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On the Melting Point of *N*-Methylacetamide–Silver Nitrate Adduct

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Synopsis. The melting point of *N*-methylacetamide-silver nitrate adduct $AgNO_3 \cdot 2NMA$ was found to be 46—47 °C which is in large disagreement with that reported by Paul and Chadha. The discrepancy was interpreted to result from the tendency of the adduct to lose NMA at high temperatures or at low partial pressures of NMA.

Formation of stable solid adducts of silver nitrate with some oxygen donor ligands was reported by Paul and Chadha.[1] Of the adducts $AgNO_3 \cdot 2NMA$ (NMA: *N*-methylacetamide) was reported to have melting point (or the temperature of decomposition) at 148 °C. We also prepared[2] the adduct in an infrared absorption spectroscopic study of the interaction between photographic gelatin and silver nitrate, and found its melting point to be 46—47 °C (in sealed tubes) and not 148 °C. The purpose of the present note is to point out and discuss the discrepancy.

Our method of preparation is as follows: solid silver nitrate was dissolved in an excess (2—3 times the equivalent) of molten NMA. The solution was cooled down to room temperature to crystallize out the adduct. This method of crystallization differs from that of Paul and Chadha who added excess benzene to the solution for the purpose of crystallization, the former taking more time and giving larger and probably purer crystals. The crystal was then ground, washed several times with benzene or carbon tetrachloride to remove excess NMA and freed from the solvent in dry streaming nitrogen. The adduct was kept in a closed vessel filled with dry nitrogen because of its high deliquescence. Drying and storing in a vacuum or in the presence of desiccating agents were avoided since the adduct tended to lose NMA (effloresce) under such conditions.

The composition of the adduct thus obtained was examined by dissolving the weighed adduct in water and measuring the absorption of nitrate ions at 300 nm. The molar ratio of NMA to $AgNO_3$ was found to be 2.00 which is in very good agreement with the expected value.

Combined thermogravimetry (TG) and differential thermal analysis (DTA) were carried out at several pressures and heating rates to find out what would happen when the $AgNO_3 \cdot 2NMA$ was heated up from room temperature to the melting point of pure silver nitrate. A Chyo Balance Corporation Type $TRDA_1$–L DTA Instrument was used. The results are given in Figs. 1 and 2. Neither NMA nor silver nitrate itself decomposed, nor did they react to each other, to a significant extent within the temperature range studied, except for an eventual slight darkening of silver nitrate near its melting point.

The endothermic peak of the DTA curve around 47 °C is distinct and reproducible. The fact that there is no change in weight at this temperature shows that this is the genuine melting point of the adduct.

Between 60 and 190 °C no definite transition was observed except for an abrupt fall of the DTA curve and a knick on the TG curve at the same time. Visual observation showed that these anomalies correspond to re-solidification of the melt due to the loss of a fraction of the initial amount of NMA. The temperature at which the anomalies appeared and the composition of the solid at that stage depended considerably on

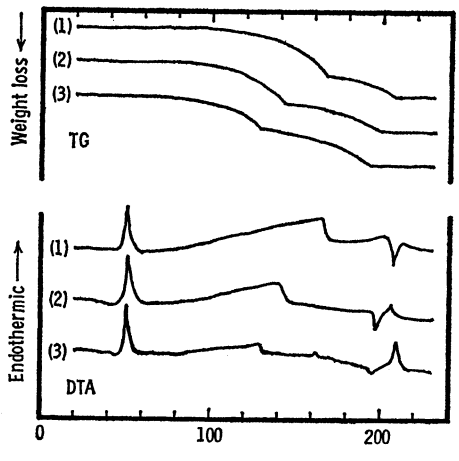

Fig. 1. TG and DTA curves of $AgNO_3$–NMA adduct at different heating rates.
Pressure: 760 mmHg. Heating rate: (1) 3.3 °C/min, (2) 1.8 °C/min, (3) 1.1 °C/min.

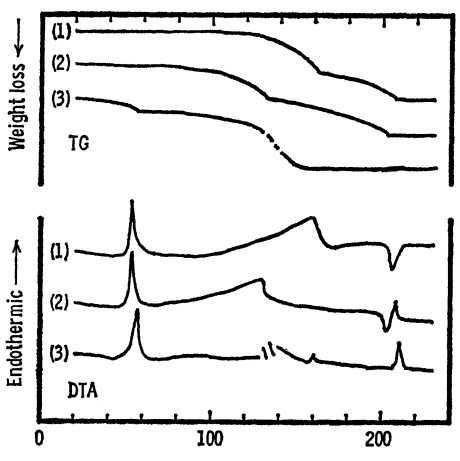

Fig. 2. TG and DTA curves of $AgNO_3$–NMA adduct at different pressures.
Heating rate: 2.6 °C/min. Pressure: (1) 760 mmHg, (2) 200 mmHg, (3) 8 mmHg.

experimental conditions. No evidence was found for the existence of another stable homogeneous phase richer in silver nitrate than the initial adduct. The cause of the knick on the TG curve would be merely the difference in the rate of vaporization of NMA from the liquid and the solid surfaces. Some DTA curves showed that the solid might contain a pure silver nitrate phase even in the presence of NMA. Traces of endothermic transition of normal silver nitrate from orthorhombic to rhombohedral structure were seen at 160 °C. (See, for example, the bottom curve in Fig. 1.)

Since we could find no "melting (or decomposition) point" at the temperature indicated by Paul and Chadha, it seems that their specimen might have lost a part of NMA during the course of drying and preservation, in particular, if the procedures had been carried out at a high temperature or at a low partial pressure of NMA, *e.g.*, in a vacuum or in the presence of desiccating agents.[3~5] On rapid heating, their specimen apparently melted at a temperature higher than the actual melting point of the adduct but lower than that of pure silver nitrate.

Attempts were made to prepare solids with NMA-content less than the adduct, by mixing powdered silver nitrate with a small amount of hot NMA and cooling the mixture rapidly in order to determine the apparent melting point of the solids in sealed tubes. Even on rapid heating, however, they melted first partly at around 50 °C, and solids coexisted with the melt. At *ca.* 140 °C generation of bubbles began to take place. This seems to correspond to the "decomposition of the adduct" mentioned by Paul and Chadha, but we consider it to be mere vaporization of NMA from the viscous melt-solid mixture.

We conclude that the actual melting point of the adduct $AgNO_3 \cdot 2NMA$ is 46—47 °C, and that the adduct is stable only at temperatures lower than this and in the presence of sufficient NMA vapor.

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