

CONTRIBUTION FROM THE DEPARTMENT OF INORGANIC CHEMISTRY,
UNIVERSITY OF MELBOURNE, PARKVILLE, VICTORIA 3052, AUSTRALIA

Use of Ion-Selective Electrodes in the Evaluation of Stability Constants of Sparingly Soluble Salts. Application to the Lead(II)-Fluoride System in Aqueous Solution

BY A. M. BOND AND G. HEFTER

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Very little data are available on the stability constants of metal ion complexes of sparingly soluble salts. Normal methods of obtaining these data cannot be applied to most of these systems because the concentration of metal ion or ligand or both remaining in solution after precipitation is insufficient to detect complex formation. The recent extensive development of ion-selective electrodes has provided a means of accurately detecting very low concentrations of ions and offers the possibility of examining complex formation occurring below the level of precipitation. In this work the possible use of ion-selective electrodes for this purpose has been investigated and results are reported on the lead(II)-fluoride system using a fluoride ion selective electrode. The system was also investigated polarographically and the results obtained are in good agreement.

Introduction

A perusal of standard reference collections of stability constant data¹ shows the amount of information available on the evaluation of stability (formation) constants for systems which involve sparingly soluble salts is miniscule, generally only the solubility product being reported.

The difficulty of measuring stability constants of these systems occurs because the usual methods of complex formation detection require such concentrations of either the metal ion, or the ligand, or both, that the solubility of the sparingly soluble salt is exceeded, the salt precipitates, and the method is no longer applicable. Exceptions are those sparingly soluble salts which are soluble in high (excess) ligand concentrations, *e.g.*, AgCl, PbI₂, etc.,¹ and those very rare cases where the method retains its applicability in spite of precipitation, *e.g.*, the polarographic determination of the lead(II)-fluoride system.² Stability constant measurements on sparingly soluble salt systems have thus presented to date a very difficult problem. Any means by which this problem may be circumvented should be capable of yielding many valuable data.

Recent extensive development of ion-selective electrodes which are very sensitive to changes in the appropriate uncomplexed ion concentrations, often down to extremely low values, presents an ideal solution to this problem. Thus, although we have restricted ourselves to the application of a fluoride ion selective electrode, most of what is written below (including the method of evaluation of stability constants, the advantages, and the limitations) may be applied directly to other ion-selective electrodes in both aqueous and nonaqueous media.

The example chosen for study is the sparingly soluble lead(II)-fluoride system. The only direct study of the fluoride complexes of lead has been that by Mesaric and Hume,² although Connick and Paul³ had pre-

viously estimated the formation constant of PbF⁺ using an indirect potentiometric method.

Mesaric and Hume were able to successfully evaluate the stability constants of the lead-fluoride system polarographically only because precipitation of PbF₂ is quite slow (taking 1-2 hr to become complete) and because the applicability of the polarographic evaluation method of DeFord and Hume⁴ is unaltered by the precipitation process. Other attempts by these workers to study this system using different techniques such as solvent extraction, potentiometry, and light absorption were, however, thwarted by the precipitation of PbF₂.

The fluoride ion selective electrode⁵ is highly specific for fluoride ion and can be used to detect concentrations of uncomplexed fluoride down to approximately 10⁻⁶ *M*. In view of this high degree of sensitivity and selectivity, the electrode should be extremely valuable for study of sparingly soluble fluoride salts. The lead(II)-fluoride system was selected for study by the fluoride electrode because results could be compared with polarographic measurements.

Experimental Section

All standard solutions were made by weighing appropriate amounts of reagent grade chemicals. Solutions for polarographic and potentiometric determinations were made up from the same standard solutions to reduce random errors.

A 1.00 *M* lead nitrate solution had a pH of 3.5. More dilute standards were prepared from this solution and the pH was raised to 5.0 by the addition of NaOH. At this pH the formation of HF and HF₂⁻ may be neglected, as may the formation of lead-hydroxy species and interference to electrode response due to hydroxide ion.

Fluoride solutions were prepared from sodium fluoride and were kept in polyethylene containers. No change was detected within the limits of experimental error (potentials constant to ±1 mV) over a period of 2 months.

