Solubility Studies on Substituted Ammonium Salts

of Halide Complexes

I. Theoretical Introduction

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The solubility of salts of anionic complexes of metal ions is used as a method for the investigation of step-equilibria in the formation of complex ions in solution. The requisite properties of such compounds are discussed and equations are derived for treating data on solubility as a function of ligand concentration for the class of compound, $(R_4N^+) (ML_m^-)$, where R_4N^+ is a quaternary ammonium ion, M a metal ion of charge $m-1$, and L a halide ion. The use of sulfuric acid as a 1:1 electrolyte to maintain constant ion normality is proposed.

During the past several years a summer student research project at Swarthmore College has shown the possibility of synthesizing a number of salts of low solubility of general formula $(R_4N^+) (ML_m^-)$, where M is an ion of a heavy metal usually in one of the groups following the transition metals, and L is a halide ion. Preliminary studies have shown that in the absence of hydrolysis, the solid phase of these salts in equilibrium with ions in solution remains pure over wide ranges of ligand (halide) concentration. Thus an easily applied method is available for the study of halide complexes of these metal ions in solution. Preliminary observations (unpublished) indicate that the method will certainly give useful results for the halide complexes of Hg(II), Sn(II), Pb(II), and Sb(III). There seems little reason to doubt its application to other central ions in halide complexes. In this paper the equations relating solubility data and concentrations of complex species and of ligand are discussed.

Most salt solubility studies in the literature are concerned with the determination of solubility products. In most cases solubility data have been used for the determination of complexity constants only in cases where equilibrium between solid phase and one complex species is of interest. For example,

Reynolds and Argersinger[1] have discussed the importance of minima in solubility curves, but limited their attention to cases involving simple ions and one complex species. Bjerrum[2] used the solubility of Gerhardtite $(Cu(NO_3)_2 \cdot 3Cu(OH)_2)$ as a function of ammonia concentration in his study of step equilibria in ammine formation. Leden[3] has made full use of the potentialities of solubility curves of AgX vs. [X⁻] in his studies of the complexes of silver ion. Since solubility data on simple salts do not distinguish mono- and polynuclear complexes, Leden generally combined solubility studies with potentiometric measurements. Recently Ahrland[4] has calculated step equilibria for BiI_{3+n}^{-n} complexes from solubility data. By introducing substituted ammonium ions as another controllable variable, it should be possible to calculate step formation constants and to detect polynuclear complex formation from solubility data alone.

MATHEMATICAL RELATIONS PERTAINING TO SOLUBILITY CURVES FOR SALTS OF THE TYPE $A^+ML_m^-$.

Definitions of terms.

S = solubility of the salt in moles per liter
C_M = Total concentration of species containing M
K_s = $[A^+][ML_m^-]$, the solubility product
K_n = $[ML_n]/[L][ML_{n-1}]$
β_n = $\prod_1^n K_n$
n = number of bound ligand atoms per metal ion in a particular complex.
$\bar{n}$ = average number of bound ligands per metal ion in solution
N = maximum coordination number for M.
[A] = concentration of substituted ammonium ion in moles per liter
[M] = Metal ion concentration in moles per liter
$[ML_n]$ = Complex ion concentration in moles per liter
[L] = Free ligand concentration in moles per liter
$[L]_0$ = Ligand concentration before dissolving any salt.

The validity of the mass action law is assumed.

I. For the case in which $A^+ML_n^-$ dissolves in a solvent containing only L⁻ and inert ions and only mononuclear complexes are formed.

$$S = [M] + [ML] + ML_2] + [ML_3] + \cdots + [ML_N] = C_M = [A] \qquad (1)$$

$$C_M = \frac{[ML_m]}{[L]^m \beta_m} + \frac{\beta_1 [ML_m]}{[L]^{m-1}\beta_m} + \cdots + \frac{\beta_n [ML_m]}{\beta_m [L]^{m-n}} + \cdots + \frac{\beta_N [ML_m][L]^{N-m}}{\beta_m}$$

Substituting for $[ML_m]$, we obtain

$$S = \frac{K_s}{[A]} \sum_{n=0}^{n=N} \frac{\beta_n [L]^n}{\beta_m [L]^m}$$

$$S^2 = K_s \sum_{n=0}^{n=N} \frac{\beta_n [L]^n}{\beta_m [L]^m} \qquad (2)$$

$$\frac{\mathrm{d}S^2}{\mathrm{d}[\mathrm{L}]} = \frac{K_s}{[\mathrm{L}]} \sum_0^N \frac{(n-m)\beta_n[\mathrm{L}]^n}{\beta_m[\mathrm{L}]^m} \tag{3}$$

$$\bar{n} = \frac{[\mathrm{ML}] + 2[\mathrm{ML}_2] + \cdots + N[\mathrm{ML}_N]}{S}$$

$$\bar{n}S = \frac{K_s}{S} \sum_0^N \frac{n\beta_n[\mathrm{L}]^n}{\beta^m[\mathrm{L}]^m}$$

$$\bar{n}S^2 = K_s \sum_0^N \frac{n\beta_n[\mathrm{L}]^n}{\beta_m[\mathrm{L}]^m} \tag{4}$$

