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Solubility Products of the Rare-Earth 8-Quinolinates

F. Henry Firsching* and Robert C. Cuca

School of Science and Technology, Southern Illinois University, Edwardsville, Illinois 62026

The solubility products of 15 rare-earth 8-quinolinates have been determined. The most soluble is lanthanum 8-quinolinate (pK = 28.06) and the least soluble is scandium 8-quinolinate (pK = 34.52). The pure rare-earth 8-quinolinates were prepared by precipitation from homogeneous solution, using the hydrolysis of urea. Saturated solutions were analyzed for pH and the concentrations of rare-earth cation and 8-quinolinol. Activity products were calculated from the experimental data. Because of the very low solubility of the rare-earth 8-quinolinates, the solubility product and the activity product are essentially the same.

Introduction

Previous work by Pyantnitskii and Gavrilova (*1*) reported on the solubility products of the rare-earth 8-quinolinates. However, their results are invalid for a variety of reasons. The two most important are failure to correct for nitrate complexation of the rare-earth cations (solutions were ~1 M in nitrate) and the calculation of a solubility product rather than an activity product. The results reported in this paper are ~10^{-3} smaller than the previously reported solubility-product values (*1*).

Wendlandt (*2*) has shown that the stoichiometric ratio or rare earth to 8-quinolinol in the pure rare-earth 8-quinolinate is 1:3. This same ratio was obtained by analyzing the composition of the saturated solutions prepared in this study.

Experimental Section

Preparation of Rare-Earth 8-Quinolinates. The rare-earth 8-quinolinates were prepared by precipitation from homogeneous solution. Some perchloric acid, 3 mmol of rare-earth perchlorate, 15 mmol of 8-quinolinol, and 2–3 g of urea were dissolved in ~800 mL of deionized water to produce a clear, uniform solution. The solution was then heated to ~90 °C, causing hydrolysis of the urea. This brought about a gradual decrease in the hydrogen-ion concentration, inducing the slow formation of a rare-earth 8-quinolinate precipitate. The resulting crystals were washed 10–20 times with deionized water in order to remove any soluble impurities or colloidal material.

Saturated Solutions. In order to dissolve enough of the rare-earth 8-quinolinate so that a suitable analysis could be made, we used perchloric acid solutions instead of pure water. Standard perchloric acid (3.80×10^{-2} or 4.89×10^{-2} M, 200 mL) was added to a 250-mL erlenmeyer flask, along with more than enough rare-earth 8-quinolinate crystals to provide a saturated solution. The flasks were stoppered and set on a shaker for 2 months. Preliminary experiments showed that in many cases a saturated solution was achieved in less than 1 month. Subsequent checks on the attainment of a saturated solution showed that 2 months was sufficient.

Analysis. Four different measurements were made on the saturated rare-earth 8-quinolinate solutions: the pH, a spectrophotometric determination of the 8-quinolinol, a spectrophotometric determination of some of the rare-earth cations (Nd, Ho, Er, and Pr), and a spectrophotometric titration of the others (Sc, Y, La, Sm, Eu, Gd, Tb, Dy, Tm, Yb, and Lu).

Table I. Analytical Values Determined for Saturated Solutions[a]

