J. Chem. Eng. Data 1993, 38, 132-133

The Solubility of the Rare-Earth-Metal Phosphates in Sea Water

F. Henry Firsching* and John C. Kell

School of Sciences, Southern Illinois University at Edwardsville, Edwardsville, Illinois 62026

The solubility and activity products of 14 rare-earth-metal phosphates in sea water have been determined at 25 ± 1 °C. The most soluble is yttrium phosphate ($pK_s = 25.60$), and the least soluble is lanthanum phosphate ($pK_s = 27.92$). Saturated solutions were analyzed for total phosphate concentration and total acidity. Activity products were calculated from the experimental data.

Introduction

The solubility of the rare-earth-metal phosphates has been determined in sea water. This work is a follow-up study of the solubility of the rare-earth-metal phosphates (*1*). Oceanographers and geologists are concerned about equilibrium conditions in the oceans, and often have little data on solubilities in sea water.

Concentrations of total rare-earth-metal cations in sea water have been determined (*2*). These give some idea about the equilibrium conditions of rare-earth-metal cations in solution, but leave much to be desired. The high ionic strength of sea water makes activity coefficient calculations uncertain.

Experimental Section

The rare-earth-metal phosphate salts from the previous solubility study (*1*) were used in this study. These were prepared from rare-earth-metal oxides that were 99.9% pure with respect to their rare-earth metal content. Only reagent grade perchloric acid, disodium hydrogen phosphate, and urea were used in the precipitation from homogeneous solution that produced the rare-earth-metal phosphates.

Synthetic sea water was prepared according to the recipe of D. Kester et al. (*3*). The concentration of all ions is within two significant figures of the natural concentration of ions in sea water. The concentrations (mol dm^{-3}) of the following ions in sea water are $Ca^{2+} = 0.010$, $Mg^{2+} = 0.056$, $Na^+ = 0.46$, $K^+ = 0.0097$, $Cl^- = 0.54$, and $SO_4^{2-} = 0.028$.

The rare-earth-metal phosphates are so insoluble (about 10^{-13} mol dm^{-3}) that the concentrations are too low for any normal analysis scheme. Therefore, a dilute solution of perchloric acid (about 0.085 mol dm^{-3}) was added to the synthetic sea water to bring a readily measurable amount of rare-earth-metal cation and phosphate into solution.

The acidified synthetic sea water was left in contact with the rare-earth-metal phosphate solids for about 18 months, before being analyzed. During this period, the flasks containing these solutions and solids were occasionally shaken. The previous study had showed that equilibrium was established after about 90 days of standing. Equilibrium was assumed.

Analysis

Two different measurements were made on the saturated solutions: the total acidity and the total phosphate concentration. The total acidity determination was made using a standard sodium hydroxide solution to the phenolphthalein end point. The concentration of total phosphate was determined spectrophotometrically using HACH Phos Ver III phosphate reagent powder pillows (*1*).

The analytical values determined for the saturated solutions are given in Table I.

Table I. Total Phosphate Concentration C_T and Total Acidity a Determined for Saturated Solutions at 25 ● 1 °C

rare-earth element	$C_T \times 10^4$/(mol dm^{-3})	a/(mol dm^{-3})	rare-earth element	$C_T \times 10^4$/(mol dm^{-3})	a/(mol dm^{-3})
Y	35.4	0.081 67	Tb	12.2	0.089 75
	24.5	0.081 67		13.5	0.081 67
	36.2	0.082 39		10.7	0.080 42
La	3.45	0.081 24	Dy	23.1	0.097 32
	1.32	0.080 75		7.3	0.090 68
	1.1	0.084 19		17.6	0.083 29
Pr	8.4	0.081 48	Ho	4.1	0.083 91
	8.1	0.081 72		18.1	0.082 81
	6.6	0.082 32		13.7	0.090 77
Nd	2.0	0.081 67	Er	4.4	0.094 21
	4.8	0.081 85		7.30	0.086 94
Sm	2.45	0.085 00		7.75	0.086 57
	2.48	0.088 88	Tm	9.50	0.080 78
	4.28	0.082 69		8.35	0.080 78
Eu	2.41	0.087 33	Yb	6.25	0.081 49
	2.64	0.085 26		4.5	0.084 54
	4.3	0.092 26		6.95	0.081 40
Gd	7.1	0.089 93	Lu	27.8	0.079 61
	9.1	0.090 29		25.8	0.082 84
				36.0	0.091 72