Combining (2), (3) and (4)

$$\frac{[L]\,\mathrm{d}S^2}{\mathrm{d}\,[\mathrm{L}]} = \bar{n}S^2 - mS^2$$

$$\frac{\mathrm{d}\log S^2}{\mathrm{d}\log[\mathrm{L}]} = \bar{n} - m \tag{5}$$

Eqn. 5 is the familiar Bjerrum equation [5] for $\bar{n}$ as a function of the species ML_n being measured. The reversal of sign is due to the measured quantity S^2 being inversely proportional to ML_m. The quantity m is given by the formula of the salt. S is measured directly. Where complexes form or dissociate to an extent which effectively alters [L] from $[\mathrm{L}]_0$, [L] must be obtained by separate measurement or by a method of successive approximations as follows:

Estimation of [L]. It can be easily shown that

$$[\mathrm{L}] = [\mathrm{L}]_0 - S(n - m) \tag{6}$$

Substituting from eqn. (3) we obtain

$$[\mathrm{L}] = [\mathrm{L}]_0 - [\mathrm{L}]\frac{2\mathrm{d}S}{\mathrm{d}[\mathrm{L}]}$$

$$[\mathrm{L}] = \frac{[\mathrm{L}]_0}{1 + 2\mathrm{d}S/\mathrm{d}[\mathrm{L}])} \tag{7}$$

The denominator of the right hans side of eqn. (7) may be estimated from the slope of the solubility curve for S *vs.* $[\mathrm{L}]_0$. An improved curve is then drawn. A second approximation for each point is usually sufficient to give the true S *vs.* [L] curve to which eqns. (1—5) apply.

An interesting consequence of eqn. (7) is that $\mathrm{d}S/\mathrm{d}[\mathrm{L}]$ has a fixed value of 0.5 for $[\mathrm{L}]_0 = 0$. This in itself is helpful in determining the solubility curve.

Finding points of integer $\bar{n}$. Beck and Huhn have discussed the significance of points where $\bar{n}$ is an integer and described different types of measurements for indicating such points [6]. At such points the concentration of the complex $\mathrm{ML}_{n=\bar{n}}$ is a maximum. Any properties of the solution depending mainly upon ML_n should also be maximal at such points. If, in the present case, a minimum appears in the solubility curve, it follows from eqn. (5) that $\bar{n} = m$ at this minimum. It can be shown by similar arguments to those used in developing eqn. (5) that the following equations also apply to the situation under discussion.

$$\text{d}\log(S^2[L])/(\text{d}\log[L]) = \bar{n} - m + 1$$

$$\text{d}\log(S^2/[L])/(\text{d}\log[L]) = \bar{n} - m - 1$$

or generally that

$$\text{d}\log(S^2[L]^{(m-n)})/\text{d}\log[L] = \bar{n} - n \qquad (8)$$

where n is an integer.

Thus a plot of $\log(S^2[L]^{(m-n)})$ vs. $\log[L]$ will show a minimum at the point where $[ML_n]$ is a maximum *.

It is thus possible using solubility data alone to determine each of the conditions for which $\bar{n}$ has integral values. It should be obvious that similar considerations apply to distribution and other types of measurements used to determine formation functions. This procedure is far simpler than undertaking a different type of measurement for each different $\bar{n}$ value depending on the charge and/or composition of ML_n as suggested by Beck and Huhn [6].

If one assumes that at the points for $[L]_{n=\bar{n}}$ only the species ML_n, ML_{n+1}, and ML_{n-1} are present, one can approximate the product of $K_n K_{n+1}$ as:

$$K_n K_{n+1} = 1/[L]_{\bar{n}}^2 \qquad (9)$$

where n is integral. At half integer values of $\bar{n}$, after Bjerrum [8] we estimate

$$K_n = 1/[L]_{\bar{n} = n - \frac{1}{2}} \qquad (10)$$

Constants so estimated may be used as a starting point for various methods of successive approximation [4,7,8] used in determining values for K_n.

Minima described generally by $\bar{n} - n = 0$ are also useful in determining the presence of higher complexes. In the following paper (II of this series) such a minimum proves the existence of $SnCl_4^{2-}$, while the absence of a second minimum suggests the absence of $SnCl_5^-$. Failure to reach a minimum does not exclude the higher complex, but the solubility curve is easily fitted with constants K_1 to K_n up to values of $n = \bar{n}$ at the unattained minimum.

