

Solvates of Arsenic Trichloride, Phosphorus Oxychloride and Selenium Oxychloride

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The liquidus curves have been studied for mixtures between each of the solutes $(\text{CH}_3)_4\text{NCl}$, $(\text{C}_2\text{H}_5)_4\text{NCl}$, SnCl_4 , SbCl_5 and the solvents AsCl_3 , POCl_3 , SeOCl_2 and also for mixtures between the solvents. The following new compounds have been found: $(\text{CH}_3)_4\text{NCl} \cdot 5 \text{SeOCl}_2$, $(\text{CH}_3)_4\text{NCl} \cdot 3 \text{SeOCl}_2$, $(\text{CH}_3)_4\text{NCl} \cdot 2 \text{SeOCl}_2$, $(\text{C}_2\text{H}_5)_4\text{NCl} \cdot 5 \text{SeOCl}_2$, $(\text{C}_2\text{H}_5)_4\text{NCl} \cdot 2 \text{AsCl}_3$, $3(\text{C}_2\text{H}_5)_4\text{NCl} \cdot 5\text{AsCl}_3$ and $\text{POCl}_3 \cdot \text{AsCl}_3$. The results are briefly discussed.

The reactions in non-aqueous ionising solvents have attracted much interest during recent years. The chemistry in arsenic trichloride, AsCl_3 , phosphorus oxychloride, POCl_3 , and selenium oxychloride, SeOCl_2 , has recently been reviewed by Gutman^{1,2} who mentions the fact that compounds between solute and solvent (solvates) often may be isolated. It has been pointed out by Lindqvist³ that the knowledge of the structures of the solid solvates is necessary for any detailed discussion of solubility and solvation conditions in these solvents. We have therefore made a survey of the binary systems between some important solutes and the three solvents AsCl_3 , POCl_3 and SeOCl_2 . This study has partly confirmed earlier results, partly led to isolation of new compounds.

EXPERIMENTAL

Chemicals used. AsCl_3 was purified as described earlier⁴ with final conductances of $0.9-1.1 \times 10^{-7} \text{ ohm}^{-1} \text{ cm}^{-1}$ at room temperature. POCl_3 was purified by distillation (boiling point $+105^\circ\text{C}$). SeOCl_2 (B.D.H. reagents) with a conductance of $8 \times 10^{-4} \text{ ohm}^{-1} \text{ cm}^{-1}$ at $+22^\circ\text{C}$ was not further purified. SnCl_4 and SbCl_5 were purified according to Dodd and Robinson⁵. $(\text{CH}_3)_4\text{NCl}$ (Eastman Kodak) was dried for 12 h at 110°C . Crude $(\text{C}_2\text{H}_5)_4\text{NCl}$ was recrystallised from acetone and dried at reduced pressure in a drying pistol at 100°C .

Analytical methods. Cl was determined by potentiometric titrations with 0.1 M AgNO_3 . N was determined by Kjeldahl distillation. Se was analysed by reduction with sulfurous acid in hydrochloric acid solution⁶. P was determined according to a method given by Scheel⁷.

Phase diagrams. The aim of the phase diagram studies has not been to obtain highly accurate data but rather to make a survey of the liquidus curves in the different binary

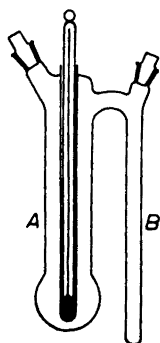


Fig 1

Fig. 1. Vessel for the phase diagram studies.

