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Solubility Products of the Trivalent Rare-Earth Arsenates

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The solubility and solubility products of 15 rare-earth arsenates in aqueous solution have been determined at 25 ± 1 °C. The most soluble compound is lanthanum arsenate ($pK_s = 21.45$). The least soluble is scandium arsenate ($pK_s = 26.72$). The rare-earth arsenates were prepared by precipitation from homogeneous solution. Saturated solutions were analyzed for the concentration of rare-earth cations, the total concentration of arsenate, and the total acidity. Activity products were calculated from the experimental data.

Introduction

The solubilities reported here involve the entire rare-earth series except for cerium and promethium. Previous solubility information about the rare-earth arsenates was almost nonexistent (*1, 2*).

Experimental Section

Satisfactory crystals of rare-earth arsenates were prepared by precipitation from homogeneous solution using the hydrolysis of urea (*3*).

Equimolar amounts (0.005 mol) of rare-earth perchlorate and disodium arsenate were added to a 1-L beaker, with 5 mL of 70% by mass $HClO_4$, to prevent the immediate precipitation of the rare-earth arsenate. Deionized water was added to bring the volume to about 900 mL. A 3–5-g amount of urea was slowly added with constant stirring. The solution was heated to hydrolyze the urea, increase the pH, and bring about the precipitation of the rare-earth arsenate. The solution was heated for an additional 1 h after precipitation began. The resulting crystals were washed 10–15 times with deionized water. The last two washings were made with a 0.100 mol dm^{-3} perchloric acid solution to remove any possible rare-earth carbonate that might be present. No fizzing was ever observed. The washing removed any excess arsenate or rare-earth ions, as well as any colloidal material that might be present. All washings were discarded.

Saturated Solutions

The rare-earth arsenates are very insoluble in water. The saturated solutions of rare-earth arsenates in pure water would contain a rare-earth concentration of about 10^{-11} mol dm^{-3}. In order to bring enough rare-earth cation into solution for accurate analysis, dilute $HClO_4$ was used to partially dissolve the rare-earth arsenates.

An equilibrium exists between the rare-earth cation and the forms of arsenate present in solution: AsO_4^{3-}, $HAsO_4^{2-}$, $H_2AsO_4^-$, and H_3AsO_4. A concentration of 0.0423 mol dm^{-3} $HClO_4$ was used for all the rare-earth arsenates except scandium arsenate. For scandium arsenate, a higher concentration of acid was needed to dissolve enough of the compound for a reasonable analysis. All the rare-earth arsenate crystals were placed in a perchloric acid solution, stoppered, and allowed to come to equilibrium with occasional shaking. Analysis was not performed on these solutions, in contact with solid rare-earth arsenate, until they had been standing for at least 18 months. Equilibrium was assumed. Scandium arsenate was the exception. The scandium arsenate solid was in contact with the acid solutions for about 60 days. During the last 20 days, the scandium arsenate–acid solutions were continuously shaken. The scandium arsenate–acid solutions were at equilibrium or close to it. Previous work with the rare-earth phosphates showed that 80 days were needed to reach equilibrium and the scandium arsenate is about as insoluble as the rare-earth phosphates.

Analysis

In this study, three different measurements were made on the saturated rare-earth arsenate solutions: an EDTA titration for the rare-earth cation concentration, an iodine titration for the total arsenate concentration, and a sodium hydroxide titration for the total acidity.

Titration Using EDTA. A 25.00-mL sample of saturated rare-earth arsenate solution was added to a 250-mL Erlenmeyer flask using a pipet. A 10-mL sample of 1.0 mol dm^{-3} ammonium acetate buffer solution was added, and the pH was adjusted to about 5.5–5.7, using either ammonia or acetic acid. Xylenol orange indicator solution (about 1%) (2 drops) was added. The purple solution was titrated with a standard 0.01 mol dm^{-3} EDTA solution until the color changed to brown-yellow.

Titration Using Iodine. A 25.00-mL sample of saturated rare-earth arsenate solution was added to a 250-mL Erlemeyer flask using a pipet. A 25-mL sample of KI solution (about 2 g) and 25 mL of 9 mol dm^{-3} H_2SO_4 solution were added. After 10 min, the solution was titrated with a standard thiosulfate solution. As the brown color of the triiodide ion faded, about 0.5 mL of starch solution (2 g/L) was added. The solution was titrated until the deep blue color disappeared.

Titration Using Base. A 10.00-mL sample of saturated rare-earth arsenate solution was added to a 250-mL Erlenmeyer flask using a pipet. Phenolphthalein indicator was added. The solution was titrated with a standard 0.025 mol dm^{-3} NaOH solution to the first permanent pink color.

