Studies on Arsenic Trichloride as a Solvent

II. On the Constitution of Solutions in Arsenic Trichloride

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The importance of ionic transfer processes in acid-base reactions in AsCl$_3$ is discussed, and the way in which they differ from Lewis' acid-base concept is pointed out. A program for experimental studies to explore the constitution of solutions in arsenic trichloride is suggested. It is partly based on a discussion of the possible similarities with aqueous solutions.

ACID-BASE CONCEPT

In connection with studies on non-aqueous solvents three main acid-base concepts have been advanced: the solvent system concept, the protonic concept and the electronic theory. They are excellently reviewed by Audrieth and Kleinberg [1] in the book "Non-aqueous solvents". In a recent paper [2] a development has been made of the solvent system concept, focussing the interest on the ionic transfer processes possible in different solvents. This represents at the same time an extension of the protonic concept to non-protonic solvents. Flood's [3] treatment of oxide melts is also included.

The new concept defines acids and bases in AsCl$_3$ in the following way: acid + Cl$^-$ = base (*cf.* acid = base + H$^+$) *or* base + solvent = acid + Cl$^-$ (*cf.* acid + solvent = base + H$^+$ in some cases [5]).

AsCl$_3$ is an ampholytic solvent and can react as an acid as well as a base: AsCl$_3$ + Cl$^-$ = AsCl$_4^-$ and AsCl$_3$ = AsCl$_2^+$ + Cl$^-$. It has therefore a characteristic auto-ionization: 2 AsCl$_3$ = AsCl$_2^+$ + AsCl$_4^-$, which is the basis for the solvent system definition.

AsCl$_4^-$ evidently corresponds to H$_3$O$^+$ in aqueous solutions and when the discussion is limited to AsCl$_3$ solutions we can therefore use the term Cl$^-$ in the same way as we use H$^+$ in aqueous solutions.

Acids will decrease and bases will increase the Cl$^-$ concentration in AsCl$_3$ (*cf.* the H$^+$ concentration in aqueous solutions).

Examples of acids are FeCl$_3$ and SnCl$_4$ which can form the ions FeCl$_4^-$ and SnCl$_6^{2-}$ and thus consume Cl$^-$ ions.

A typical base is $(CH_3)_4NCl$ which as a salt contributes Cl^- ions to the solution. Another base to be discussed later is pyridine.

The new concept is more to be considered as a *method* for a *unified treatment* of what we call *acid-base reactions* in non-aqueous solvents and salt melts than as a contribution to the discussion of the *formal definition* of *acids and bases*. For that purpose there exist more symmetrical definitions [4] which, however, are purely formal.

It is of particular interest to compare the new concept with Lewis' theory, according to which an acid is an electron pair acceptor, a base is an electron pair donor. The difference in the two concepts is best shown in the two different ways of considering the reaction between pyridine and arsenic trichloride:

$$C_5H_5N: \; + AsCl_3 = C_5H_5N:AsCl_3 = C_5H_5N:AsCl_2^+ + Cl^-$$
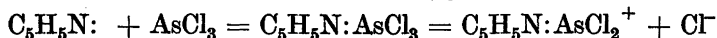
The acid-base process is here, according to Lewis, the first step, that is *the formation of an electron pair bond*. That reaction would not change the Cl^- concentration in $AsCl_3$, however. The acid-base process described as *a transfer of chloride ions* would obviously be the second step.

The two definitions evidently have different aims. The reactions included in the Lewis theory are the same as those which cause the colour changes of indicators. The new concept on the other hand focuses interest on the transfer processes of ions, which can be studied indirectly with indicators but more directly with electrochemical methods.

THE EXPERIMENTAL STUDY OF IONIC TRANSFER PROCESSES

If the chloride ion transfer is the fundamental reaction in $AsCl_3$ there must exist $AsCl_2^+$ and $AsCl_4^-$ ions. The existence of such ions has only been proved indirectly and we have no knowledge of their structures.

