functional side chains. *Chemical Communications, 19*, 2010-2011.

Abbott, A. P., Capper, G., Davies, D. L., Rasheed, R. K., & Tambyrajah, V. (2003). Novel solvent properties of choline chloride/urea mixtures. *Chemical Communications, 1*, 70-71.

Abbott, A .P., Boothby, D., Capper, G., Davies, D. L., & Rasheed, R. K. (2004). Deep Eutectic Solvents Formed between Choline Chloride and Carboxylic Acids: Versatile Alternatives to Ionic Liquids. *Journal of the American Chemical Society, 126*, 9142-9147.

Abbott, A. P., Capper, G., McKenzie, K. J., & Ryder, K. S. (2007). Electrodeposition of zinc-tin alloys from deep eutectic solvents based on choline chloride. *Journal of Electroanalytical Chemistry, 599*, 288-294.

Brady, J. E., Russel, J. W., & Holum, J. R. (2000). *Chemistry: Matter and Its changes*. New York, United States: John Wiley & Sons Inc. pp. 45-46.

Buzzeo, M. C., Evans, R. G., & Compton, R. G. (2004). Non-haloaluminate room-temperature ionic liquids in electrochemistry–a review. *European Journal of Chemical Physics and Physical Chemistry, 5*, 1106-1120.

Chen, N., Morikawa, J., & Hashimoto, T. (2005). Effect of cryoprotectans on eutectics of NaCl–$2H_2O$/ice and KCl/ice studied by temperature wave analysis and differential scanning calorimetry. *Thermochimica Acta, 431*, 106-112.

Ford, J. L., & Timmins, P. (1989). *Pharmaceutical Thermal Analysis - Techniques and Applications*. Chichester, England: Ellis Horwood. pp. 60-63.

Hou, Y., Gu, Y., Zhang, S., Yang, F., Ding, H., & Shan, Y. (2008). Novel binary eutectic mixtures based on imidazole. *Journal of Molecular Liquids, 143*, 154-159.

Kanchanomai, C., Miyashita, Y., & Mutoh, Y. (2002). Strain-rate effects on low cycle fatigue mechanisms of a eutectic Sn–Pb solder. *International Journal of Fatigue, 24*, 987-993.

Table 1. Physical appearances of eutectic mixtures at room temperature (25ºC)

Eutectic mixture	Appearance
ammonium chloride + urea	White solid
methanaminium chloride + urea	White solid
dimethylammonium chloride + urea	White solid
trimethylammonium chloride + urea	White solid
tetramethylammonium chloride + urea	White solid
dodecyltrimethylammonium chloride + urea	White solid
hexadecyltrimethylammonium chloride + urea	White solid
phenyltrimethylammonium chloride + urea	White solid
benzyltrimethylammonium chloride + urea	White solid
(vinylbenzyl)trimethylammonium chloride + urea	White solid

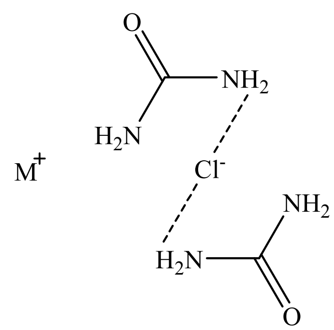
Table 2. Melting points of eutectic components as obtained from MSDS data

Eutectic component	Melting point, T_m (ºC)*
ammonium chloride	340
methanaminium chloride	229-233
dimethylammonium chloride	170-173
trimethylammonium chloride	283-284
tetramethylammonium chloride	>300
dodecyltrimethylammonium chloride	246
hexadecyltrimethylammonium chloride	232-237
phenyltrimethylammonium chloride	246-248
benzyltrimethylammonium chloride	239
(vinylbenzyl)trimethylammonium chloride	240
urea	132-135

* obtained from Sigma Aldrich

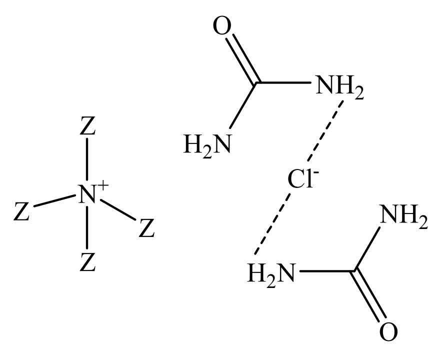
Table 3. Melting points of eutectic mixtures as determined from DSC data

Eutectic mixture	Melting point, T_m (ºC)
ammonium chloride + urea	286.51
methanaminium chloride + urea	210.28
dimethylammonium chloride + urea	123. 61
trimethylammonium chloride + urea	215.12
tetramethylammonium chloride + urea	240.06
dodecyltrimethylammonium chloride + urea	145.75
hexadecyltrimethylammonium chloride + urea	120.09
phenyltrimethylammonium chloride + urea	213.16
benzyltrimethylammonium chloride + urea	180.48
(vinylbenzyl)trimethylammonium chloride + urea	170.55



M^+ = ammonium based cation

Figure 1. Formation of hydrogen bonding between eutectic components in the eutectic mixtures



Z = hydrogen > alkyl > phenyl > benzyl > vinylbenzyl > fatty alkyl

Figure 2. The order of melting point reduction for varying functional groups