Derivation of the Solubility Product Equation

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

$$LnAsO_4(s) = Ln^{3+}(aq) + AsO_4^{3-}(aq) \qquad (1)$$

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

$$K_{sp} = [Ln^{3+}][AsO_4^{3-}] \qquad (2)$$

The activity product is

$$K_{sp,c} = a_{Ln^{3+}}\, a_{AsO_4^{3-}} \qquad (3)$$

In the saturated solution there is only one mathematically significant form of the rare-earth ion and that is Ln^{3+}. Calculations indicate that other possible species such as

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$Ln(OH)^{2+}$ are not present in significant quantities at the pH conditions in the saturated solutions. H_3AsO_4 is the most significant form of arsenate in the saturated solutions. A smaller fraction of the total concentration of arsenate is present as $H_2AsO_4^-$.

The concentration of the free arsenate anion AsO_4^{3-} cannot be analytically determined, and therefore it cannot be used directly in the K_{sp} expression. However, the concentration of the arsenate anion can be calculated by using the total concentration of arsenate and the weak acid dissociations of arsenic acid.

The dissociation constants of arsenic acid (*4*) used in this study are

$$K = 6.0 \times 10^{-3}$$

$$K = 1.05 \times 10^{-7}$$

$$K = 3.0 \times 10^{-12}$$

The analytical concentration of total arsenate is given by

$$C_T = [H_3AsO_4] + [H_2AsO_4^-] + [HAsO_4^{2-}] + [AsO_4^{3-}] \tag{4}$$

$$\alpha_3 = \frac{[AsO_4^{3-}]}{C_T} = \frac{K_1K_2K_3}{[H^+]^3 + [H^+]^2K_1 + [H^+]K_1K_2 + K_1K_2K_3} \tag{5}$$

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

$$K_{sp,c} = \frac{[Ln^{3+}]f_{Ln^{3+}}C_Tf_{AsO_4^{3-}}}{[H^+]^3f_{H^+}^{\ 3}/K_1K_2K_3 + [H^+]^2f_{H^+}^{\ 2}/K_2K_3 + [H^+]f_{H^+}/K_3 + 1} \tag{7}$$

From the solubility data given in Table I, the activity products were calculated. The ionic strength was determined by using the concentration of both the hydrogen and rare-earth cations, and including the only significant anion, the perchlorate. The ionic strengths of most saturated solutions were less than 0.1. Those of the scandium arsenate saturated solutions were higher. The extended Debye–Huckel equation gives reliable results within this ionic strength range. The base titration gave the total acidity, which is a combination of the free hydrogen ion as well as the protonated forms of the arsenate. From the total arsenate concentration and total acidity, the concentrations of free hydrogen ion and the various protonated arsenate forms can be calculated. The activity coefficients for the hydrogen ion, the rare-earth cation, and the arsenate anion were then calculated. The calculated activity products are given in Table II. The molar solubilities are plotted in Figure 1.

There are a variety of limiting factors involved in this study. One is the individual variation of one saturated solution from another. There are titration errors. In doing an EDTA titration, with a 0.01 mol dm^{-3} solution, small volumes such as 5 or 10 mL were often encountered. The same is true for the iodine titration data where small titration volumes of less than 5 mL were commonly encountered. The hydrogen ion concentration is cubed. Any small error is significantly enlarged by the cubing operation. The K_a values for the arsenic acid are given to two-figure accuracy. Nevertheless, the final results appear to be valid to at least one-figure accuracy. The scandium value is the most uncertain.

Table I. Rare-Earth Concentration *C*, Total Arsenate Concentration C_T, and Total Acidity *a*, Determined for Saturated Solutions at 25 ± 1 °C

rare-earth element	10^3C, mol dm^{-3}	10^3C_T, mol dm^{-3}	10^2a, mol dm^{-3}
Sc	0.50	0.75	20
	0.38	0.11	15
	0.32	0.09	11
Y	2.92	3.47	4.30
	2.96	3.53	4.30
	2.93	3.38	4.57
La	6.10	2.40	3.33
	6.48	2.14	3.31
	6.29	2.27	3.68
Pr	4.20	1.25	3.11
	4.15	1.15	3.11
	4.20	1.10	3.01
Nd	5.76	5.6	4.42
	5.54	4.5	4.43
	5.35	5.1	4.32
Sm	2.60	2.60	4.12
	2.70	2.65	4.41
	2.75	2.95	4.66
Eu	3.89	1.98	4.17
	3.80	1.85	4.14
	3.86	1.89	4.13
Gd	4.85	7.1	4.00
	4.70	7.3	4.04
	4.85	7.6	4.01
Tb	1.90	1.80	4.44
	2.00	2.71	4.72
	2.10	2.88	4.93
Dy	2.30	2.25	4.31
	2.35	2.40	4.19
	2.50	2.45	4.23
Ho	2.50	2.05	4.08
	2.45	2.05	4.27
	2.50	2.20	4.54
Er	4.14	3.82	4.83
	3.66	3.20	4.44
	3.64	3.60	4.41
Tm	1.74	2.33	4.40
	1.70	2.29	4.42
	1.68	2.18	4.28
Yb	2.50	3.33	4.47
Lu	2.83	3.29	4.57
	2.92	3.46	4.61
	2.90	3.45	4.66

