particular mole fraction nor even well-defined; in fact it disappears at higher temperatures where the water structure is already partially destroyed.

It is interesting to note the different trend of the diffusion and viscosity activation energies. Both have a maximum at a DMF mole fraction ca. 0.2, which corresponds approximately to the composition range where a wider DMF–H_2O clusterlike structure can grow, according to model b.

At high DMF mole fraction, the diffusion activation energy exhibits also a minimum, which is absent in the viscosity activation energy trend.

Such a difference can be related to the different mechanism used in molecule and momentum transport.

In the range of low DMF concentrations the diffusion process corresponds to an actual motion of DMF molecules and a simple rearrangement of water molecules.

However, the DMF molecule's motion requires the breaking and rebuilding of the water hydration shell around each $-CH_3$ group and that of H_2O–DMF hydrogen bonds.

It is reasonable to assume that the barrier to this process increases with increasing DMF concentration.

On the other hand, in the DMF-rich composition range, diffusion corresponds to the motion of H_2O molecules and a rearragement of DMF around them.

Such a motion can be achieved by the simple rotation of a DMF–H_2O couple inside the hole containing them without any extensive participation of the surrounding solvent structure (*24*).

For this reason increasing water concentration promotes a decreasing of diffusion activation energy.

The momentum transport connected with the viscous flow implies a contribution of the bulk of solution so only the maximum is observed, connected with the building of DMF–H_2O extended structures.

Finally we note that unfortunately activity coefficient data are missing and it is impossible to use the Ogston formula (*25*) for the calculation of mobilities.

Registry No. DMF, 68-12-2.

Literature Cited

(1) Guarino, G.; Ortona, O.; Sartorio, R.; Vitagliano, V. *J. Chem. Eng. Data* **1985**, *30*, 366–368.
(2) Kesting, R. E. In "Synthetic Polymeric Membranes"; McGraw Hill: New York, 1971.
(3) Loeb, S.; Sourirajan, S. *Adv. Chem. Ser.* **1962**, *38*, 117–132.
(4) Strathmann, H.; Kock, K. *Desalination* **1977**, *21*, 241–255.
(5) Koenhen, D. N.; Mulder, M. H.; Smolders, C. A. *J. Appl. Polym. Sci.* **1977**, *21*, 199–215.
(6) Sourirajan, S.; Kunst, B. In "Synthetic Membranes"; Sourirajan, S., Ed.; Natl. Res. Council., Canada: Ottawa, 1977; p 129.
(7) Hertz, H. G.; Leiter, H. *Z. Phys. Chem.* (*Wiesbaden*) **1982**, *133*, 45–67.
(8) Weissberger, A. In "Physical Methods of Chemistry"; Wiley: New York, 1972.
(9) International Critical Tables, Vol. 7, p 13.
(10) Assarson, P.; Eirich, F. R. *J. Phys. Chem.* **1968**, *72*, 2710–2719.
(11) Symons, M. C. R.; Harvey, J. M.; Jackson, S. E. *J. Chem. Soc., Faraday Trans. 1* **1980**, *76*, 256–265.
(12) Oncescu, T.; Jurconi, E. *Rev. Roum. Chim.* **1971**, *16*, 1033–1038.
(13) de Visser, C.; Perron, G.; Desnoyers, J. E.; Heuvelsland, W. J. M.; Somsen, G. *J. Chem. Eng. Data* **1977**, *22*, 74–79.
(14) Saphon, S.; Bittrich, H. J. *Z. Phys. Chem.* **1971**, Bd. 252, H.1/2.
(15) de Visser, C.; Somsen, G. *Z. Phys. Chem.* (*Wiesbaden*) **1974**, *92*, 159–162.
(16) Dawber, J. G. *J. Chem. Soc., Faraday Trans. 1* **1982**, *78*, 1127–1130.
(17) Assarson, P.; Chen, N. Y.; Eirich, F. R. *Chem. Abstr.* **1975**, *82*, 176109.
(18) Sasaki, Y. et al. *Chem. Abstr.* **1983**, *98*, 153533.
(19) Assarson, P. et al. *Chem. Abstr.* **1969**, *70*, 14825.
(20) Murthy, N.; Manohara, et al. *Chem. Abstr.* **1983**, *99*, 129139.
(21) Rohdewald, P.; Moldner, M. *J. Phys. Chem.* **1973**, *77*, 373–377.
(22) Singh, D.; Bahadur, Lal; Ramanamurti, M. V. *J. Solution Chem.* **1977**, *6*, 703–715.
(23) Stockausen, N.; Utzel, H.; Seitz, E. *Z. Phys. Chem.* (*Wiesbaden*) **1982**, *133*, 569–577.
(24) Hirtschfelder, J. O.; Curtiss, C. F.; Bird, R. B. In "Molecular Theory of Gases and Liquids"; Wiley: New York, 1954; pp 624–629.
(25) Ogston, A. G. *J. Chem. Soc., Faraday Trans. 1* **1954**, *50*, 1303–1311.

Received for review December 26, 1984. Accepted July 5, 1985. This research was supported by the Italian C.N.R.: Progetti finalizzati—Chimica Fine e Secondaria.