II. In cases where it is convenient to decrease solubilities by including a high (virtually constant) concentration of A^+ in the solvent the derived equations must be modified as follows because S is no longer equal to $[A^+]$.

$$S = \frac{K_s}{[A^+]} \sum_{n=0}^{n=N} \frac{\beta_n[L]^n}{\beta_m[L]^m} \qquad (2a)$$

$$\frac{\text{d}\log S}{\text{d}\log[L]} = \bar{n} - m \qquad (5a)$$

$$[L] = \frac{[L]_0}{1 + \text{d}S/\text{d}[L]} \qquad (7a)$$

$$\frac{\text{d}\log(S[L]^{(m-n)})}{\text{d}\log[L]} = \bar{n} - n \qquad (8a)$$

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* It is possible to show from eqn. 7 that plots of $S^2[L]^{(m-n)}$ vs. $[L]$ and plots of $S[L]^{(m-n)}$ vs. $[L]$ give minima at the same points — namely at $[L]_{n=\bar{n}}$. Thus the points $[L]_{n=\bar{n}}$ are easily determined from the solubility curve when $[L] = [L]_0$.

Other cases can be imagined in which modifications of eqns. (1—7) are required. For instance salts of polyvalent anions such as $(R_4N^+)_2$ $(SnCl_6^{2-})$ would require that $S = [A^+]/2$ in case I and substitution of $[A^+]^2$ for $[A^+]$ in the equations under case II, and that $K_s = [A^+]^2[ML_m]$.

Detecting polynuclear complexes. If solubilities are measured at different values of $[A^+]$ and other conditions remain the same, polynuclear complexes will be detected if S is not inversely proportional to $[A^+]$. Some consequences of polynuclear complex formation in studies involving simple salts are illustrated in Leden's work on silver iodide [3g] and silver thiocyanate [3e].

Is is also possible to alter the solubility of the salt by altering the cation. For instance with $SnCl_3^-$ it is possible to prepare salts with $(CH_3)_3C_6H_5N^+$, (o-phenanthroline H^+), and $(CH_3)_4N^+$. Many other univalent cations which might be useful may readily be imagined.

It may be useful to use one cation in the region of the solubility minimum and another at the ends of the curve where solubilities may become very high. If the data overlap the combined curves can be easily used to determine the formation curve.

Solvent media. It is generally customary in studies involving multiple equilibria involving ions to make measurements, if possible, in solutions containing a high and constant concentration of inert ions. The anion generally employed is the perchlorate ion which, unfortunately, precipitates substituted ammonium ions. Sulfates and bisulfates of such ions are very soluble, however. Stokes and Robinson [10] have emphasized that sulfuric acid is a 1:1 electrolyte in solutions more concentrated than 1.0 M. The molarity *vs.* molality and Hammett H_0 functions *vs.* weight percent curves are virtually identical [11] for sulfuric and perchloric acids in the range 1 to 10 M. It thus appears reasonable that sulfuric acid can be used in place of perchloric acid to maintain constant ion normality in concentration regions where the dissociation of the bisulfate ion is suppressed. The following paper describes the use of sulfuric acid in this capacity for a study of the solubility of tetramethylammonium trichlorostannate(II) as a function of chloride ion concentration.

Advantages and limitations. The use of solubilities as suggested will have definite advantages in situations where no good reversible electrode is available for potentiometric measurements, as, for instance, in the studies of complexes of Bi(III) and Sb(III). Measurements should, in general, be less subject to errors from trace impurities in solutions than electrometric measurements.

Solubility studies on the other hand do not in general permit free variation of total concentration of metal ion. Often solubilities are so high that dissociation of ML_n complexes of low n is impossible. In the BiI_n^{3-n} system, Ahrland [4] could not obtain solutions with $\bar{n}$ less than 3 from the solubility of BiI_3, and the author has found (unpublished) that the solubility of tetramethylammonium trichloromercuriate(II) is so high as to prohibit the study of the dissociation of $HgCl_2$ and $HgCl^+$ by this method.

Solubility studies break down if there is a change in the solid phase as the composition of the solution is varied. (If the change is well defined, the solubilities of the various solid phases can be employed in finding step constants, *cf.* Leden [3a,e]).

It is possible that K_s will vary with change in medium. Leden [3b] found that K_s for AgCl changed about 40 % in changing from 5 M $NaClO_4$ to 5 M NaCl. The example treated in the following paper [9] indicates that even smaller variation is to be encountered with complex salts of the type under discussion.

An application of the considerations of this paper to the study of $SnCl_n^{2-n}$ complexes is presented in the following paper [9]. As a rule, the method, using solubilities of salts of complex ions will serve best for information on complexes of higher n, but, as in the illustration to follow, for salts of weakly formed complexes, the entire formation curve may be obtained from the solubility curve. The substituted ammonium salt solubilities appear to have particular applicability to the halide complexes of ions of heavy metals following the transition groups.

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