Table II. p$K_{sp,c}$ of the Rare-Earth Arsenates

rare-earth element	p$K_{sp,c}$	rare-earth element	p$K_{sp,c}$
Sc	26.72 ± 0.27	Tb	23.07 ± 0.09
Y	22.60 ± 0.06	Dy	23.83 ± 0.06
La	21.45 ± 0.12	Ho	22.87 ± 0.08
Pr	22.03 ± 0.02	Er	22.47 ± 0.04
Nd	21.86 ± 0.11	Tm	23.08 ± 0.01
Sm	22.73 ± 0.08	Yb	22.72
Eu	22.53 ± 0.03	Lu	22.66 ± 0.01
Gd	21.67 ± 0.04		

Discussion

The results of this study are not in agreement with the work of Komissarova et al. (*1*), who determined a solubility of 2 × 10^{-5} mol dm^{-3} for scandium arsenate. No method of analysis was given. Despite this value, the solubilities of the rare-earth arsenates in this paper are very similar to the solubilities of the rare-earth phosphates (*3*). The arsenates are slightly more soluble than the phosphates, as would be expected from charge density considerations of the phosphate and arsenate anions.

The solubilities of the rare-earth arsenates are so low that

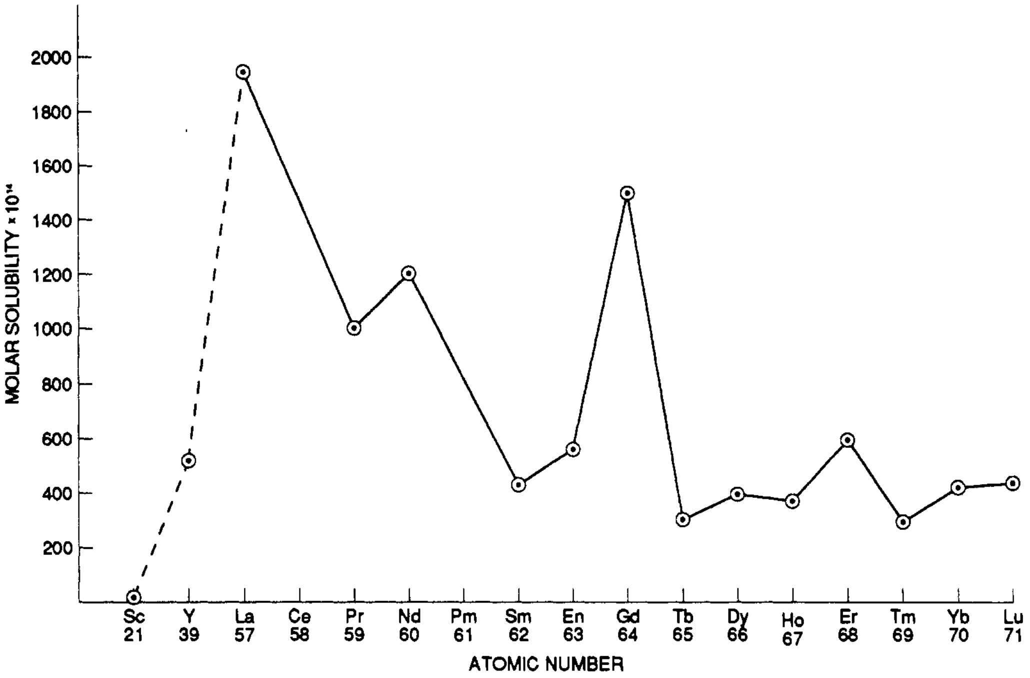

Figure 1. Solubilities of the rare-earth arsenates.

the solubility product and the activity products have essentially the same value.

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Registry No. $ScAsO_4$, 15479-88-6; $YAsO_4$, 14214-03-0; $LaAsO_4$, 14214-04-1; $PrAsO_4$, 15479-86-4; $NdAsO_4$, 15479-84-2; $SmAsO_4$, 15479-87-5; $EuAsO_4$, 22816-52-0; $GdAsO_4$, 14214-05-2; $TbAsO_4$, 28548-41-6; $HoAsO_4$, 28548-43-8; $ErAsO_4$, 28548-44-9; $TmAsO_4$, 28548-45-0; $YbAsO_4$, 15479-89-7; $LuAsO_4$, 18490-52-3.