# Liquid Adducts Consisting of Ammonia and Aliphatic Acid

Shizuo NAKAMURA
*Sagami Chemical Research Center, Sagamihara, Kanagawa*
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A curious phenomenon is described herewith which takes place when a certain solid compound is added to liquid ammonia in a sealed glass tube. The compound turns liquid and remains at the bottom without being mixed with the liquid ammonia. The phenomenon does not seem to have been reported.

The following four compounds show the phenomenon: imino diacetic acid (IDA), glutaric acid (GLA), glutamic acid (GMA) and aspartic acid (ASP).

The liquid is viscous and sticky like the solution of a high molecular compound. It is not a compound in the usual sense. The ammonia content of the liquid varies with temperature. In the case of IDA the molar ratio of $NH_3$/IDA is 8 at dry ice temperature, and 6.5 at room temperature. The liquid becomes stiffer with the fall of temperature. At −78°C the liquid turns transparent, colorless caramel which does not flow; at −196°C it turns glassy, while liquid ammonia solidifies into a white mass. With the rise of temperature the liquid becomes turbid, but becomes transparent when left to stand for some time. The turbid liquid turns clear at once if temperature falls. This takes place at temperatures −30°C—+100°C. The phenomenon above 100°C was not studied.

The liquid is stable at room temperature under the pressure of saturated ammonia. In the case of IDA, the decomposition pressure is 2.1—2.4 atm at 22°C.

TABLE 1. TUBE SIZE AND EXPERIMENTAL CONDITIONS

| Tube size | | | Maximum temp. °C | Maximum pressure atm. |
|---|---|---|---|---|
| Inner dia. mm | Outer dia. mm | Length cm | | |
| 12 | 17.5 | 28 | 37 | 14 |
| 3[a)] | 8[a)] | 17 | 100 | 62 |
| 2.5 | 9 | 17 | | |
| 20 | 26 | 13 | 37 | 14 |
| 2.3 | 5 | 15 | 35 | 13 |

a) The tube burst after being kept at 100°C for one hour.

When the pressure is reduced, ammonia gas bubbles out from the viscous liquid giving rise to the formation of a white foamed mass (in the case of GLA, the mass is less sticky than in other cases, the foam being smaller). The mass is sticky at first, but turns brittle after complete separation of ammonia. It is an ammonium salt of the acid which is also dissolved forming a liquid phase like its free acid.

The liquid obtained from the four dibasic acids differ in their ammonium contents. Rough estimate at room temperature gives the results: IDA-6.5$NH_3$, GLA-7$NH_3$, GMA-6$NH_3$ and ASP-5$NH_3$.

NMR spectra of IDA-$NH_3$ and GLA-$NH_3$ at 35°C show that there is no ammonia molecule of ordinary liquid ammonia, *viz.*, NMR signal of the ammonia proton shifts from $\delta=9.88$ (ordinary liquid ammonia) to $\delta=4.74$ in the case of IDA, and to $\delta=4.26$ in the case of GLA.

The facts that the liquid does not mix with liquid ammonia, it is viscous and sticky, it exists between −196°C and +100°C, and its NMR signal of ammonia proton shifts largely from that of liquid ammonia, suggest that ammonia molecules are surrounded by atoms of acid molecules forming clathrate-like liquid structure.

*Experimental.* Thick glass tubes were used in order to prevent explosion. Tube size and experimental conditions are shown in Table 1.

Decomposition pressure was estimated by reading the temperature of liquid ammonia, whose vapor pressure balanced with that of the viscous liquid. The temperature range was −15°C (2.33 atm) to −17°C (2.14 atm).

In order to measure the ammonia content in the liquid, the liquid ammonia (upper phase) was made to volatilize gradually at room temperature. With the disappearance of upper phase, the tube was sealed off immediately, and weighed. The pressure was then reduced for the formation of foamed mass, and the vessel was evacuated and weighed. The results are given in Table 2. The accuracy of weighing is ±0.01 g.

TABLE 2. MASS BALANCE OF THE VISCOUS LIQUID

| | Acid used g | Viscous liquid g | Ammonia content g | Molar $NH_3$/acid ratio | Remaining solid | |
|---|---|---|---|---|---|---|
| | | | | | g | Formula |
| IDA-$NH_3$ | 0.50 | 0.91 | 0.41 | 6.4 | 0.57 | $NH_4$-$C_4H_6O_4N$ |
| IDA-$NH_3$[a)] (−78°C) | 0.50 | 1.02 | 0.52 | 8.1 | 0.58 | $NH_4$-$C_4H_6O_4N$ |
| GLA-$NH_3$ | 0.50 | 0.96 | 0.46 | 7.1 | 0.65 | $(NH_4)_2$-$C_5H_6O_4$ |
| GLA-$NH_3$ | 0.70 | 1.32 | 0.62 | 6.9 | 0.88 | $(NH_4)_2$-$C_5H_6O_4$ |
| GMA-$NH_3$ | 0.50 | 0.83 | 0.33 | 5.7 | 0.58 | $NH_4$-$C_5H_8O_4N$ |
| ASP-$NH_3$ | 0.50 | 0.83 | 0.33 | 5.2 | 0.55[b)] | $NH_4$-$C_4H_6O_4N$ ? |

a) Separation of the two phases was carried out by decantation.
b) Hygroscopic.