# THE SOLUBILITY OF BARIUM MONOFLUOROPHOSPHATE

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ABSTRACT.—The solubility of barium monofluorophosphate, $BaPO_3F$, in water at 25°C has been determined to be $(7.7 \pm 0.6) \times 10^{-4}$ g-moles/liter. Mean activity coefficients of $BaPO_3F$, as a function of ionic strength, approach the limiting Debye-Huckel slope for a 2-1 electrolyte.

For the sparingly soluble salt, $BaPO_3F$, the following equilibium equation applies:

$$BaPO_3F_{(s)} = Ba^{+2} + PO_3F^{=} \quad (1)$$
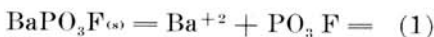
The solubility product constant is expressed as

$$K_{SP} = a_{Ba}^{+2} \, a_{PO3F}^{=} \quad (2)$$

where K_{SP} is the thermodynamic solubility product constant of the salt.

Equation (2) may be rewritten as:

$$K_{SP} = c_{Ba}^{+2} c_{PO_3F}^{=} \cdot \gamma_{Ba}^{+2} {}_{PO_3F}^{=} \quad (3)$$

where c_{Ba+2} and $c_{PO_3F}^{=}$ represent the molarities of the ions and γ the respective ionic activity coefficients.

Allowing

$$K_{SP} = c_{Ba}^{H} \, c_{POF}^{=} \quad (4)$$

$$\gamma^2_{\pm} = \gamma_{Ba}^{+2} \gamma_{PO_3F}^{=} \quad (5)$$

where $K_{SP'}$ is the concentration solubility product and $\gamma_{\pm}$ is the mean activity coefficient of $BaPO_3F$, then from (3)

$$K_{SP} = K_{SP'} \, \gamma^2_{\pm} \quad (6)$$

Since $\gamma_{\pm}$ is dependent on the ionic strength of the solution, $K_{SP'}$ must vary as ionic strength varies. From (4)

$$K_{SP'} = S^2 \quad (7)$$

where S is the solubility of the salt. So,

$$K_{SP} = S^2\gamma^2_{\pm} \quad (8)$$

The Debye-Huckel Theory predicts that the activity coefficients of solutions of electrolytes decrease as ionic strength increases in dilute solutions, hence one would expect an increase in solubility of the salt as the ionic strength of the solution is increased by the addition of an inert electrolyte.

The thermodynamic solubility product constant is independent of the ionic strength of the solution so that we may write the equation:

$$K_{SP} = S^2\gamma^2_{\pm} = S_o^2 \, \gamma_o^2 \quad (9)$$

where S and $\gamma_{\pm}$ are for solutions of a certain ionic strength and S_o and γ_o are for a solution of zero ionic strength. Taking the square root of equation (9) and the logarithm of that equation; we obtain the result

$$\log S = \log S_o\gamma_o - \log \gamma_{\pm} \quad (10)$$

In this linear equation, $\log S_o\gamma_o$ is a constant and $\log \gamma_{\pm}$ is linearly

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dependent on the square root of the ionic strength, μ, by virtue of the Debye-Huckel limiting law. Therefore, a plot of log S against $\sqrt{\mu}$ should be linear, the intercept at $\mu = 0$ yielding the true thermodynamic solubility product, K_{SP}. The slope of the line should be such that, as the square root of the ionic strength increases, log S should increase. The mean activity coefficients of $BaPO_3F$ in solutions may be calculated from (10).

Procedures

$BaPO_3F$ was prepared by adding 0.5 molar Na_2PO_3F to 0.5 molar $BaCl_2$. The resulting precipitate of $BaPO_3F$ was washed and dried to constant weight over $CaCl_2$. The salt was analyzed for total barium (Pierce, Haenisch and Sawyer, 1958) and total fluoride (Armstrong, 1933). These analyses established a 95% purity for the $BaPO_3F$ with barium ortho- and meta-phosphates as the probable impurities.

A stock solution of potassium chloride was prepared by weight from Analytical Reagent grade KCl oven-dried at 110°C. A stock solution of magnesium chloride was prepared from reagent-grade $MgCl_2$ • $6H_2O$ and analyzed for chloride ion by the Mohr method.

A series of KCl and $MgCl_2$ solutions of varying ionic strengths were prepared by dilution of the stock solutions. Each of these solutions was saturated with $BaPO_3F$ by adding solid $BaPO_3F$ to the solution and heating to 35°C for 15 minutes. The solutions were then allowed to equilibrate at 25.00 ± 0.02°C in an oil bath.

About 15 ml of the saturated supernatant liquid was separated by filtration and acidified with 5 ml of 12 molar HCl. The acidified solution was heated on a steam bath for 15 minutes to hydrolyze the monofluorophosphate to orthophosphate and fluoride ions (Lange, 1950) and the resulting solution analyzed for orthophosphate by the spectrophotometric molybdo-vanadate method (Quinlan and DeSea, 1955). The concentration of $BaPO_3F$ was then calculated directly from the orthophosphate concentration.