All measurements with the fluoride ion electrode were made at constant ionic strength, maintained by sodium perchlorate. Under the conditions of the experiments (extremely low fluoride ion concentrations and nearly constant lead(II) concentration) the ionic environment present for all measurements will be

(1) "Stability Constants of Metal-Ion Complexes," Special Publication No. 17, The Chemical Society, London, 1964.

(2) S. S. Mesaric and D. N. Hume, *Inorg. Chem.*, **2**, 788 (1963).

(3) R. E. Connick and A. D. Paul, *J. Am. Chem. Soc.*, **80**, 2069 (1958).

(4) D. D. DeFord and D. N. Hume, *ibid.*, **73**, 5321 (1951).

(5) M. S. Frant and J. W. Ross, *Science*, **154**, 1553 (1966).

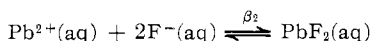
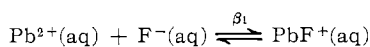
essentially the same, and the activity coefficients of all species will be constant at constant ionic strength.⁶ Measurements on more concentrated electrolyte solutions⁷ indicate that any variation in activity coefficients at the concentrations used in this investigation will be well within the limits of experimental error.

The fluoride ion selective electrode (Model 94-09, Orion Research Inc., Cambridge, Mass.) was used in conjunction with a fiber-type saturated calomel electrode to reduce leakage of chloride to a negligible level. Readings were made at $15 \pm 1^\circ$ with a Philips PR9400 pH meter, on a total solution volume of about 25 ml using a Teflon-coated magnetic stirrer. Potentials reached equilibrium generally within 2 min and were reproducible to ± 1 mV (*i.e.*, within instrumental error) for more than 8 hr, either in glass or Teflon beakers. This justifies the use of glass apparatus at pH 5 and in situations in which measurements can be made reasonably quickly.

Polarographic results were obtained at $15.0 \pm 0.1^\circ$ using a constant lead(II) concentration of 4.00×10^{-4} M and an ionic strength of 1.00 maintained by sodium perchlorate. Polarograms were obtained with a Metrohm Polarecord E 261. Ac polarography was carried out using the Metrohm ac Modulator E393 with an ac voltage of 10 mV, rms at 50 cps. To minimize cell impedance the modulating ac voltage was applied through an auxiliary tungsten electrode. Rapid polarographic techniques and a controlled drop time of 0.16 sec were achieved with a Metrohm Polarographic Stand E354. Argon was used to deaerate the solutions.

Theory

As Mesaric and Hume² detected only two complexes, PbF^+ and PbF_2 , even at very high fluoride ion concentrations, it can be assumed that these are the only species present in appreciable quantities. Thus the only equilibria which need to be considered are



for which the equilibrium concentration stability constants β_1 and β_2 , obtained by neglecting activity coefficients, are given by

$$\beta_1 = \frac{[\text{PbF}^+]}{[\text{Pb}^{2+}][\text{F}^-]} \quad (1)$$

$$\beta_2 = \frac{[\text{PbF}_2]}{[\text{Pb}^{2+}][\text{F}^-]^2} \quad (2)$$

The usual concentration relationships

$$[\text{F}^-]_{\text{T}} = [\text{F}^-] + [\text{PbF}^+] + 2[\text{PbF}_2] \quad (3)$$

$$[\text{Pb}^{2+}]_{\text{T}} = [\text{Pb}^{2+}] + [\text{PbF}^+] + [\text{PbF}_2] \quad (4)$$

also apply. The subscripts T refer to the total (or analytical) concentrations.

