

The composition was checked by DTA, and adjusted by addition of AlF_3 if necessary.

The experimental methods and equipment used during the investigation (DTA, X-ray and density measurements) were the same as described previously.^{2,3,5}

Results and discussion. The phase diagram is presented in Fig. 1. The experimental points were obtained from DTA cooling curves. The phase diagram of this system is similar to the two systems $\text{Li}_3\text{AlF}_6 - \text{K}_3\text{AlF}_6$ and $\text{Li}_3\text{AlF}_6 - \text{Rb}_3\text{AlF}_6$.³ The system contains one incongruently melting compound, $2\text{Cs}_3\text{AlF}_6 \cdot \text{Li}_3\text{AlF}_6$, corresponding to $\text{Cs}_2\text{LiAlF}_6$. A peritectic point was found at 670°C and 85.5 mol % Cs_3AlF_6 while a eutectic point was established at 555°C and 40 mol % Cs_3AlF_6 .

A preliminary investigation of the structure of the compound $\text{Cs}_2\text{LiAlF}_6$ was carried out. The X-ray data for the compound $\text{Cs}_2\text{LiAlF}_6$ are given in Table 1. Single crystal X-ray diffraction analysis indicated that the compound has an orthorhombic structure with a C-centered lattice and the cell constants $a = 6.21 \pm 0.04$ Å; $b = 10.72 \pm 0.03$ Å; $c = 4.99 \pm 0.01$ Å. This gives a calculated density of 4.14 g cm^{-3} (2 formula units in the cell) compared to a measured value at 25°C of 4.04 g cm^{-3} .

Acknowledgements. One of the authors (M.A.) was supported during his stay in Norway by a fellowship from NORAD. The Royal Norwegian Council for Scientific and Industrial Research is thanked for financial support.

- Holm, J. L. *Undersøkelser av struktur og faseforhold for en del systemer med tilknytning til aluminium-elektrolysen*, Lic. Thesis, Institute of Inorganic Chemistry, NTH, Trondheim 1963.
- Holm, J. L. and Jenssen Holm, B. *Acta Chem. Scand.* **24** (1970) 2535.
- Grjotheim, K., Holm, J. L., Malinovsky, M. and Mikhael, S. A. *Acta Chem. Scand.* **25** (1971) 1695.
- Henry, J. L. and Dreisbach, S. H. *J. Am. Chem. Soc.* **81** (1959) 5274.
- Holm, J. L. and Jenssen Holm, B. *Thermochem. Acta* **5** (1973) 273.
- Holm, J. L. and Jenssen Holm, B. *Acta Chem. Scand.* **23** (1969) 1065.

Received May 8, 1973.

Perchlorate and Fluoride Complexes of Thallium(I) in Aqueous Solution

LARS JOHANSSON

Division of Inorganic Chemistry 1, Chemical Center, P.O. Box 740, S-220 07 Lund 7, Sweden

When weak complex systems are investigated in perchlorate media, different experimental methods may give different apparent stability constants, if the perchlorate ion is not completely inert but forms a complex with the central ion.¹ Central ion measurements, in a wide sense, give lower values of the stability constants than do ligand measurements. In the extreme case, when the perchlorate complex is stronger than that of the ligand studied, central ion measurements may give negative apparent constants. The $\text{Tl}^+ - \text{F}^-$ system appears to behave in this manner. The system has been previously studied with potentiometric and polarographic methods.²⁻⁴ As the effects observed are small, it might be argued that they are caused mainly or in part by changes, at constant ionic strength, in liquid junction potentials and activity coefficients. Such changes are, however, not likely to be the same for different methods. Therefore, in the present work, the system has been studied with other methods than those used earlier, viz. two solubility methods, the first being, in effect, a central ion measurement, the second a ligand measurement. The measurements have been carried out at 25°C in a NaClO_4 medium of $I = 0.5$, where

$$I = [\text{L}] + [\text{A}] \quad (1)$$

L and A denote fluoride and perchlorate ion, respectively.

Solubility of $\text{TlIO}_3(s)$. Solutions in the range $0 \leq [\text{L}] \leq 0.5$ M were saturated in a column with $\text{TlIO}_3(s)$, and analyzed for IO_3^- by the thiosulphate method.⁵ The solubilities could be reproduced within 1%.