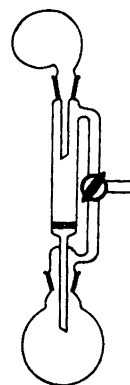


Fig 2

Fig. 2. Apparatus for the analysis.

systems, particularly for large mole fractions of solvent. A rather simple apparatus could therefore be used for these experiments (Fig. 1). With liquid solutes, the solute and solvent are poured or directly distilled into either of the two legs *A* or *B* which have been cooled to -50°C . The amount added to the *A* part has first been weighed and as the *B* tube has been calibrated, the volume of liquid transferred from *B* to *A* during the experiments can be determined (as well as the weight, because the densities are known). Solid solute is added in weighed amounts to the solvent in *A*. The error in the mole fractions obtained in this way is mainly due to adherence of liquid to the glass walls during the transfer from *B* to *A* or to vapor phase reactions, but the accuracy is good enough for our purposes. The thermometer does not dip directly into the liquid (which would have increased the difficulties of working in a closed system) but the thermal contact is improved by a small mercury drop at the bottom of the inner tube. Tests have shown that the reproducibility of the temperature reading is within $\pm 1^{\circ}$. The temperature values may, however, have systematic errors of $2-3^{\circ}$ which is of no importance in this type of study (compare also the good agreement with the results of more elaborate measurements). The results are not sensitive to small impurities if the solvates formed have congruent melting points, that is when the reactants completely crystallise as solids.

The analyses were made in an apparatus (Fig. 2) which permitted filtration and washing of the crystals formed. The crystals were then dissolved on the filter in an alkaline water solution and their mole ratios could be determined by analyses. Absolute analyses of weighed amounts of the solvates were also made in some cases but are difficult to carry out because of the extreme sensitivity of these compounds to moisture.

When our investigation was finished, we were informed by Dr. Gutmann, Vienna, of a thesis by Groeneveld, Leyden. Groeneveld has already studied three of our systems: $\text{SnCl}_4-\text{POCl}_3$, $\text{SbCl}_5-\text{POCl}_3$ and $\text{SnCl}_4-\text{SeOCl}_2$ with a more elaborate experimental technique. His phase diagrams, which have never been published, are in very good agreement with ours. The melting points he obtained for the solvates are given together with our results for comparison in the following. The good agreement proves that the very simple and rapid technique used by us was adequate for our purposes.

RESULTS

Tetramethyl ammonium chloride, $(\text{CH}_3)_4\text{NCl}$

1. $(\text{CH}_3)_4\text{NCl} \cdot \text{AsCl}_3$ and $(\text{CH}_3)_4\text{NCl} \cdot 3 \text{AsCl}_3$ have been prepared earlier^{8,9}. Part of the phase diagram has now been studied (Fig. 3 *a*) and no higher

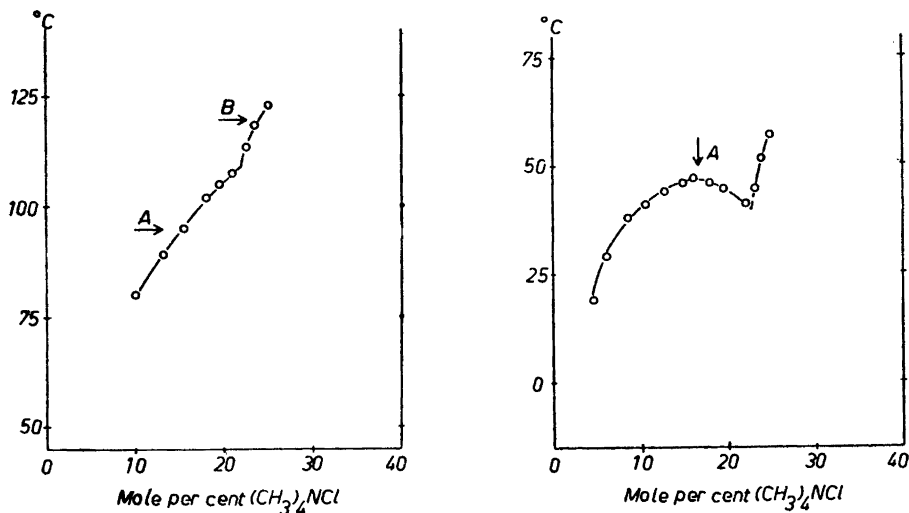


Fig. 3. *a.* The system $(\text{CH}_3)_4\text{NCl}-\text{AsCl}_3$. Liquidus curves for $A = (\text{CH}_3)_4\text{NCl} \cdot 3\text{AsCl}_3$, $B = (\text{CH}_3)_4\text{NCl} \cdot \text{AsCl}_3$. *b.* The system $(\text{CH}_3)_4\text{NCl}-\text{SeOCl}_2$. Liquidus curve for $A = (\text{CH}_3)_4\text{NCl} \cdot 5\text{SeOCl}_2$.

solvates have been discovered. Mole fractions of $(\text{CH}_3)_4\text{NCl}$ larger than 0.25 cannot be studied because of the boiling of the solvent.