Derivation of the Solubility Product Equation

The equilibrium between solid rare-earth-metal phosphate and the dissolved ions is

$$LnPO_4(s) = Ln^{3+}(aq) + PO_4^{3-}(aq) \qquad (1)$$

(Ln = any rare-earth element). The solubility product expression for this equilibrium is

$$K_{sp} = [Ln^{3+}][PO_4^{3-}] \qquad (2)$$

The activity product is

$$K_{sp,c} = [Ln^{3+}]f_{Ln}[PO_4^{3-}]f_{PO_4} \qquad (3)$$

In the saturated solution there is only one mathematically significant form of the rare-earth-metal ion that is Ln^{3+}. Calculations indicate that other possible species such as $Ln(H_2PO_4)^{2+}$, $Ln(OH)_2^+$, and $Ln(HPO_4)^+$ are not present in significant quantities at the pH conditions found in the saturated solutions (*4*). H_3PO_4 is the only significant form of phosphate in the saturated solutions.

In order to calculate the solubility product, it is essential to use the concentration of PO_4^{3-}. The concentration of PO_4^{3-} cannot be analytically determined, and therefore it cannot be used directly in the K_{sp} expression. The concentration of phosphate ion can be determined by using the weak acid dissociations of phosphoric acid.

The dissociation constants of phosphoric acid selected were a median of all the reported values at 25 °C with an ionic

0021-9568/93/1738-0132$04.00/0

Table II. $K_{sp,c}$ of the Rare-Earth-Metal Phosphates

rare-earth element	$K_{sp,c} \times 10^{28}$	rare-earth element	$K_{sp,c} \times 10^{28}$	rare-earth element	$K_{sp,c} \times 10^{28}$
Y	250	Eu	1.8	Er	8.6
La	1.2	Gd	12	Tm	21
Pr	14	Tb	32	Yb	8.4
Nd	3.4	Dy	49	Lu	190
Sm	2.3	Ho	49		

Table III. Conditional K_{sp} of the Rare-Earth-Metal Phosphates without Using Activity Coefficient Corrections

rare-earth element	$K_{sp} \times 10^{25}$	rare-earth element	$K_{sp} \times 10^{25}$	rare-earth element	$K_{sp} \times 10^{25}$
Y	120	Eu	7.4	Er	3.4
La	3.1	Gd	5.5	Tm	8.3
Pr	4.5	Tb	13	Yb	2.9
Nd	1.1	Dy	22	Lu	100
Sm	4.4	Ho	13		

strength approaching zero (*5*):

$$K_1 = 7.11 \times 10^{-3}$$

$$K_2 = 6.34 \times 10^{-8}$$

$$K_3 = 4.17 \times 10^{-13}$$

The analytical concentration of total phosphate is given by

$$C_T = [H_3PO_4] + [H_2PO_4^-] + [HPO_4^{2-}] + [PO_4^{3-}] \tag{4}$$

$$\alpha_3 = \frac{[PO_4^{3-}]}{C_T} = \frac{K_1K_2K_3}{[H^+]^3 + [H^+]^2K_1 + [H^+]K_1K_2 + K_1K_2K_3} \tag{5}$$

Suitable algebraic manipulations yield the solubility product

$$K_{sp} = \frac{[Ln^{3+}]C_T}{[H^+]^3/K_1K_2K_3 + [H^+]^2/K_2K_3 + [H^+]/K_3 + 1} \tag{6}$$