rare earth	10^3(rare-earth-ion concn), M	10^3(8-quinolinol concn), M	pH	10^4(hydrogen-ion activity)
Sc	6.6	20.0	3.27	5.3
	6.6	19.7	3.26	5.6
	7.2	21.5	3.20	6.0
Y	6.2	18.5	3.57	2.7
	6.2	18.5	3.55	2.8
	6.3	19.0	3.62	2.4
La	6.5	19.5	4.40	0.40
	6.5	19.5	4.38	0.42
	6.5	19.5	4.41	0.39
Pr	6.3	19.0	4.05	0.89
	6.2	18.7	3.60	2.5
	6.3	19.0	4.07	0.80
	5.9	18.4	4.26	0.54
	5.8	17.8	4.09	0.80
	5.5	16.2	3.55	2.8
Nd	6.2	18.4	3.81	1.5
	6.2	18.4	3.95	1.1
	6.3	18.8	3.96	1.1
	6.3	17.8	4.13	0.73
Sm	6.5	19.2	3.98	1.1
	6.2	18.7	3.76	1.7
	6.3	19.2	3.92	1.2
Eu[b]	8.0	24.0	3.83	1.5
	7.8	23.5	3.73	1.9
	8.0	24.0	3.75	1.8
Gd	6.6	19.7	3.88	1.3
	6.5	19.5	3.73	1.8
	6.5	19.5	3.74	1.8
Tb	5.6	16.5	3.68	2.1
	5.5	16.5	3.68	2.1
	5.5	16.3	3.75	1.8
Dy	6.1	18.7	3.56	2.8
	6.1	19.0	3.64	2.3
	6.1	19.0	3.67	2.1
Ho	6.2	18.5	3.66	2.2
	6.4	19.0	3.78	1.7
	6.3	19.2	3.69	2.0
Ho[b]	8.0	24.0	3.68	2.1
	7.9	23.7	3.63	2.3
	7.9	23.7	3.52	3.0
Er[b]	7.9	23.7	3.53	3.0
	8.0	23.7	3.47	3.4
	7.9	23.7	3.55	2.8
Tm[b]	7.5	22.5	3.33	4.6
	7.6	27.7	3.55	2.8
	7.6	27.7	3.61	2.5
Yb	6.5	19.5	3.69	2.0
	6.4	19.2	3.67	2.1
	6.4	19.2	3.37	4.3
Yb[b]	7.6	23.0	2.90	13.0
	7.9	23.7	3.02	9.3
	8.0	24.0	3.36	1.9
Lu	6.0	18.0	3.39	4.0
	6.1	18.0	3.37	4.2
	6.1	18.5	3.56	2.8

[a] Starting $HClO_4$ concentration – 3.8×10^{-2} M except where otherwise indicated. [b] Starting $HClO_4$ concentration = 4.89×10^{-2} M.

The pH measurements were made with a Corning Model 12, expanded-scale pH meter. Experimental results were reproducible to two-figure accuracy.

The 8-quinolinol analyses were made with a Cary 14 spectrophotometer. Even though three possible forms of 8-quinolinol

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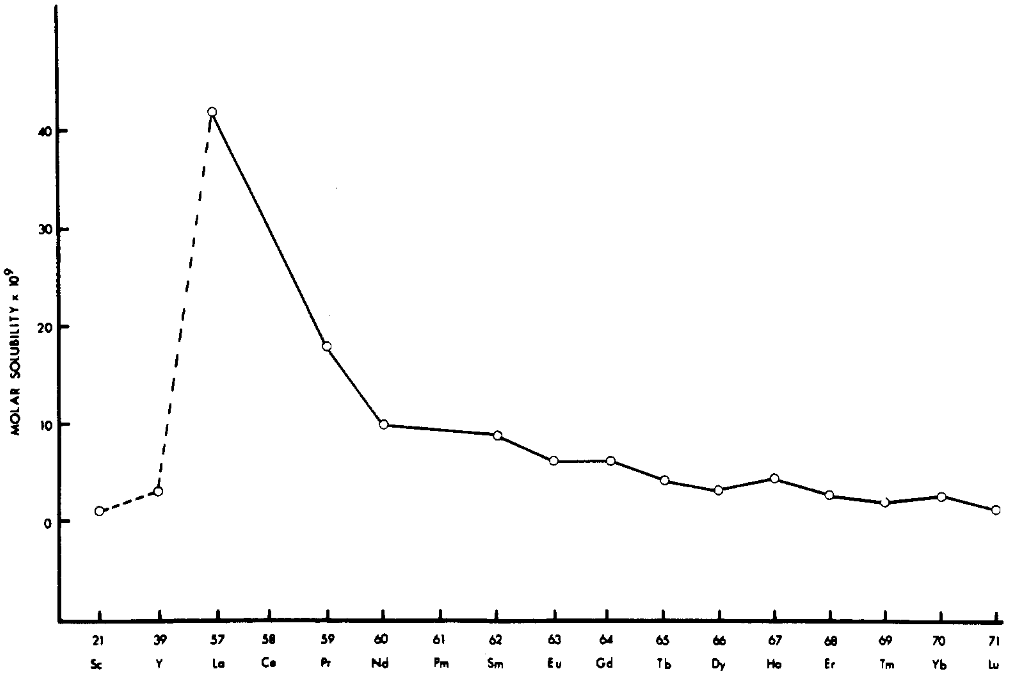

Figure 1. Molar solubility vs. rare-earth atomic number.

can be present in solution, H_2Ox^+, HOx, and Ox^-, the solutions to be analyzed were made very acid so that essentially only one form, the H_2Ox^+, was present. Unknown solutions were adjusted to ca. pH 1.2 and compared to standard solutions by using a wavelength of 367.5 nm.