Solubility Products of the Rare-Earth Carbonates

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The solubility and the solubility products of 15 rare-earth carbonates in aqueous solution have been determined at 25 ± 1 °C. The most soluble are lanthanum carbonate (pK = 29.91) and erbium carbonate (pK = 28.25) and the least soluble is scandium carbonate (pK = 35.77). Some of the rare-earth carbonates were prepared by precipitation from homogeneous solution with trichloroacetic acid. Saturated solutions were analyzed for pH and the concentrations of rare-earth cation. Activity products were calculated from the experimental data. The solubility of the rare-earth carbonates is so low that the solubility product and activity product are essentially the same value. A thorough search of chemical literature showed only limited information on the solubility of rare-earth compounds in general, and nothing on the solubility of the rare-earth carbonates. Solubility information is essential for general use by scientists. Furthermore, the difference in the solubilities of rare-earth carbonates may provide suitable separation procedures for some lanthanides.

Experimental Section

Preparation of Rare-Earth Carbonates. The rare-earth carbonates can be prepared in major quantities by precipitation from homogeneous solutions with trichloroacetic acid. Decomposition of the rare-earth trichloroacetates in a warm homogeneous solution yields pure crystalline rare-earth carbonates (*1*). Approximately 10 g of rare-earth oxide was dissolved in a slight excess of trichloroacetic acid. The solution was then heated to 90 °C, causing the decomposition of the trichloroacetates. A slight excess of trichloroacetic acid was originally required to dissolve the rare-earth oxide, and the carbonate would not precipitate until the excess acid had been decomposed. Heating was continued for nearly 7 h following the initial formation of the carbonate precipitate. The resulting crystals were washed 10–20 times with deionized water in order to remove any soluble impurities or colloidal material.

Saturated Solutions. The rare-earth carbonates are very insoluble in water. The pure saturated solutions of rare-earth carbonates would contain a rare-earth cation concentration that is on the order of 10^{-7}–10^{-8} M. In order to bring enough

0021-9568/86/1731-0040$01.50/0

rare-earth cations into solution for accurate analysis, dilute $HClO_4$ was used to partially dissolve the rare-earth carbonates.

There exists an equilibrium between the carbonate ion, CO_3^{2-}, hydrogen carbonate, HCO_3^-, carbonic acid, the partial pressure of carbon dioxide above the solution, and dissolved or hydrated CO_2. In this study Erlenmeyer flasks with screw caps were used to keep the carbon dioxide from escaping during the saturation period. Standard perchloric acid (1.0×10^{-2} M, 250 mL) was added to a 250-mL Erlenmeyer flask with a screw cap, along with enough rare-earth carbonate (usually ROC/RJC and Apache reagent grade, 99.9% pure) to provide a saturated solution. The flasks were filled up to the neck so that very little space was left above the solution. The caps were secured tightly and the flasks were shaken at frequent intervals for 3 months at 25 ± 1 °C. Preliminary studies illustrated that about 1 month produced equilibrium in the saturated solution. Some rare-earth carbonates might take longer to reach equilibrium, so that the 3-month period was taken to assure reaching equilibrium.

Analysis. Analytical procedures used for the determination of the solubility of some insoluble rare-earth compounds are reported by various workers (*2*). Four different measurements were made on the saturated solutions of the rare-earth carbonates: the pH, complexometric titration of rare-earth cations (Sc, Y, La, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, and Lu), photometric titration of some rare-earth cations (Sc, Y, La, Sm, Dy, Tb, and Yb), and spectrophotometric analysis of the others (Nd, Ho, Sm, Er, and Pr).

The pH measurements were made with a Corning Model 4500 digital pH meter. Analytical results were reproducible to two figures.

Concentration of all the rare-earth cations were determined directly by EDTA titration using xylenol orange as an indicator. The unknown saturated solution (10 mL) was pipetted into a 100-mL beaker. Deionized water (20 mL), 10 mL of 1 M ammonium acetate, and two drops of xylenol orange were added. The pH of this solution was adjusted to 5.5 during the titration. This solution was titrated with standard EDTA solution (0.0100 M) to the end point. The numerical results are reproducible to two-figure accuracy and are given in Table I.

The photometric titration was performed as follows. The unknown saturated solution (10 mL) was pipetted into a 100-mL beaker, 20 mL of deionized water, 10 mL of 1 M ammonium acetate, and two drops of xylenol orange were added. The pH of this solution was then adjusted to 5.5 by using ammonium hydroxide or acetic acid as needed. The standard EDTA 0.0100 M was added from a buret until the purple color began to fade. A small portion of this solution was then placed in a cuvette of a Welch Chem Anal spectrophotometer with wavelength set at 630 nm. Transmittance of this solution was then measured. The solution in the cuvette was quantitatively transferred back into the unknown solution, and 0.2-mL aliquots of EDTA were added. (The transmittance was read after each addition until three or four beyond the end point). A plot of transmittance vs. the volume of the added EDTA was used to determine the end point.