In a separate experiment, IO_3^- but no F^- was added. The solubility, S , then was inversely proportional to $[\text{IO}_3^-]$. Thus, no

Table 1. Solubility of $\text{TlIO}_3(s)$: $[\text{L}]/\text{M}$, $S \times 10^3/\text{M}$; 0.000, 3.289; 0.100, 3.245; 0.200, 3.219; 0.300, 3.159; 0.400, 3.107; 0.500, 3.057.

complexes containing IO_3^- are likely to be formed. It is assumed that the only complexes formed are ML and MA (stability constants β_1 and γ_1 , respectively). Thus

$$S = [\text{IO}_3^-] = [\text{M}] + [\text{ML}] + [\text{MA}] \quad (2)$$

and the following equation applies

$$(S/S_0)^2 = 1 + \beta_1(1)[\text{L}] \quad (3)$$

where S_0 is the solubility when $[\text{L}] = 0$, and

$$\beta_1(1) = \frac{\beta_1 - \gamma_1}{1 + \gamma_1 I} \quad (4)$$

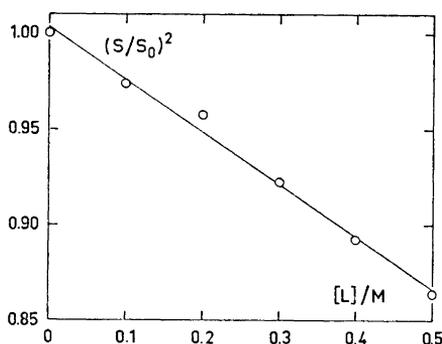


Fig. 1. Solubility of $\text{TlIO}_3(\text{s})$: $(S/S_0)^2$ vs. $[\text{L}]$.

As shown in Fig. 1, $(S/S_0)^2$ decreases linearly with increasing $[\text{L}]$. Giving the points equal weight

$$\beta_1(1) = -0.27 \pm 0.03 \text{ M}^{-1}$$

is obtained. Errors refer to the 99 % confidence level.

Solubility of $\text{BaF}_2(\text{s})$. Solutions with $0 \leq C_{\text{L}'} \leq 0.040 \text{ M}$ and $0 \leq C_{\text{M}} \leq 0.100 \text{ M}$ were saturated with $\text{BaF}_2(\text{s})$. The initial concentration of L is denoted by $C_{\text{L}'}$. At equilibrium, the total concentration is $C_{\text{L}} = C_{\text{L}'} + 2S$. The column technique proved to be too tedious, so solution and solid samples were shaken to equilibrium in a thermostat. The shaking time was four weeks, although equilibrium was shown to be reached in about half that time. The saturated solutions were analyzed for Ba^{2+} by adding an excess of EDTA and titrating the excess with Mg^{2+} . Thallium, which interfered, was precipitated and removed as $\text{TlI}(\text{s})$. The reproducibility was relatively poor, within 5 % with few exceptions.

In investigations of this kind, S is normally ^{1,6} plotted vs. $C_{\text{L}'}$ for different

constant C_{M} values, the curves then being cut at constant S , giving $C_{\text{L}'}$ as a function of C_{M} :

$$C_{\text{L}'} = [\text{L}] + \bar{n}_{\text{Ba}} S + \bar{n} C_{\text{M}} \quad (5)$$

where \bar{n}_{Ba} refers to the $\text{Ba}^{2+} - \text{F}^-$ system, and \bar{n} to the $\text{Tl}^+ - \text{F}^-$ system:

$$\bar{n} = \frac{\beta_1[\text{L}]}{(1 + \gamma_1 I) + (\beta_1 - \gamma_1)[\text{L}]} \quad (6)$$

Thus, \bar{n} may be obtained as a function of $[\text{L}]$. The present measurements as well as literature data ⁷ indicate $\text{Ba}^{2+} - \text{F}^-$ complex formation to be negligible in the range studied. Moreover, for constant $C_{\text{L}'}$, the solubility appeared to be roughly independent of C_{M} , implying that \bar{n} and also β_1 are close to zero. It was therefore possible to treat the data in the following way, which is rational from a statistical point of view.

For each $C_{\text{L}'}$, the average solubility, S_{av} , and the quotient S/S_{av} were computed. As S is a function of $C_{\text{L}'}$ and C_{M} , generally

$$\left(\frac{\partial S}{\partial C_{\text{M}}}\right)_{C_{\text{L}'}} = -\left(\frac{\partial S}{\partial C_{\text{L}'}}\right)_{C_{\text{M}}} \left(\frac{\partial C_{\text{L}'}}{\partial C_{\text{M}}}\right)_S \quad (7)$$

Further, from eqns. (5) and (6), approximately

$$\left(\frac{\partial C_{\text{L}'}}{\partial C_{\text{M}}}\right)_S = \bar{n} = \beta_1(2) C_{\text{L}'} \quad (8)$$

where $\beta_1(2) = \frac{\beta_1}{1 + \gamma_1 I}$ (9)

Eqns. (7) and (8) give, approximately

$$\left(\frac{\partial(S/S_{\text{av}})}{\partial C_{\text{M}}}\right)_{C_{\text{L}'}} = -\left(\frac{\partial \log S}{\partial \log C_{\text{L}'}}\right)_{C_{\text{M}}} \beta_1(2) = 2\beta_1(2) \quad (10)$$

The slope of a plot of S/S_{av} vs. C_{M} is thus independent of $C_{\text{L}'}$.