The simplest indirect experimental evidence is obtained by preparations of compounds that may contain those groups. Thus the compound $AsSbCl_8$ has been interpreted as $AsCl_2SbCl_6$[7], and the formula $(CH_3)_4NAsCl_4$[7] as an indication of the presence of a $AsCl_4^-$ ion. These ideas have also been checked by conductometric neutralisation titrations[7], and must be considered to be well founded, although not conclusively so. Successive heating of the compound $(CH_3)_4NAsCl_4 \cdot 2\ AsCl_3$ also indicates that one $AsCl_3$ is more strongly bound than the two others [8].

If we thus confidently assume the existence of groups $AsCl_2^+$ and $AsCl_4^-$ it remains to be found whether there is any sense in speaking of a Cl^- concentration in $AsCl_3$. The existence of a pCl value is a condition for a successful quantitative application of the set of formulae already developed in the Brönsted theory to describe protolytic processes. In H_2O the pH values can be determined by electrochemical methods and the analogy would demand the possibility of determining pCl in a similar way. The problem is of course to find a reversible Cl^- sensitive electrode. AgCl is classified as very slightly soluble in $AsCl_3$[7] and the possibility is then given of measuring concentration elements in $AsCl_3$. The cell would be

$$\text{Ag, AgCl} \mid Cl^- \; (C_1) \text{ in } AsCl_3 \parallel Cl^- \; (C_2) \text{ in } AsCl_3 \mid \text{AgCl, Ag}$$

Such measurements have been made and will be reported in a following paper [9]. It is a difficult task to determine Cl^- concentrations in this way because of the large activity correction connected with the low dielectric constants of $AsCl_3$. ($SeOCl_2$ would be a more suitable solvent for exact investigations.) The shape of titration curves, pCl (emf.) against acid added to a base, show, however, without doubt the analogy with pH measurements in water. It also proves the existence of a defined ionic product $C_{AsCl_2}^+ \cdot C_{AsCl_4}^- = K$, characteristic for auto-ionized solvents.

Measurements of electrical conductivity have mostly been used in connection with conductometric titrations [7], but an effort has recently been made to prove the validity of the Onsager-Debye-Hückel theory for a strong electrolyte in $AsCl_3$ and to determine the acidity constants of some weak acids (V. Gutmann [10]). Determinations of transference numbers would also be of interest. Of course, measurements of all kinds of osmotic properties would give interesting information, too.

Studies of frequency shifts in As—Cl vibration spectra with different methods might give valuable indications about the degree of association in liquid $AsCl_3$ and about the interaction between acids or bases and $AsCl_3$.

COMPARISON WITH WATER AND AQUEOUS SOLUTIONS

The preliminary experimental investigations indicate the importance of chloride ion transfer in acid-base reactions in $AsCl_3$. The effect on pCl can be considered as a formal expression of an ionic transfer process but does not give any information about the mechanism of the transfer. An atomistic description of the constitution of $AsCl_3$ solution has still to be given. No structural work has as yet been done but a comparison with water and aqueous solutions may lead to a crude hypothetical picture apt to incite essential experimental studies.

The present state of knowledge about water and the compounds obtained from aqueous solutions is here briefly summarized for the purpose of comparison without any pretentions of completeness.

The structure of ice is well established. Each oxygen atom is surrounded tetrahedrally by four others. (This low coordination may be compared with 12 for dense packing.) The hydrogen atoms are distributed between the oxygen atoms, two hydrogen atoms being closely associated with each oxygen atom. The O—H...O bond is called a hydrogen bond.

When ice melts the lattice is partly broken down [11, 12], because part of the hydrogen bonds are broken [11, 12] or bent [13]. As a result of the partial dense packing, the average coordination number of oxygen is increased [11] from 4 to 4.9 at 80° C. The resulting differential increase of density is compensated at 4° C by the thermal expansion which makes the average distances longer. There is no doubt about the association of the water molecules to an ice-like structure, it may then be described as a "broken down ice structure" [11] or as a "network of pliable, branched chains of tetrahedra" [12].