The activity product form of eq 6 is

$$K_{sp,c} = \frac{[Ln^{3+}]f_{Ln}C_Tf_{PO_4}}{(a_{H^+})^3/K_1K_2K_3 + (a_{H^+})^2/K_2K_3 + a_{H^+}/K_3 + 1} \tag{7}$$

From the solubility data given in Table I, the activity products were calculated using this equation. The ionic strength was determined by using the known perchlorate ion concentration, the hydrogen ion concentration, the rare-earth-metal cation concentrations, and the ionic strength of the synthetic sea water component. The activity coefficient for each rare-earth-metal cation was calculated from the extended Debye–Huckel expression (*6*). The activity products were then calculated. These are given in Table II.

Due to the uncertainty of the extended Debye–Huckel equation at such a high ionic strength, conditional solubility products were calculated without using activity coefficient corrections. These are given in Table III.

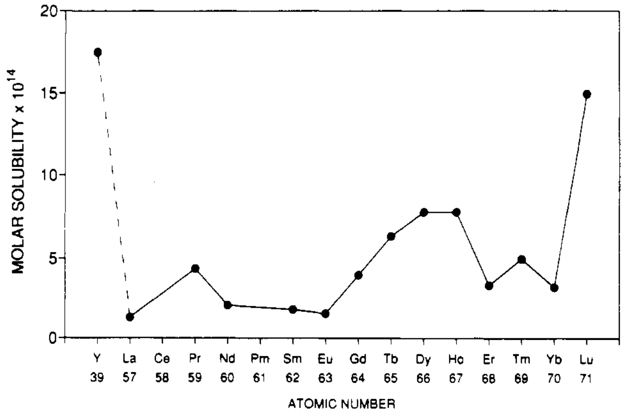

Figure 1. Molar solubilities of rare-earth-metal phosphates in sea water.

Discussion

The quantitative analysis of total phosphate is reproducible within two-figure accuracy. The total acidity determination is considerably better. Yet the final results are of about one-figure accuracy.

There are a variety of limiting factors involved in this study. An important factor is the individual variation of one saturated solution from another. See Table I. La and Dy values vary by more than 3, and Ho by more than 4.

Several mathematical manipulations also influence the overall accuracy. The total phosphate concentration is equal to the rare-earth-metal cation concentration, which is then squared. The calculated hydrogen ion is cubed. Any small error in the experimental values would be magnified by the mathematical operation. Nevertheless, the final results appear to be valid to at least one-figure accuracy. The calculated molar solubilities are given in Figure 1.

The activity products of the rare-erath-metal phosphates determined in acidified sea water are very similar to the values determined in dilute acid solution (*1*). This similarity infers that the extended Deby–Huckel expression may be fairly valid, even for solutions as concentrated as sea water (ionic strength about 0.7).

Acknowledgment

We thank William P. Hildebrand and Thomas Stone for their assistance in the laboratory.

Literature Cited

(1) Firsching, F. H.; Brune, S. N. *J. Chem. Eng. Data* **1991**, *36*, 93.
(2) Goldberg, E. D.; Koide, M.; Schmitt, R. A.; Smith, R. H. *J. Geophys. Res.* **1963**, *68*, 4209.
(3) Kester, D. R.; Duedall, I. W.; Connors, D. N.; Pytokowicz, R. M. *Limnol. Oceanogr.* **1967**, *12*, 176.
(4) Bingler, L. S.; Byrne, R. H. *Polyhedron* **1989**, *8*, 1315.
(5) Sillen, L. G.; Martell, A. E. *Stability Constants*; The Chemistry Society, Burlington House: London, 1964.
(6) Kolthoff, I. M.; Sandell, E. B.; Meehan, E. J.; Bruckenstein, S. *Quantitative Chemical Analysis*, 4th ed.; MacMillan: New York, 1969.

Received for review June 23, 1992. Revised September 24, 1992. Accepted October 2, 1992.