2. The solubility of $(\text{CH}_3)_4\text{NCl}$ in POCl_3 is very small below $+200^\circ\text{C}$ and does not permit a phase study of this type. (Gutmann¹⁰ found 2 g/l at $+20^\circ\text{C}$ corresponding to a mole fraction of 0.0016.)

3. The phase diagram (Fig. 3 *b*) $(\text{CH}_3)_4\text{NCl}-\text{SeOCl}_2$ shows a maximum at the composition $(\text{CH}_3)_4\text{NCl} \cdot 5 \text{SeOCl}_2$ where the entire liquid phase solidifies. The melting point is $+45-47^\circ\text{C}$. The analysis of this compound is very difficult to carry out accurately, because the crystals lose SeOCl_2 when washed with, *e.g.*, ether, and small amounts of liquid adhere to the solid without being washed. The position of the maximum has, however, been studied by direct comparison of the melting points of different accurately weighed mixtures of solute and solvent.

The white residue obtained after washing with a small amount of ether had the composition $(\text{CH}_3)_4\text{NCl} \cdot 3 \text{SeOCl}_2$. Mole ratio N : Se : Cl calculated 1 : 3 : 7, found 1.00 : 3.04 : 7.01. A thorough washing with ether gave a compound $(\text{CH}_3)_4\text{NCl} \cdot 2 \text{SeOCl}_2$. Mole ratio N : Se : Cl calculated 1 : 2 : 5, found 1.00 : 2.01 : 5.00. In the latter case an absolute analysis proved that no ether had entered the solid compound. Calculated for N : 3.17 %, found 3.17 %.

The two compounds $(\text{CH}_3)_4\text{NCl} \cdot 2 \text{SeOCl}_2$ and $(\text{CH}_3)_4\text{NCl} \cdot 3\text{SeOCl}_2$ could not be obtained by cooling of solutions of $(\text{CH}_3)_4\text{NCl}$ in SeOCl_2 because these solutions become very viscous and are always supercooled at mole fractions of $(\text{CH}_3)_4\text{NCl}$ larger than 0.25.

