ARTICLE

Characterization of Adductive Crystal of Trimesinic Acid

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ABSTRACT

The adductive crystals formed by trimesinic acid and N-methyl pyrrolidone were measured and characterized by HPLC, TG and XRD. The results show that adduct is a kind of crystal with one trimesinic acid molecule and three N-methyl pyrrolidone molecules by O–H···O hydrogen-bonding. The crystal is unstable above 75 °C, which it is prone to decomposition in some certain solvents. The computational hydrogen-bonding energy between trimesinic acid and N-methyl pyrrolidone is -127.9 KJ mol^{-1}, which can be categorized to the strong hydrogen bond.

KEYWORDS

Trimesinic acid, N-Methyl pyrrolidone, Adductive crystallization.

INTRODUCTION

Trimesinic acid is a sort of vital chemical intermediate, which is mainly used for preparing the solid fuel crosslinking agent of rocket, aldol resin, water-soluble paint, the reverse osmosis membrane material of polyamide-sulfoxide and so on. Trimesinic acid (TMA) is prepared by the method of mesitylene liquid oxidation [1] and the crude trimesinic acid is refined by hydrofining process under high temperature. The hydrofining process has harsh conditions and costs high. When impure trimesinic acid was in some specific solvents, trimesinic acid and the solvents could spontaneously form a new crystal with high selectivity [2]. Trimesinic acid is concentrated in solid, but impurities are concentrated in liquid. The new crystal generated is unstable and may be resolved when it is in water or is heated. Thus, it is easy to get trimesinic acid with high purity, which is separated from solvents. The phenomenon that solute and solvent are crystallized out together with high selectively is called adductive crystallization and it is very different from conventional methods such as cooling down, evaporation, salting out and solvent-out crystallization. It was reported that the structure and property of adductive crystal formed with benzene-1,2,3-tricarboxylic acid and dimethyl formamide [3,4]. However, the adductive crystallization of trimesinic acid (TMA) and N-methyl pyrrolidone (NMP) hasn't been reported. This paper reports synthesis and characterization of adductive crystal TMA-NMP in order to understand the characteristics of adductive crystallization and lay the foundation of exploitation this new separation technique.

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EXPERIMENTAL

Preparation of adductive crystal TMA-NMP: A certain amount of trimesinic acid (TMA) (chemically pure, production in American Alpha Company) was dissolved in N-methyl pyrrolidone (NMP) at 120 °C, then made it cool down at the room temperature. The crystal appeared after cooling, it was the adductive crystal of trimesinic acid and N-methyl pyrrolidone. The crystal is easy to react with water and weaken in air, so the sample should be refrigerated at low temperature and the structure of crystal should also be determined in low temperature.

Thermogravimetric analysis: STA409PC thermogravimetric analyzer (German NETZSCH Company) whose heating rate is 20 °C/min and heating range is 25-300 °C under nitrogen atmosphere is used in the present study.

X-ray single crystal diffraction: The single crystal diffraction instrument was produced by Japanese Rigaku R-AKIS RAPID. The big and distinct crystal was fixed on the top of glass fiber. The diffraction data were collected on single crystal diffraction instrument. With the scanning method of ω-2θ and MoK_α radial (λ = 0.71073) of graphite monochromatization to collect data between the range of $3.1° \le 2\theta \le 24.99°$. The crystal structure was solved by SHELX-97 procedure in direct method. Finally, least square method and difference Fourier method were used to correct repeatedly to find all the non-hydrogen atoms. Hydrogen atoms were gained by the theory of hydrogenation.

RESULTS AND DISCUSSION

Constitute and stability of TMA-NMP adductive: The composition of crystal TMA-NMP was analyzed by Agilent LC, the molar ratio of trimesinic acid and N-methyl pyrrolidone is 1:3. Fig. 1 shows thermogravimetric analysis of the adductive crystal TMA-NMP. Crystal begins to decompose at 75 °C and ends at 225 °C with weight loss 56 %. In this process, NMP molecules with low boiling point are lost, while high boiling point trimesinic acid molecules are remained. It can thus be seen that trimesinic acid and N-methyl pyrrolidone adductive crystal is unstable in high temperature and easy to decompose.

Crystal structure of TMA-NMP adductive: According to the crystallography data of XRD, the adductive crystal formed by trimesinic acid and N-methyl pyrrolidone is P-1 and their cell parameters are a = 8.2105(16), b = 12.480(3), c = 13.135(3), α = 70.02(3), β = 82.96(3), γ = 86.50(3), Z = 2; TMA and NMP are tied by O–H···O hydrogen-bonding. A TMA molecule and three NMP molecules form a crystal unit by hydrogen-bonding (O–H···O). Fig. 2 shows the molecule structure formula of the adductive crystal TMA-NMP. Fig. 3 shows the crystal structure according to the crystallography data determined.