The crystal structures of the compounds $HNO_3 \cdot H_2O$ [14] and $HNO_3 \cdot 3 H_2O$ [15] show that there are hydrogen bonds between oxygen atoms in the nitrate groups and the water molecules. It has even been possible to prove the complete proton transfer from HNO_3 to H_2O in $HNO_3 \cdot 3 H_2O$. The structure

suggested for aqueous HNO_3 solutions [16] is not quite in agreement with the structure found in the solid state. The discrepancy is probably due to the fact that Finbak [16] has overemphasized the importance of the tetrahedral coordination around the water molecules. In the solid state water molecules are found, which actually have triangular coordination [14, 15]. The assumption of an arrangement of the H_2O molecules around HNO_3 in such a way as to permit a proton transfer from HNO_3 to H_2O along hydrogen bonds is not influenced by this discrepancy. In dilute solutions of the strong acid HNO_3 the proton transfer is complete while only part of the protons are transferred from a weak acid to H_2O (or hydrogen bonds are formed with other acid molecules). The hydrogen bonds have of course a dynamical character in solutions, they are broken and redistributed and there is an average number of hydrogen bonds [12] determined by the temperature and by the nature and concentration of the solute.

In the same way NH_3 molecules form hydrogen bonds with the water molecules along which protons are partly transferred from H_2O to NH_3 forming NH_4^+ and OH^- ions.

An addition of acid evidently results in an excess of protons in the water structure, symbolized as H_3O^+. In a similar way a base gives rise to a proton deficiency symbolized as OH^-. The pH value of a solution is dependent on this proton excess or proton deficiency.

The arrangement of water molecules around ions which do not function as acids or bases has been extensivily studied in the solid state structures of salt hydrates. It has been shown in an excellent review [17] that the water molecule does not exhibit any tetrahedral character in such compounds but demonstrates one positive and one negative side. The hydration of ions in aqueous solutions is usually explained in a similar way. In the case of large ions with small charges, such as Cs^+, the water molecules around the ion will still belong to the water structure. With decreasing size or increasing charge hydrated ions such as $Mg(H_2O)_6^{2+}$ are formed. A further change will lead to a proton repulsion as in the case of Al^{3+}, causing the acidic properties of an $AlCl_3$ solution.

It seems as if proton transfer is intimately connected with the existence of hydrogen bonds along which the transfer can take place without any other structural changes. There are, however, acid-base reactions which involve drastic structural changes: $7 MoO_4^{2-} + 8 H^+ = Mo_7O_{24}^{6-} + 4 H_2O$.

The existence of hydrogen bonds may be considered as due to the smallness of the proton which makes any other oxygen coordination than two around the protons very little probable. The hydrogen bond thus cannot be expected necessarily to have an analogy in other ionic transfer processes.

As a basis for discussion of the constitution of $AsCl_3$ solutions we have no more knowledge than of the structure of the free $AsCl_3$ molecule [18], a pyramid with the As—Cl distances 2.16 ± 0.03 Å and the Cl—As—Cl angles $103 \pm 3°$. It can also be described as a slightly distorted tetrahedron with one vacant position. The cohesive forces in the solid $AsCl_3$ are probably determined by the interaction between such molecules. It would therefore be interesting to know the coordination around an $AsCl_3$ molecule and whether the structure is such as to permit the existence of chlorine bonds and thus ionic transfer (at the auto-ionization) without any other structural changes. It is easy to derive such

structures making different assumptions, but it is not worth-while to discuss them all because they are quite arbitrarily obtained. To demonstrate the principles one single case will be mentioned, namely the formation of chains of distorted $AsCl_4$ tetrahedra in the structure. That would include chlorine bonds from one arsenic atom to the other

$$\begin{array}{cccccc}
& Cl & & Cl & & Cl \\
\ldots Cl{-}As & \ldots & Cl{-}As & \ldots & Cl{-}As. \\
& Cl & & Cl & & Cl
\end{array}$$

Formation of $AsCl_2^+$ and $AsCl_4^-$ would then be possible by a simple transfer process without any further structural changes.