Table 2. Solubility of $\text{BaF}_2(\text{s})$: $C_{\text{M}} \times 10^3/\text{M}$, weight (= number of points), average of S/S_{av} ; 0, 20, 1.0017; 25, 18, 1.0042; 50, 16, 0.9845; 75, 16, 1.0078; 100, 9, 1.0022.

If the individual points are given equal weight, the present data (79 points, Table 2) give the slope $(6 \pm 90) \times 10^{-3}$, and thus

$$\beta_1(2) = 0.00 \pm 0.05 \text{ M}^{-1}$$

Conclusions. The difference observed here between $\beta_1(1)$ and $\beta_1(2)$ is small, and medium effects cannot be excluded

as the major cause of the difference. However, the present results compare favourably with literature data. Thus, $\beta_1(1) = -0.20 \pm 0.02$ may be estimated from Nilsson's potentiometric data² in 1 M NaClO₄. Bond,³ studying the formation of TlClO₄ in 1 M NaF with a type of central ion measurement, obtained the constant 0.32 ± 0.04 . A ligand measurement method gave^{3,4} for the formation of TlF $\beta_1(2) = 0 \pm 0.4$, in 1 M NaClO₄ as well as in 1 M NaNO₃. From the good agreement with the present results (activity coefficients are probably not very different in 0.5 M and 1 M media), one tends to conclude that medium effects are small. Assuming these to be negligible, the present data yield the following values of the individual constants (eqns. (4) and (9))

$$\beta_1 = 0.00 \pm 0.06 \text{ M}^{-1}$$

$$\gamma_1 = 0.32 \pm 0.07 \text{ M}^{-1}$$

As discussed in more detail elsewhere,¹ there is also more direct evidence of Tl⁺ - ClO₄⁻ association, e.g. from studies of Raman spectra.⁸ For Tl⁺ - F⁻, Bell and George⁵ estimated a value of β_1 at $I=0$, but according to the authors⁵ no importance should be attached to this value.

This work has been supported financially by the Swedish Natural Science Research Council.

1. Johansson, L. *Coord. Chem. Rev.* **11** (1973). Submitted for publication.
2. Nilsson, R. O. *Arkiv Kemi* **10** (1957) 363.
3. Bond, A. M. J. *Phys. Chem.* **74** (1970) 331.
4. Bond, A. M. and O'Donnell, T. A. J. *Electroanal. Chem.* **26** (1970) 137.
5. Bell, R. P. and George, J. H. B. *Trans. Faraday Soc.* **49** (1953) 619.
6. Johansson, L. *Coord. Chem. Rev.* **3** (1968) 293.
7. Connick, R. E. and Tsao, M. S. *J. Amer. Chem. Soc.* **76** (1954) 5311.
8. Jones, M. M., Jones, E. A., Harmon, D. F. and Semmes, R. T. *J. Amer. Chem. Soc.* **83** (1961) 2038.

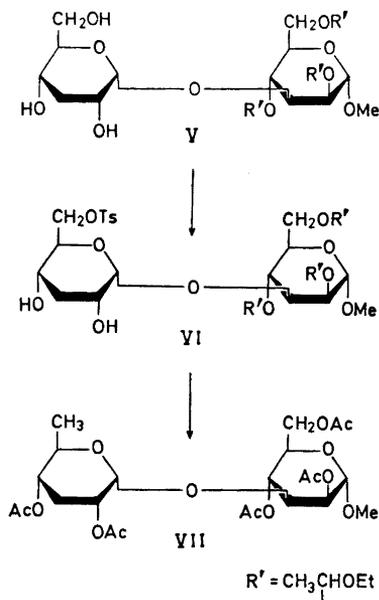
Received May 30, 1973.

Corrections to: Synthesis of Methyl 3-O-(3,6-Dideoxy- α -D-ribohexopyranosyl)- α -D-mannopyranoside*

GUNNEL ALFREDSSON and
PER J. GAREGG

Institutionen för organisk kemi, Stockholms universitet, S-104 05 Stockholm 50, Sweden

Formulae V, VI, and VII are in error. The correct formulae are depicted below.



Received June 15, 1973.

* *Acta Chem. Scand.* **27** (1973) 556.