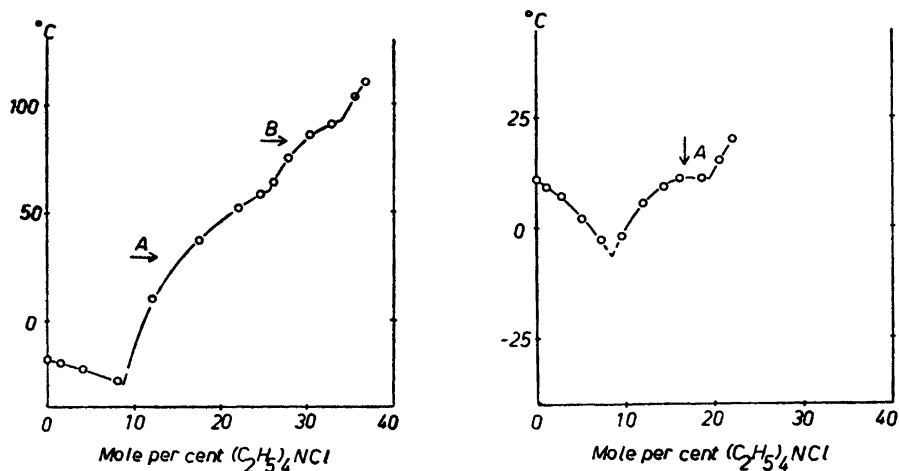


Fig. 4. *a.* The system $(\text{C}_2\text{H}_5)_4\text{NCl}-\text{AsCl}_3$. Liquidus curves for $A = (\text{C}_2\text{H}_5)_4\text{NCl} \cdot 2\text{AsCl}_3$, $B = 3(\text{C}_2\text{H}_5)_4\text{NCl} \cdot 5\text{AsCl}_3$. *b.* The system $(\text{C}_2\text{H}_5)_4\text{NCl}-\text{SeOCl}_2$. Liquidus curve for $A = (\text{C}_2\text{H}_5)_4\text{NCl} \cdot 5\text{SeOCl}_2$.

Tetraethyl ammonium chloride, $(\text{C}_2\text{H}_5)_4\text{NCl}$

1. The phase diagram is shown in Fig. 4 *a.* No congruently melting compounds are obtained in the concentration range studied and the compositions of the phases in equilibrium with the solution have been determined by distillation at reduced pressure at different temperatures. The same method has been used earlier¹⁰ in the study of the compounds between $(\text{CH}_3)_4\text{NCl}$ and AsCl_3 . We started with a dilute solution of $(\text{C}_2\text{H}_5)_4\text{NCl}$ in AsCl_3 and distilled at 0°C until the weight was constant. The mole ratio $\text{AsCl}_3 : (\text{C}_2\text{H}_5)_4\text{NCl}$ was then 2.06 in agreement with a compound $(\text{C}_2\text{H}_5)_4\text{NCl} \cdot 2\text{AsCl}_3$. The temperature of the distillation was then increased to $+22^\circ\text{C}$ when more AsCl_3 was lost until the mole ratio became 1.69 in agreement with a compound $3(\text{C}_2\text{H}_5)_4\text{NCl} \cdot 5\text{AsCl}_3$. This is no definite proof that these formulae are correct but this system has shown such interesting features that we plan a more detailed study of it.

2. The solubility of $(\text{C}_2\text{H}_5)_4\text{NCl}$ in POCl_3 below $+200^\circ\text{C}$ is very low and does not permit a phase study of this type.

3. The phase diagram $(\text{C}_2\text{H}_5)_4\text{NCl}-\text{SeOCl}_2$ is shown in Fig. 4 *b.* Here the same obstacles to accurate analysis are encountered as in the case of $(\text{CH}_3)_4\text{NCl}$ but the phase diagram indicates a compound with the composition $(\text{C}_2\text{H}_5)_4\text{NCl} \cdot 5\text{SeOCl}_2$. Its melting point is $+11-12^\circ\text{C}$ so that the compound cannot be isolated at room temperature and no other washings have been made.

At mole ratios larger than 0.22 it is impossible to determine the melting points with any accuracy with our methods.