Rearranging eq 1 and 2 and substituting into eq 3 the relationship

$$[\text{F}^-]_{\text{T}} = [\text{F}^-] + \beta_1[\text{Pb}^{2+}] + 2\beta_2[\text{Pb}^{2+}][\text{F}^-]^2$$

is obtained, which on rearrangement gives

$$\frac{[\text{F}^-]_{\text{T}} - [\text{F}^-]}{[\text{Pb}^{2+}][\text{F}^-]} = \beta_1 + 2\beta_2[\text{F}^-]$$

In order to simplify calculations and to ensure that the changes in free fluoride ion concentration are detectable, it is most convenient to work with a large excess of

metal ion relative to fluoride ion. Under these conditions the approximation $[\text{Pb}^{2+}] = [\text{Pb}^{2+}]_{\text{T}}$ holds; *i.e.*, the free or uncomplexed lead ion concentration is equal to the total lead ion concentration. Using this, the above equation becomes

$$\frac{1}{[\text{Pb}^{2+}]_{\text{T}}} \left\{ \frac{[\text{F}^-]_{\text{T}}}{[\text{F}^-]} - 1 \right\} = \beta_1 + 2\beta_2[\text{F}^-] \quad (5)$$

All terms on the left-hand side of this equation either are known or can be determined experimentally. Hence, the stability constants β_1 and β_2 may be obtained simply from a graphical plot of the left-hand side of eq 5 vs. fluoride ion concentration, which should yield a straight line with intercept β_1 and slope $2\beta_2$. Equation 5 is in fact a particular form of a general expression used previously by Bond and O'Donnell,⁸ and for further details this work should be consulted.

Results and Discussion

(a) **Polarographic Determination.**—The polarographic investigation by Mesaric and Hume² was repeated using rapid ac techniques as applied to the DeFord–Hume theory.⁴ The general scope, uses, advantage, and validity of the ac technique have been discussed elsewhere.^{9,10}

The polarographic ac lead(II) wave in sodium fluoride–sodium perchlorate media was well defined, symmetrical, and reversible with a half-width of 49 ± 1 mV (theoretical, approximately 45 mV).

Conventional DeFord–Hume plots⁴ indicated the presence of PbF^+ and PbF_2 only, for fluoride ion concentrations up to 0.8 M in sodium fluoride. The overall stability constants at ionic strength 1.0 obtained graphically were $\beta_1 = 34 \pm 5$ and $\beta_2 = 390 \pm 30$ at 15° . These values may be compared with Mesaric and Humes' $\beta_1 = 18$ and $\beta_2 = 356$ at 25° and ionic strength of 2.0. As stability constants usually increase with decreasing ionic strength and vary with temperature, the agreement between these values is satisfactory.

It must be emphasized, however, that the applicability of the polarographic method to the lead(II)–fluoride system is fortuitous and results only from the slowness of precipitation of PbF_2 and some other unusual conditions which prevail for this system² and would be therefore inapplicable to most other sparingly soluble systems.

(b) **Fluoride Ion Selective Electrode Determination.**—It is essential to work in a completely homogeneous solution, below the point of precipitation of any sparingly soluble species.

Since the formation constants of PbF^+ and PbF_2 are known to be small, it is desirable to have as high a fluoride ion concentration as possible. However, the validity of the method (see Theory) is dependent on an excess of metal ion over fluoride ion, which should be at least 100-fold. Limits of detectability and calculation errors must also be borne in mind when dealing with very dilute solutions. Taking into account these re-

(6) R. A. Robinson and R. H. Stokes, "Electrolyte Solutions," Butterworth and Co. Ltd., London, 1959, Chapter 15.

(7) See, for example, J. E. Prue and A. J. Read, *J. Chem. Soc., A*, 1812 (1966).

(8) A. M. Bond and T. A. O'Donnell, *J. Electroanal. Chem.*, in press.

(9) A. M. Bond, *ibid.*, **20**, 223 (1969).

(10) A. M. Bond, *ibid.*, **23**, 277 (1969).

strictions, a lead(II) ion concentration of $10^{-2} M$ was chosen.

The solubility product of lead fluoride is reported² as 2.5×10^{-7} at 25° and an ionic strength of 2.0. Thus if we take $K_s(\text{PbF}_2) = [\text{Pb}^{2+}][\text{F}^-]^2$ as being approximately 10^{-7} at the temperature and ionic strengths used, it can be seen that the concentrations employed are well below the solubility limit of PbF_2 .

