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THERMAL ANALYSIS AND STRUCTURAL STUDIES OF SYSTEMS OF $SbCl_3$ WITH DIPHENYLAMINE, TRIPHENYLAMINE, ANILINE HYDROCHLORIDE AND SULPHUR

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ABSTRACT

Structures and phase relations in the systems of $SbCl_3$ with diphenylamine, triphenylamine, sulphur, and aniline hydrochloride were investigated by means of DTA and X-ray techniques.

Compounds of various compositions were identified:

2:1 and 1:1 in the system $SbCl_3$/diphenylamine

2:1 in the system $SbCl_3$/triphenylamine and

1:1 and 1:2 in the system $SbCl_3$/aniline hydrochloride.

The system $SbCl_3$/sulphur is a simple eutectic one.

INTRODUCTION

The investigation of the present systems forms part of a study of the acceptor properties of $SbCl_3$. It was previously reported that $SbCl_3$ is an acceptor towards N-atoms (ref. 1,2) and π-systems (ref. 3) of amines as well as towards Cl^- ions of amine hydrochlorides (ref. 4) and that SbI_3 forms a molecular complex with sulphur (ref. 5).

In this paper phase diagrams are discussed as a result of DTA methods and X-ray powder patterns.

EXPERIMENTAL

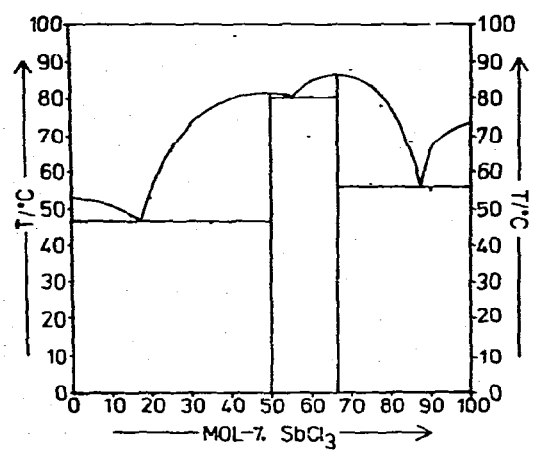
Special DTA ampoules were filled with the samples required for DTA measurement under argon atmosphere and sealed at vacuum. The mixtures were homogenized and tempered about 10° below the eutectic temperatures. Samples for X-ray powder patterns were treated the same way.

DTA measurements of heating curves were carried out on different DTA-systems (ref. 6,7). Heating rates were varied between 0.75 and 2° per minute depending on the required resolution of the curves. Nickel-chrome nickel thermocouples were used for temperature measurements. The reference material was $TeCl_4$ and schamotte. For powder patterns the Guinier technique was used.

RESULTS

System $SbCl_3$-Diphenylamine (Fig. 1)

The system is quasi binary with two congruently melting compounds. Melting points are 86 to 88° for the 2:1 and 81 to $85^{\circ}C$ for the 1:1 phases, respectively. The eutectic mixtures are at 87.5, 55.5 and 17.5 mol-% $SbCl_3$, the eutectic temperatures at 55.5, 80.5 and $47^{\circ}C$. The structures of the compounds are built up of $SbCl_3$ and diphenylamine molecules. The adducts are stabilized by Sb...π and Sb...Cl interactions.



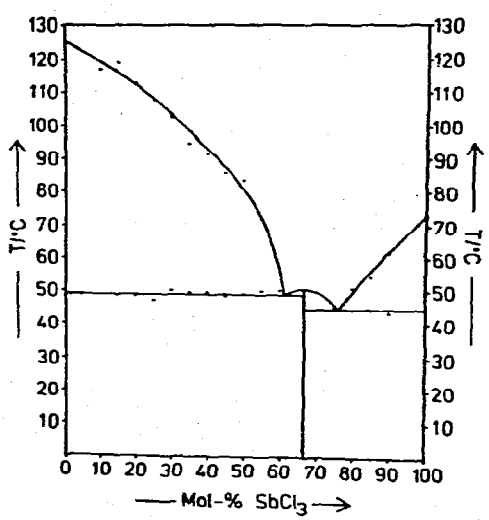


Fig. 1. Phase diagram $SbCl_3$-diphenylamine
Fig. 2. Phase diagram $SbCl_3$-triphenylamine