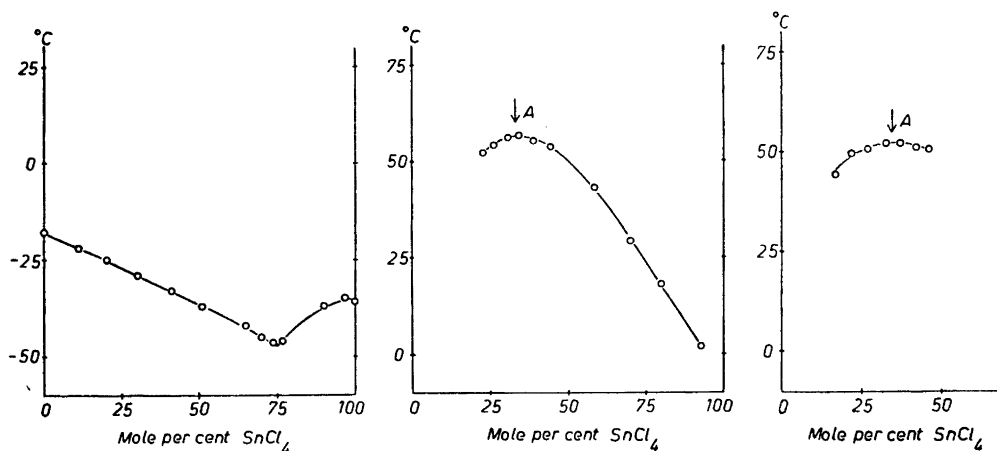


Fig. 5. a. The system $\text{SnCl}_4\text{—AsCl}_3$. b. The system $\text{SnCl}_4\text{—POCl}_3$. Liquidus curve for $A = \text{SnCl}_4 \cdot 2\text{POCl}_3$. c. The system $\text{SnCl}_4\text{—SeOCl}_2$. Liquidus curve for $A = \text{SnCl}_4 \cdot 2\text{SeOCl}_2$.

Tin tetrachloride, SnCl_4

1. The phase diagram, given in Fig. 5 a, does not indicate any compound formation.

2. The phase diagram $\text{SnCl}_4\text{—POCl}_3$ (Fig. 5 b) has only one, well defined maximum corresponding to the compound $\text{SnCl}_4 \cdot 2\text{POCl}_3$ with a melting point of $+55\text{—}57^\circ\text{C}$ (Groeneveld 56°C). Three compounds have earlier been described: $2 \text{SnCl}_4 \cdot \text{POCl}_3$ by Oddo and Tealdi¹¹, $\text{SnCl}_4 \cdot \text{POCl}_3$ and $\text{SnCl}_4 \cdot 2 \text{POCl}_3$ by Gutmann¹² who, however, did not definitely prove the existence of a definite compound $\text{SnCl}_4 \cdot 2 \text{POCl}_3$. The existence of that solvate was proved by Payne¹³ who found a melting point of $+59 \pm 0.5^\circ\text{C}$. The compound $\text{SnCl}_4 \cdot \text{POCl}_3$ was obtained by Gutmann from $\text{SnCl}_4 \cdot 2 \text{POCl}_3$ at low pressure. It is evident that it does not exist in the closed system which we have studied, nor does $2 \text{SnCl}_4 \cdot \text{POCl}_3$.

3. The phase diagram (Fig. 5 c) shows the existence of a compound $\text{SnCl}_4 \cdot 2 \text{SeOCl}_2$ with a melting point of $+52\text{—}54^\circ\text{C}$ (Groeneveld $\sim 52^\circ\text{C}$). The system could not easily be studied for mole fractions of SnCl_4 larger than 0.50 because of the formation of two liquid phases. $\text{SnCl}_4 \cdot 2 \text{SeOCl}_2$ has already been reported by Wise¹⁴.

Antimony pentachloride, SbCl_5

1. The phase diagram $\text{AsCl}_3\text{—SbCl}_5$ (Fig. 6 a) does not show any indication of compound formation. Gutmann⁸, however, obtained a small residue of the approximate composition $\text{AsCl}_3 \cdot \text{SbCl}_5$ by evaporation *in vacuo* at $+30\text{—}35^\circ\text{C}$. That compound obviously must be the result of a slow irreversible reaction.