Results

Table 1 summarizes the data for the solubility, S, in moles per liter and the mean activity coefficient, $\gamma_\pm$, of $BaPO_3F$ as a function of ionic strength in solutions of $MgCl_2$ and KCL. A plot of $-$log S vs $\sqrt{\mu}$ yields a straight line as predicted by the Debye-Huckel limiting law. Least-squares analysis of the data for KCL and $MgCl_2$ solutions give the limiting values of $-$log S_0 of 3.109 ± 0.034 and 3.117 ± 0.035 respectively. Averaging these values gives a value of $S_0 = (7.7 \pm 0.6) \times 10^{-4}$ g-moles/liter. This compares favorably with the value of 6×10^{-4} at 20°C determined by Lange (1950).

In Figure 1 we have plotted the calculated values of log $\gamma_\pm$ of $BaPO_3F$ versus $\sqrt{\mu}$ in KCL and

TABLE 1.—Solubilities and Mean Activity Coefficients of $BaPO_3F$.

| In Solutions of KCl		
$\sqrt{\mu}$	$-$log S	$\gamma\pm$
0.6810	2.68	0.38
0.4832	2.73	0.43
0.3431	2.93	0.68
0.2221	2.96	0.73
0.1638	2.99	0.78
0.1485	2.99	0.78
0.1125	3.04	0.87
0.08418	3.06	0.91
0.2009	2.96	0.73
In Solutions of $MgCl_2$		
$\sqrt{\mu}$	$-$log S	$\gamma\pm$
0.7736	2.53	0.27
0.5504	2.63	0.34
0.3521	2.77	0.47
0.2518	2.93	0.68
0.1637	3.03	0.85
0.2283	2.88	0.60
0.1140	3.04	0.87
0.08949	3.07	0.93
0.2763	2.84	0.55
0.3170	2.78	0.48

MgCl$_2$ solutions. It can be seen that the data very nearly approximate the behavior of a 2-1 electrolyte rather than a 2-2 electrolyte as one might expect at first consideration. The lines on the graph represent the limiting form of the Debye-Huckel equation for the dependence of the mean activity coefficient upon the ionic strength of a solution. The expression for the Debye-Huckel equation is:

$$\log \gamma_\pm = -A\ Z_+Z_-\ \sqrt{\mu} \qquad (11)$$

where A is a constant dependent upon type of solvent and temperature and has the value 0.509 for water at 25°C and Z_+Z_- represents the charge of the cation and anion of the electrolyte in question.

The observed behavior of BaPO$_3$F as a 2-1 electrolyte is readily explained. The second dissociation constant of monofluorophosphoric

acid, H$_2$PO$_3$F, has a value of 1.2 X 10^{-5} (Bruns, 1963). In solutions of such low concentration of PO$_3$F$^=$ as are encountered in this study, the hydrolysis of the ion to form HPO$_3$F$^-$, because of the weakly acidic nature of the second hydrogen ion, is nearly complete, that is to say

$$PO_3F^= + H_2O \rightarrow HPO_3F^- + OH^- \qquad (12)$$
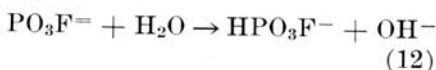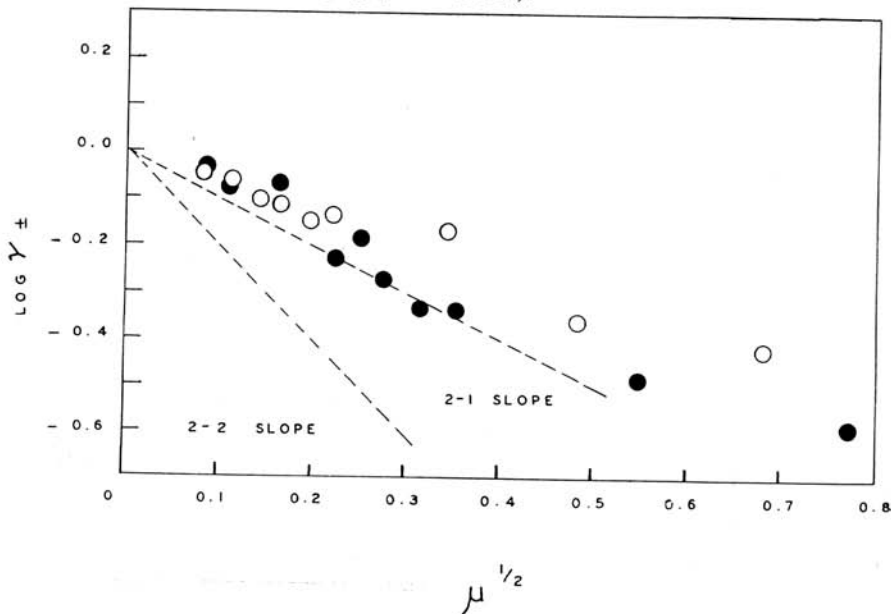
Hence the physical properties of aqueous solutions would, indeed be expected to approximate those of an electrolyte with a doubly charged cation and singly charged anion.

ACKNOWLEDGMENT

FIGURE 1.—Mean activity coefficients vs. $\sqrt{\mu}$ for BaPO$_3$F in aqueous solutions of KCl (open circles) and MgCl$_2$ (filled circles).

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