For many reasons this hypothesis is not very probable. It is recognized that the lone electron pair in $AsCl_3$ is of importance for the structure, and it is often arbitrarily assumed to be situated in the fourth corner of the tetrahedron

$\begin{array}{l} Cl \\ :As{-}Cl. \\ Cl \end{array}$ In the same way the structure of $AsCl_4^-$ would be determined by the

following electron distribution $\begin{bmatrix} Cl \\ | \diagup Cl \\ :As \\ | \diagdown Cl \\ Cl \end{bmatrix}^-$ and thus have a trigonal bipyr-

amidal structure with one vacant position and not a tetrahedral structure.

Only structure determinations can give a definite answer to this problem and thus indirectly to the question how a chloride ion excess or deficiency is distributed in the liquid structure.

Comparison with the structures of some other solid non-aqueous solvents supports, however, the idea that chlorine bonds do not exist. If the structure of the solids is mainly preserved in the liquid state ionic transfer without other structural changes is not possible in SO_2[19] or $COCl_2$[20].

A consideration of the solution of $SnCl_4$ in $AsCl_3$ will give further aspects of the problem. The $SnCl_4$ molecule has a tetrahedral structure and must increase its coordination to an octahedral structure in the acid-base reaction $SnCl_4 + 2 AsCl_3 = SnCl_6^{2-} + 2 AsCl_2^+$. The chloride ion transfer here is connected with a complete change in the distribution of the chloride ions around the Sn atoms. Of course there is a possibility that an intermediate compound $SnCl_4(ClAsCl_2)_2$ exists with an octahedral coordination. This possibility has a perfect analogy in aqueous solutions: $CO_2 + H_2O = H_2CO_3 = H^+ + HCO_3^-$.

Evidently such molecules or ions will function as acids which have a chloride ion affinity. This may partly be determined by purely geometrical considerations. The low chloride ion affinity of bases can in some cases be explained as a repulsion effect. There is thus an analogy between the two reactions:

$$C_5H_5NAsCl_3 = C_5H_5NAsCl_2^+ + Cl^- \qquad (N{-}Cl\ repulsion)$$

and

$$Al(OH_2)_6^{3+} = Al(OH)(OH_2)_5^{2+} + H^+ \qquad (Al{-}H\ repulsion)$$

Whatever is the mechanism of the ionic transfer processes in $AsCl_3$, it will result in chloride ion excess or deficiency, which can be measured.

All the problems discussed here are evidently very much dependent on the charge distribution in $AsCl_3$. Ions such as $(CH_3)_4N^+$ are probably surrounded by $AsCl_3$ molecules turning their negative sides against the positive ion. The knowledge of the structures of solvates is thus of fundamental importance for any effort to discuss solvation processes or to obtain a picture of the structure of solutions in $AsCl_3$.

PERTINENT STRUCTURAL PROBLEMS

An attempt has been made to show that our present knowledge permits only vague ideas about the constitution of $AsCl_3$-solutions and to point out some pertinent structural problems which are here summarized:

1. The structure of solid and liquid $AsCl_3$ is of basic importance in any structural discussion of $AsCl_3$ solutions.

2. The structures of the ions $AsCl_2^+$ and $AsCl_4^-$ might explain how Cl^- excess or deficiency is manifested in the liquid structure.

3. The knowledge of the structures of solid solvates is necessary for any detailed discussion of solubility and solvation conditions in $AsCl_3$-solutions.

Of course these points apply directly to the study of other auto-ionizing solvents.

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