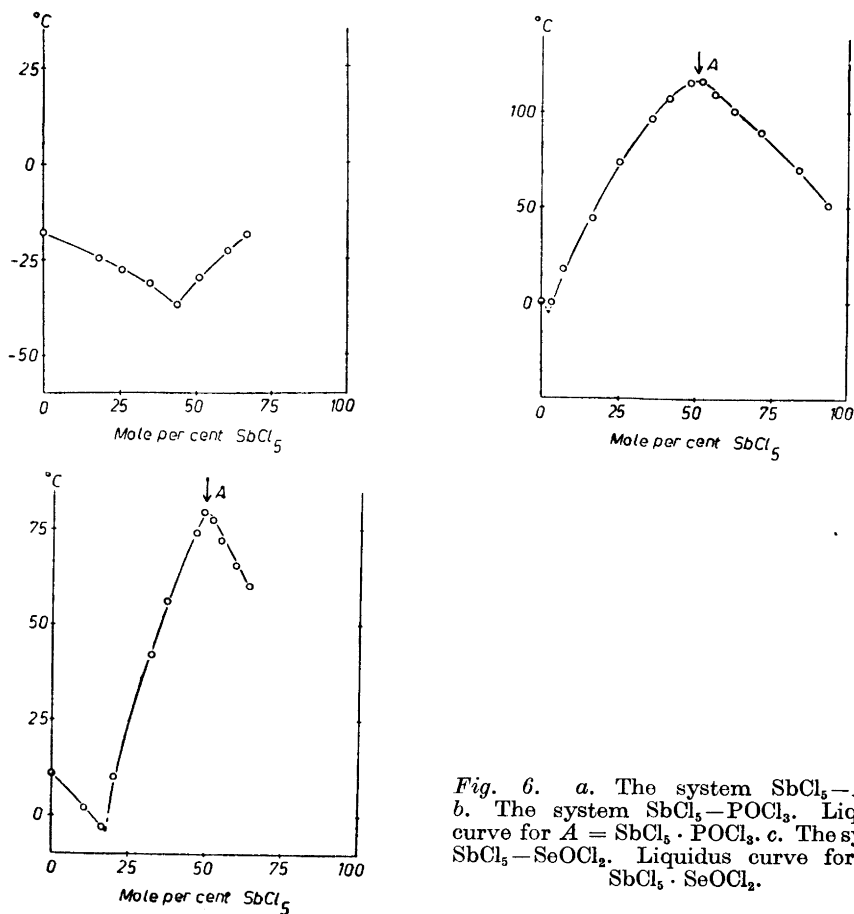


Fig. 6. a. The system SbCl_5 — AsCl_3 . b. The system SbCl_5 — POCl_3 . Liquidus curve for $A = \text{SbCl}_5 \cdot \text{POCl}_3$. c. The system SbCl_5 — SeOCl_2 . Liquidus curve for $A = \text{SbCl}_5 \cdot \text{SeOCl}_2$.

2. The phase diagram SbCl_5 — POCl_3 (Fig. 6 b) confirms the existence of the compound $\text{SbCl}_5 \cdot \text{POCl}_3$, earlier described by Weber¹⁵ and Gutmann¹². The melting point is $+115$ — 117°C (Groeneveld 117°C). The statement by Gutmann that the compound is not soluble in SbCl_5 is not in agreement with our results.

3. The phase diagram SbCl_5 — SeOCl_2 (Fig. 6 c) shows the existence of only one compound, $\text{SbCl}_5 \cdot \text{SeOCl}_2$, with a melting point of $+79$ — 80°C . Weber¹⁵ has already described the same solvate but Wise¹⁴ found $\text{SbCl}_5 \cdot 2 \text{SeOCl}_2$, the existence of which we have not been able to confirm.

Binary systems between the solvents

1. We have also studied the binary systems between the solvents. Fig. 7 a shows the system POCl_3 — AsCl_3 . The existence of a compound $\text{AsCl}_3 \cdot \text{POCl}_3$ with a melting point of -23 — 25°C has definitely been established.

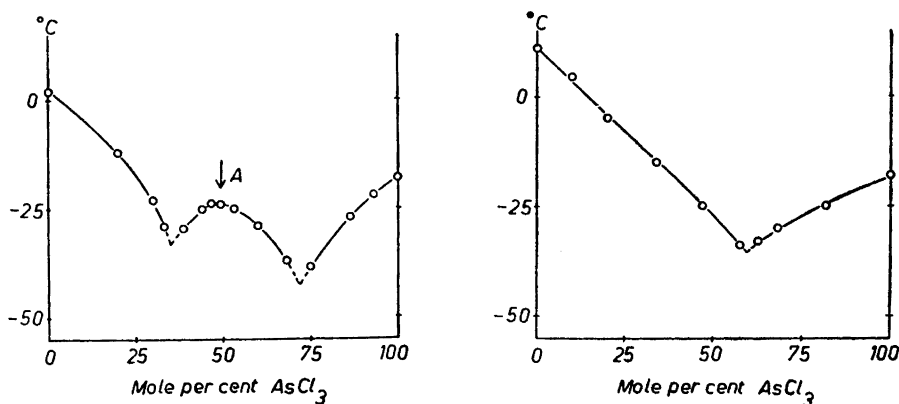


Fig. 7. a. The system $\text{AsCl}_3\text{--POCl}_3$. Liquidus curve for $A = \text{AsCl}_3 \cdot \text{POCl}_3$.
b. The system $\text{AsCl}_3\text{--SeOCl}_2$.