The results obtained at two different ionic strengths along with the fluoride ion concentrations employed are shown in Tables I and II. Calibration graphs for determining free fluoride ion concentrations at the appropriate ionic strength were found to be strictly linear with slopes of 57 mV/decade. The values in the final columns of Tables I and II indicate the presence of only

concentration range used, the amount of PbF_2 relative to PbF^+ is always very low so that detection of the second complex would not be expected.

For example, using the polarographic values $\beta_1 = 34$ and $\beta_2 = 390$ (15° , $I = 1.0$) with $[\text{Pb}^{2+}]_T = 10^{-2} M$, when (a) $[\text{F}^-] = 10^{-4} M$, then

$$[\text{PbF}^+] = \beta_1[\text{Pb}^{2+}][\text{F}^-] = 3.4 \times 10^{-6} M$$

and

$$[\text{PbF}_2] = \beta_2[\text{Pb}^{2+}][\text{F}^-]^2 = 3.9 \times 10^{-8} M$$

or when (b) $[\text{F}^-] = 5 \times 10^{-6} M$, then

$$[\text{PbF}^+] = 1.7 \times 10^{-6} M$$

and

$$[\text{PbF}_2] = 9.8 \times 10^{-11} M$$

The results obtained are thus in reasonable agreement with the polarographic results and are a good indication of the validity of this technique.

The values obtained from this investigation and that of Mesaric and Hume² definitely indicate that the earlier, indirect determination of $\beta_1 < 2$ by Connick and Paul³ is incorrect.

Inability to detect formation of PbF_2 (and consequently determine β_2) illustrates the only severe limitation of the ion-selective method. The number of stepwise stability constants which can be evaluated by this method will depend chiefly on the accessible concentrations of metal and ligand ions (*i.e.*, on the solubility of the sparingly soluble salt) and especially on the strength of the complexes. The method would break down under a combination of extremely low solubility and very weak complexes.

This drawback, however, must be seen in context: the use of ion-selective electrode techniques as outlined above may be the only means for determining any stability constant data for a wide range of metal-ligand systems, and the species detected would normally be the only one present in any significant amount at the concentration of metal ion and ligand remaining after precipitation occurs. Data obtained by ion-selective electrodes would, therefore, be sufficient for most calculations.

TABLE I^aDATA FOR $[\text{Pb}^{2+}] = 1.00 \times 10^{-2} M$, $I = 1.0$, AND 15°

$[\text{F}^-]_T, M$	$[\text{F}^-], M$	$\frac{1}{[\text{Pb}^{2+}]_T} \left(\frac{[\text{F}^-]_T}{[\text{F}^-]} - 1 \right)$
8.00×10^{-6}	5.96×10^{-6}	34
1.00×10^{-5}	6.95×10^{-6}	44
2.80×10^{-5}	1.97×10^{-5}	42
4.00×10^{-5}	2.82×10^{-5}	42
6.00×10^{-5}	4.22×10^{-5}	42
1.00×10^{-4}	6.68×10^{-5}	50

^a Average $\beta_1 = 42 \pm 3$.

TABLE II^aDATA FOR $[\text{Pb}^{2+}] = 1.00 \times 10^{-2} M$, $I = 0.10$, AND 15°

$[\text{F}^-]_T, M$	$[\text{F}^-], M$	$\frac{1}{[\text{Pb}^{2+}]_T} \left(\frac{[\text{F}^-]_T}{[\text{F}^-]} - 1 \right)$
8.00×10^{-6}	6.03×10^{-6}	67
1.00×10^{-5}	6.76×10^{-6}	48
2.80×10^{-5}	1.80×10^{-5}	56
4.00×10^{-5}	2.63×10^{-5}	52
6.00×10^{-5}	3.94×10^{-5}	52
1.00×10^{-4}	6.76×10^{-5}	48

^a Average $\beta_1 = 54 \pm 5$.

one complex, PbF^+ , having an overall stability constant $\beta_1 = 42 \pm 3$ at an ionic strength of 1.0 and 15° and $\beta_1 = 54 \pm 5$ at an ionic strength of 0.10 and 15° .

Simple calculations show that over the fluoride ion