The rare-earth cation spectrophotometric analyses were made with a Cary 14 spectrophotometer. An unknown solution was placed in a 10-cm cell and compared to standards at the appropriate wavelength (*3*).

The spectrophotometric titration was performed as follows. The unknown saturated solution (5 mL) was pipetted into a 50-mL beaker. Deionized water (25 mL), 5 mL of 1 M ammonium acetate, and two drops of xylenol orange were added, and the pH was adjusted to between 5.5 and 5.7 by using ammonium hydroxide or acetic acid as needed. The resulting solution was then placed in a titration cell of a Welch Chem Anal spectrophotometer with the wavelength set at 630 nm. A 10-mL buret was used to add increments of a 0.0100 M EDTA standard solution to the titration cell. The solution was stirred, and a transmittance reading recorded after each increment added. A plot of the data was used to determine the end point. The results obtained from these analyses are given in Table I.

Derivation of the Solubility-Product Equation. The equilibrium between solid rare-earth 8-quinolinate and the dissolved ions is

$$LnOx_3 = Ln^{3+} + 3Ox^-$$

(Ln = any rare earth and HOx = 8-quinolinol). The solubility product expression for this equilibrium is

$$[Ln^{3+}][Ox^-]^3 = K_{sp} \quad (1)$$

There is only one mathematically significant form of the rare earth present in the solutions used in this study and that is Ln^{3+}. Other forms such as $Ln(OH)^{2+}$, $Ln(OH)_2{}^+$, $LnOx^{2+}$, and $LnOx_2{}^+$ are not present in mathematically significant quantities. However, the 8-quinolinol can be present in three distinct forms: H_2Ox^+, HOx, and Ox^-. In order to calculate the solubility product directly, one must use the concentration of Ox^-. Unfortunately this cannot be determined directly because of the extremely low concentration that is present in the saturated solutions. Nevertheless, the total 8-quinolinol concentration can be determined. This necessitates the use of the two weak-acid dissociation constants for 8-quinolinol in any calculation (*4*):

$$[H^+][HOx]/[H_2Ox^+] = K_1 = 1.23 \times 10^{-5} \quad (2)$$

$$[H^+][Ox^-]/[HOx] = K_2 = 1.55 \times 10^{-10} \quad (3)$$

From the stoichiometry of the rare-earth 8-quinolinate

$$3[Ln^{3+}] = [HOx]_{total} = [H_2Ox^+] + [HOx] + [Ox^-] \quad (4)$$

Both $[H_2Ox^+]$ and [HOx] can be expressed in terms of $[Ox^-]$ by using the dissociation equations.

$$3[Ln^{3+}] = [H^+]^2[Ox^-]/(K_1K_2) + [H^+][Ox^-]/K_2 + [Ox^-] \quad (5)$$

Equation 5 can be solved for $[Ox^-]$ and substituted into eq 1.

$$K_{sp} = [Ln^{3+}]\left\{\frac{3[Ln^{3+}]}{[H^+]^2/(K_1K_2) + [H^+]/K_2 + 1}\right\}^3 \quad (6)$$

$$K_{sp} = 27[Ln^{3+}]^4(K_1K_2)^3/([H^+]^2 + [H^+]K_1 + K_1K_2)^3 \quad (7)$$

The activity-product form of eq 7 is

$$K_{AP} = 27[Ln^{3+}]^4(f_{Ln^{3+}})^4(K_1K_2)^3/\{(a_{H^+})^2 + a_{H^+}K_1 + K_1K_2\}^3 \quad (8)$$

The ionic strength was calculated from the known perchlorate-ion concentration and the determined concentration of rare earth and total 8-quinolinol. Other ionic concentrations were not mathematically significant. Using the extended Debye–Huckel equation (*5*), we calculated the activity coefficients for the rare-earth cations.

Discussion

The mathematical operations of the activity-product equation, i.e., the activity of the hydrogen ion to the sixth power, the rare-earth concentration to the fourth power, etc., magnify the experimental errors. This means that only approximately one-figure accuracy was reasonable in the final solubility-product value.