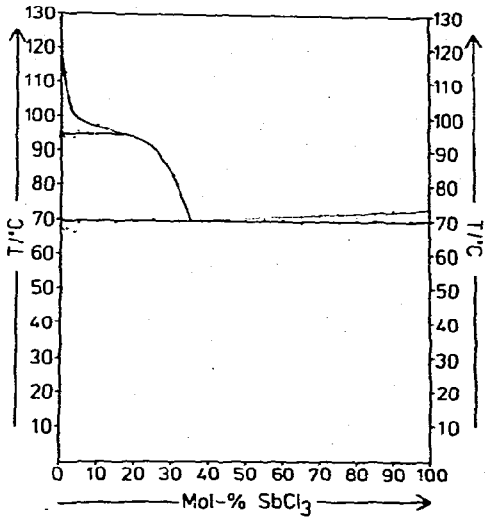
System $SbCl_3$-Triphenylamine (Fig. 2)

The 2:1 compound melts congruently at 51 to 54° with a small dystecticum. Eutectic mixtures are at 61.5 and 76 mol-%, eutectic lines at 49 and 44.5°C. X-ray structure analysis showed that $2SbCl_3$.triphenylamine is a molecular compound which is stabilized by Sb...π and Sb...Cl interactions.

System $SbCl_3$-Sulphur (Fig. 3)

A molecular adduct between $SbCl_3$ and sulphur does not exist. Samples had only been heated little above the liquid temperatures at preparation to avoid breaking of sulphur rings. The eutectic is at 35 mol-% $SbCl_3$ and 70°C.

Phase transition of sulphur ocurred at 95° except for sulphur itself which showed overheating effects.



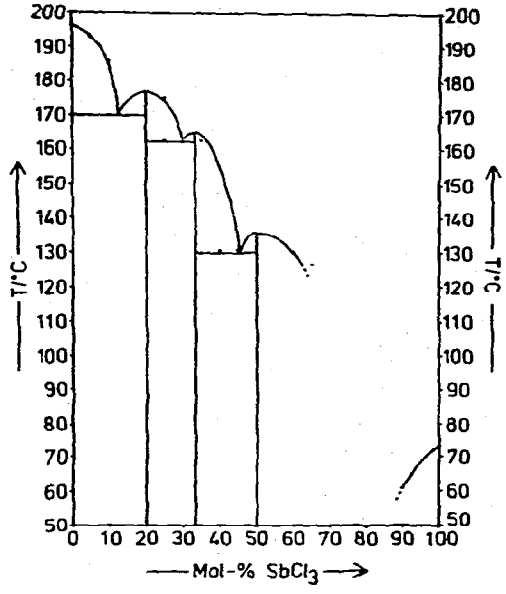


Fig. 3. Phase diagram $SbCl_3$-sulphur

Fig. 4. Phase diagram $SbCl_3$-aniline hydrochloride

System $SbCl_3$-Aniline Hydrochloride (Fig. 4)

Two congruently melting phases with compositions of 1:1 and 1:2 were identified. Melting points are 137 to 140°C, and 165 to 168°C, respectively. The eutectic line in the range of 0 to 20 mol-% $SbCl_3$ and the maximum at 20 mol-% $SbCl_3$ as well as X-ray powder patterns indicate the existence of a further compound. Its composition is

still dubious, for the heating curve of the 20:80 sample matches the eutectic line as well as the liquid curve, which indicates that the phase diagram might be pseudobinary.

The eutectic line in the range from 50 to 100 mol-% $SbCl_3$ could not yet be located probably due to glass formation, for some samples are liquid but do not show reproducible effects by low temperature DTA method, and other samples look partially recrystallized after tempering at different temperatures.

As result of X-ray structure determination the compounds might be described as intermediates between anilinium chloroantimonates and adducts of $SbCl_3$ with anilinium chlorides.

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