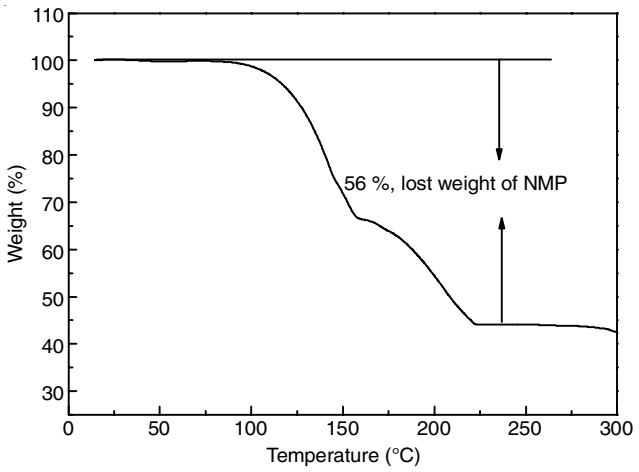

Fig. 1. Thermogravimetric analysis of TMA-NMP adductive crystal

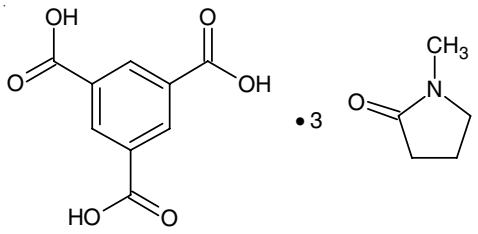

Fig. 2. Molecular formula of TMA-NMP adductive crystal

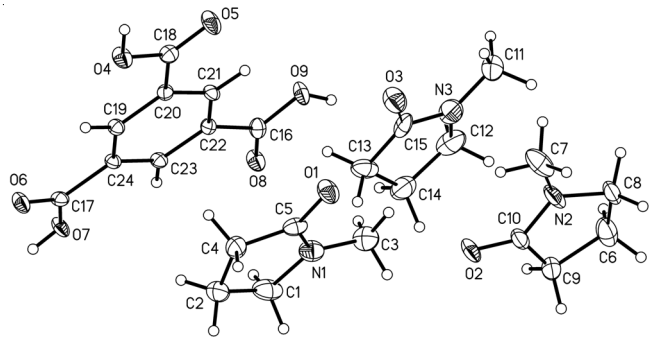

Fig. 3. Structure of TMA-NMP adductive crystal

Calculation of hydrogen bond energy of adductive crystal TMA-NMP: Solute and solvent of adductive crystal are joined by hydrogen bond [3-5]. The strength and function of hydrogen bond make a big difference with the properties of crystals. It is believed that the stronger hydrogen bond is, the easier product adductive crystal is formed. The energy of hydrogen bond is between the energy of ordinary double bond and van der Waals force, whose numerical value is about 8-50 kcal mol^{-1}. In general, H-bond energy belongs to the strong hydrogen bonding interaction at the range of 15-40 kcal mol^{-1} and it is the medium interaction at the range of 4-15 kcal mol^{-1}. Hydrogen bond energy, which is less than 4 kcal mol^{-1} belongs to the weak hydrogen bonding interaction [6]. The O–H···O hydrogen bonding, joining trimesinic acid and N-methyl pyrrolidone, can be calculated by Gaussian038 software package. It should be calculated by Boys and Bernardi's counterpoise procedure [7] to eliminate the basis set superposition error (BSSE). Relevant results are listed on the Table-1. The binding energy between TMA and NMP is 127.9 KJ mol^{-1} [$\%E_{(TMA\cdot 3NMP)} = E_{(TMA\cdot 3NMP)}-E_{(TMA)}-3E_{(NMP)}$], which is about 30

TABLE-1
BINDING ENERGY OF TMA-NMP ADDUCTIVE CRYSTAL

Compound	E/Hartree
Trimesinic acid (TMA)	-798.2
N-Methyl pyrrolidone (NMP)	-326.0
TMA·3NMP	-1776.3 (BSSE after correction)

kcal mol^{-1}. It belongs to the strong hydrogen bonding, so it can form the stable adductive crystal at room temperature.

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REFERENCES

1. D. Yang, W.J. Zhang, R.X. Li, M. Han and D.F. Chang, *Chem. Eng.*, **35**, 72 (2007) (Chinese Journal).
2. X. Guo, Y.W. Cheng and X. Li, *Acta Crystallogr. Sect. E Struct. Rep. Online*, **65**, o1794 (2009); https://doi.org/10.1107/S1600536809025793.
3. S.H. Dale and M.R.J. Elsegood, *Acta Crystallogr. C*, **60**, o444 (2004); https://doi.org/10.1107/S010827010400976X.
4. M. Hemamalini, P.T. Muthiah, G. Bocelli and A. Cantoni, *Acta Crystallogr. Sect. E Struct. Rep. Online*, **59**, o14 (2003); https://doi.org/10.1107/S1600536802021670.
5. G. Peng, *Asian J. Chem.*, **25**, 8821 (2013); https://doi.org/10.14233/ajchem.2013.15749.
6. G.M. Sheldrick, *Acta Crystallogr. A*, **64**, 112 (2008); https://doi.org/10.1107/S0108767307043930.
7. S.F. Boys and F. Bernardi, *Mol. Phys.*, **19**, 553 (1970); https://doi.org/10.1080/00268977000101561.