The Formation of Trilaurylammonium Carbonate

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During work in this laboratory with trilaurylamine (TLA) [1,2] (tridodecylamine) it was noticed that a white precipitate appeared on the bottom of containers filled with the liquid amine. In an attempt to find out the composition of this solid it was filtered off and washed with petroleum ether and dried in air. Elemental analysis gave the following results:

	C	H	N
Found	76.29	13.28	2.69
$TLAH_2CO_3$	76.09	13.29	2.40
$TLAH_2CO_3H_2O$	73.82	13.23	2.33

It seems evident that the experimentally found composition corresponds to the formation of a carbonate salt. The formation of a hydrate, $TLAH_2CO_3H_2O$, does not seem likely.

The salt $TLAH_2CO_3$ could be prepared by bubbling CO_2(g) through TLA(l) in contact with pure water. The reaction proceeds slowly; during one night enough solid had been formed permitting elemental analysis. The analysis confirmed the composition $TLAH_2CO_3$. On bubbling N_2(g) through TLA(l) overnight the solid disappeared.

Infrared spectra were run on $TLAH_2CO_3$(s), $TLAH_2CO_3$ dissolved in benzene, and on $TLAH_2CO_3$ in benzene treated with sulfuric acid.

Fig. 1 gives the IR spectrum of $TLAH_2CO_3$ dissolved in benzene and that of TLA itself. A new band appears in the range 1540 – 1640 cm^{-1}. In the literature absorption has been found in the range 1410 – 1450 cm^{-1} for inorganic carbonates [3a] and from the values for inorganic carbonates up to ≈1800 cm^{-1} for organic carbonates.[4] The values recorded for $TLAH_2CO_3$ are thus in the IR range to be expected. The infrared spectrum of the solution of trilaurylammonium carbonate in benzene treated with sulfuric acid showed peaks at 1140 cm^{-1} and 630 cm^{-1} confirming the formation of a sulfate.[3b]

It has been observed that the secondary amine, dilaurylamine (didodecylamine), similarly to TLA seems to absorb CO_2 readily from air.[5]

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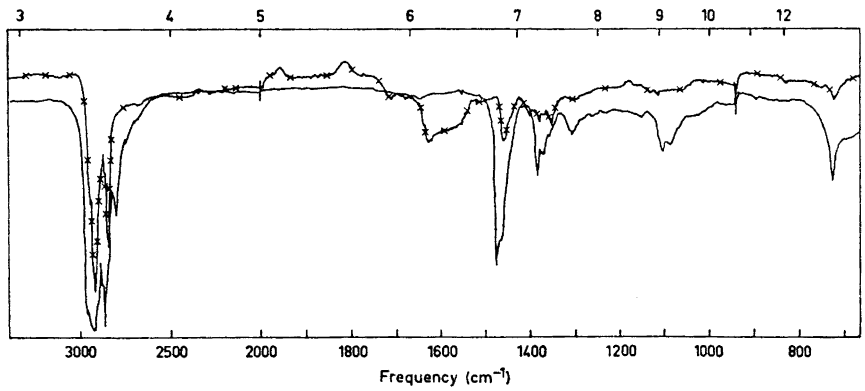

Fig. 1. IR spectrum of TLA ———. IR spectrum of $TLAH_2CO_3$ × – ×. The concentrations of TLA and $TLAH_2CO_3$ are not the same.

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On the Phase Diagram Na_2CO_3—Na_2S

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At STFI a thermodynamic study of reactions in the recovery of spent pulping liquors is in progress. For this investigation a reliable phase diagram for the system $Na_2CO_3 - Na_2S$ was needed. The only earlier studies on this system in the literature seem to be those by Tammann and Oelsen,[1] and by Courtois.[2] The result of the former authors seems to be quite uncertain mainly due to the use of impure Na_2S. Courtois' result is doubtful as his experimental method [3] is unsuitable for two-component systems. Therefore a redetermination seemed necessary and was performed at the Department of Inorganic Chemistry at Umeå University.

The sodium carbonate – sodium sulfide system has been studied mainly by high temperature microscopy (HTM) and differential thermal analysis (DTA).

Experimental. Pure anhydrous Na_2S was prepared as described in Ref. 4. The product was white, analyzed ≥ 99.5 % Na_2S (iodometrically),[5] and had a melting point of 1175°C ± 10°C. Na_2CO_3 (May and Baker, *p.a.*) was dried at 500°C under CO_2 and had a melting point of 858°C. All handling, *e.g.*, mixing and weighing of samples, was made in dry N_2 atmosphere in a glove-box.

A Leitz high temperature microscope (HTM) with a 1350 Hot-stage was used. The temperature was measured with a Pt – Pt(Rh) thermocouple. The sample mixture was pressed into a small disc and was then placed between two sapphire plates for direct observation (at 100× magnification) of melting and solidification processes under a protective atmosphere of N_2. Heating and cooling was done very slowly near the transition temperatures.

The DTA equipment was a Netzsch model 404. The sample and the reference substance (Al_2O_3-powder) were packed in small alumina cups (with graphite lids) placed on the thermocouples. The heating and cooling rate was 5°/min, and was done in an atmosphere of 90 % N_2 and 10 % H_2.

Result and discussion. The results are are shown in Fig. 1. The system has a single eutectic at a mol fraction Na_2S (x_{Na_2S}) of 0.40 and at 762°C. Also there is some evidence of solid solubility, at least on the Na_2CO_3 side of the phase diagram. The liquidus temperatures obtained by HTM

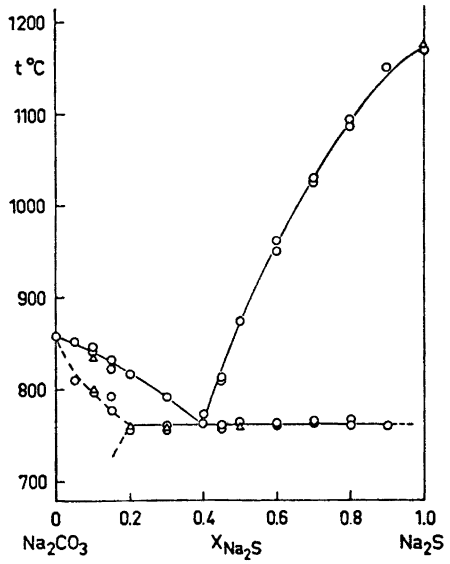

Fig. 1. The phase diagram $Na_2CO_3 - Na_2S$. ○ HTM data. △ DTA data.