2. The system $\text{AsCl}_3\text{--SeOCl}_2$ (Fig. 7 b) does not show any indications of compound formation.

3. When SeOCl_2 and POCl_3 are mixed a yellowish insoluble precipitate is formed after some hours at low mole fractions of POCl_3 ; immediately at mole fractions larger than 0.35–0.45. The composition of this precipitate corresponds to a formula $3 \text{SeOCl}_2 \cdot 2\text{POCl}_3$ (calculated mole ratio P:Se:Cl = 2 : 3 : 12, found 2.00 : 3.04 : 11.94). When we tried to determine the melting point, part of the compound formed a red-brown vapour at about $+170^\circ\text{C}$ quite like SeCl_4 . We could not definitely ascertain whether a compound had formed or not, but we decided that a chemical reaction $3 \text{SeOCl}_2 + 2 \text{POCl}_3 \rightarrow 3 \text{SeCl}_4 + \text{P}_2\text{O}_5$ had probably taken place. SeCl_4 and P_2O_5 are both almost insoluble in SeOCl_2 as well as in POCl_3 . The reaction therefore would always lead to a product of the approximate composition $3 \text{SeOCl}_2 \cdot 2 \text{POCl}_3$ or $3 \text{SeCl}_4 \cdot \text{P}_2\text{O}_5$.

The stability of solutions of SbCl_5 in SeOCl_2

The findings in the preceding section open the question of whether solutions in AsCl_3 , POCl_3 and SeOCl_2 are stable or only metastable.

We have made one experiment to investigate this problem further. Sb_2O_5 and SeCl_4 were mixed in an ampoule, which was sealed (but not evacuated). After one day the mixture looked wet and the colour had become red-brown. When heated to $+60^\circ\text{C}$ it partly melted, as would be expected if the reaction $\text{Sb}_2\text{O}_5 + 5 \text{SeCl}_4 \rightarrow 2 \text{SbCl}_5 + \text{SeOCl}_2$ had taken place. This experiment strongly indicates that at least the solution of SbCl_5 in SeOCl_2 is a stable solution.

DISCUSSION

We do not want to make any far-going theoretical speculations based on this investigation but a few observations in connection with the present study may be summarised:

1. The behaviour of POCl_3 is quite different from AsCl_3 and SeOCl_2 in reactions with $(\text{CH}_3)_4\text{NCl}$ and $(\text{C}_2\text{H}_5)_4\text{NCl}$. These two salts have a very low solubility in POCl_3 (of a different order than in AsCl_3 and SeOCl_2) and give no solvates. This indicates that the solvation energy of Cl^- is smaller in POCl_3 than in AsCl_3 and SeOCl_2 . Using the acid-base concept suggested by Gutmann and Lindqvist¹⁶ this means that POCl_3 is a weaker acid than AsCl_3 and SeOCl_2 .

2. AsCl_3 reacts with SnCl_4 and SbCl_5 quite unlike POCl_3 and SeOCl_2 . The latter solvents form congruently melting solvates but AsCl_3 gives only eutectic mixtures (the compound $\text{SbCl}_5 \cdot \text{AsCl}_3$ can be prepared only under special conditions). In a previous paper¹⁷ on the reactions in solutions of POCl_3 the reasons for the difference have been discussed.

3. $(\text{CH}_3)_4\text{NCl}$ is less soluble than $(\text{C}_2\text{H}_5)_4\text{NCl}$ in these solvents. (KCl has a still smaller solubility.) It would be interesting to study quaternary ammonium salts with larger cations to see how far the solubility increases with the cation radius.

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