Table II. pK_{sp} of the Rare-Earth 8-Quinolinolates

rare earth	pK_{sp}	rare earth	pK_{sp}
Sc	34.52 ± 0.11	Tb	32.09 ± 0.23
Y	32.64 ± 0.18	Dy	32.38 ± 0.40
La	28.06 ± 0.09	Ho	31.89 ± 0.32
Pr	29.59 ± 0.45	Er	32.50 ± 0.36
Nd	30.50 ± 0.62	Tm	33.03 ± 0.85
Sm	30.80 ± 0.65	Yb	32.60 ± 1.12
Eu	31.39 ± 0.33	Lu	33.46 ± 0.60
Gd	31.38 ± 0.45		

The fact that the solubility of the rare-earth 8-quinolinates is so low, $\sim 10^{-9}$ M, means that saturated solutions of only the pure rare-earth 8-quinolinate and pure water are approaching infinite dilution. This means that the activity product and the solubility product are essentially the same value. These values are given in Table II.

The molar solubilities were calculated from the solubility products and are given in Figure 1. This curve is characteristic of other rare-earth solubility curves given in the chemical literature. A "gadolinium break" is present, and the yttrium solubility coincides with the heavy-rare-earth solubility. Both features are typical of similar rare-earth curves.

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Diffusion Coefficients for the Liquid System Acetone–Cyclohexane at 298.15 K

Aleksandar Ž. Tasić,* Bojan D. Djordjević, Slobodan P. Šerbanović, and Dušan K. Grozdanić

Faculty of Technology and Metallurgy, University of Beograd, 11000 Beograd, Karnegieva 4, Yugoslavia

The diaphragm cell technique has been used to measure mutual diffusion coefficients for the system acetone–cyclohexane at 298.15 K over the complete composition range. The obtained diffusivities have been compared with the results predicted by the correlations of Sanchez and Clifton, Rathbun and Babb, and Haluska and Colver. The corresponding absolute mean deviations are computed as 1.32%, 3.77%, and 28.33%.

Introduction

Liquid-phase diffusion coefficients are important data from the fundamental as well as the practical point of view. During a mass-transfer study, the composition dependence of the diffusion coefficients is essential. This information is particularly needed for a proper design and rational operation of the separation process equipment.

Diffusion coefficients can be obtained either from experimental measurements or from the existing theoretical or empirical prediction correlations. A number of these models, applicable to nearly ideal and nonassociating systems, have been proposed in the literature (*2*, *4*, *5*, *9*, *14*, *29*). Correlations, intended to be applied to the nonideal systems and to the systems containing associated constituents, are scarce (*8*, *20*, *23*).

Since the predictive abilities of some models, cited above, are far from satisfactory, and since the others have to be more fully tested, a necessity for further experimental measurements exists. Furthermore, permanent experimental studies represent an important help in developing new theories for better describing the diffusion mechanism.

Table I. Densities and Refractive Indexes of Purified Compounds at 298.15 K

	density, g cm^{-3}		refractive index	
compd	exptl	lit.	exptl	lit.
acetone	0.785 12	0.785 01 (*28*) 0.785 07 0.785 08	1.3556	1.355 99 (*28*) 1.356 09
cyclohexane	0.773 88	0.773 87 (*1*)	1.4231	1.423 54 (*1*)

The present article reports the experimentally obtained diffusion coefficients for the binary system acetone–cyclohexane at 298.15 K through the entire range of composition. The obtained data have been compared with the values predicted by the correlations of Haluska and Colver (*8*), Rathbun and Babb (*20*), and Sanchez and Clifton (*23*). These models have been selected according to the existing information on the behavior of the investigated binary system (*3*, *17*, *19*).

Experimental Section

Chemicals. Analytical-grade acetone supplied by Merck and "RP" cyclohexane purchased from Carlo Erba, used in this work, have been further purified as described previously (*19*). Reagent-grade potassium chloride (Merck), purified as proposed by Kruis (*13*), and double-distilled water have been used to determine the diaphragm cell constant and the volumes of the cell compartments. All solutions have been prepared by weight, using a Mettler balance type H-20 and a mixing cell designed specially to minimize evaporation during weighing. Some physical properties of the purified chemicals are compared with selected published values in Table I.

Analysis. The concentration differences of the potassium chloride between the samples have been determined by a Carl Zeiss interferometer type LI 3 with a resolution of 2 × 10^{-6} R.I. units.

Composition of the acetone–cyclohexane solutions, used in the diffusion experiments, have been obtained from density measurements by means of an oscillator-type densimeter (DMA 02C, Anton Paar) (*25*). The density-composition curve for this system at 298.15 K shows a minimum at ~0.37 mole fraction of acetone. Hence, in the range 0.25–0.55 mole fraction of acetone the composition has been obtained from refractive-index measurements at 298.15 K, using a Carl Zeiss Abbe

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