The rare-earth cation spectrophotometric analyses were made with a Cary 219 spectrophotometer. A cylindrical cell, 10-cm long, was used to hold the unknown sample. Immediately following the analysis of the unknown saturated solution, a known standard solution containing rare-earth perchlorate was then analyzed at the same control settings. The concentration of rare-earth cations of the unknown sample was determined by comparison with a standard at the appropriate wavelength (*3*).

Derivation of the Solubility Product Equation. The equilibrium between solid $Ln_2(CO_3)_3$ and the dissolved ion is

$$Ln_2(CO_3)_3(s) = 2Ln^{3+}(aq) + 3CO_3^{2-}(aq) \qquad (1)$$

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

$$K_{sp} = [Ln^{3+}]^2[CO_3^{2-}]^3 \qquad (2)$$

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

rare earth	rare earth ion concn × 10^3, M	pH	rare earth	rare earth ion concn × 10^3, M	pH
Sc	4.55	4.70	Dy	3.56	5.04
	4.62	4.68		3.50	5.00
	4.80	4.61		3.46	5.06
Y	4.25	5.31	Ho	3.41	5.12
	4.25	5.42		3.42	5.06
	4.25	5.49		3.40	5.11
La	3.65	5.74		3.15	5.63
	3.68	5.73		3.15	5.43
	3.70	5.74	Er	2.55	5.90
	3.65	5.72		2.50	5.80
Pr	3.45	5.21		2.50	5.65
	3.42	5.19		2.50	6.08
	3.42	5.10		2.93	6.12
Nd	3.50	5.10		2.88	6.12
	3.44	4.94		3.18	6.18
	3.50	5.00		3.24	6.09
Sm	2.91	4.95		2.93	6.15
	2.64	5.17		2.86	6.05
	2.94	5.22	Tm	3.52	5.43
Eu	3.42	4.82		3.50	5.50
	3.48	4.85		3.42	5.41
	3.45	4.90	Yb	3.58	5.40
Gd	3.18	4.81		3.58	5.30
	3.19	4.79		3.37	5.59
	3.22	4.81	Lu	3.65	5.38
Tb	3.34	4.82		3.70	5.32
	3.40	4.89			
	3.36	4.80			
	3.36	5.05			

[a] Starting $HClO_4$ concentration 1.00×10^{-2} M.

In the saturated solution there is only one mathematically significant form of rare-earth ion and that is Ln^{3+}. Calculations indicated that other possible species such as $Ln(HCO_3)^{2+}$, $Ln(CO_3)^+$, and $Ln(OH)_2^+$ are not present in significant quantities at the pH condition found in the saturated solutions. In the equilibrated solution containing carbonate, the H_2CO_3, HCO_3^-, and CO_3^{2-} are present in different concentrations. H_2CO_3 is the only significant form in saturated solution, and its concentration can be calculated from the pH of the solution. In order to calculate the solubility product, it is essential to use the concentration of CO_3^{2-}. The concentration of CO_3^{2-} cannot be analytically determined, and therefore it cannot be used directly in the K_{sp} expression. The concentration of carbonate can be determined by using two weak-acid dissociation constants.

The two dissociation constants for carbonic acid involve the following equilibria, provided that the system under study is closed to the atmosphere:

$$H_2CO_3 \overset{K}{\rightleftharpoons} H_2O + CO_2(aq) \qquad (3)$$

$$H_2CO_3^* \overset{K_1}{\rightleftharpoons} H^+ + HCO_3^- \qquad (4)$$

$$H_2CO_3 \overset{K_{H_2CO_3}}{\rightleftharpoons} H^+ + HCO_3^- \qquad (5)$$

$$HCO_3^- \overset{K_2}{\rightleftharpoons} H^+ + CO_3^{2-} \qquad (6)$$

In the carbonate solution the analytical distinction between CO_2 and carbonic acid is difficult. The following equation describes the total concentration of dissolved CO_2 and carbonic acid (*4*).

$$[H_2CO_3^*] = [CO_2(aq)] + [H_2CO_3] \qquad (7)$$

where $H_2CO_3{}^*$ is defined as composite carbonic acid for all dissolved CO_2, both hydrated and H_2CO_3. The five solute components of the carbonate system can be described by four dissociation constants, K, K_1, $K_{H_2CO_3}$, and K_2. The true carbonic acid (*5*) is a much stronger acid ($pK_{H_2CO_3} = 3.5$) than the composite $H_2CO_3{}^*$ ($pK = 6.3$). These two acidity constants are interrelated (see dissociation equlibria K, K_1, and $K_{H_2CO_3}$).

$$K_1 = \frac{[H^+][HCO_3^-]}{[H_2CO_3] + [CO_2(aq)]} = \frac{K_{H_2CO_3}}{1 + K} \qquad (8)$$

The equilibrium constant, K, presents the hydration equilibrium of CO_2, and has a value of 400-670 at 20-25 °C (*6*). Since $K \gg 1$ then eq 7 can be simplified to

$$K_1 = K_{H_2CO_3}/K \qquad (9)$$

The dissociation constants of carbonic acid were selected as an average of all the reported values of 25 °C with an ionic strength approaching zero (*7*). Accordingly

$$K_1 = [H^+][HCO3^-]/[H_2CO_3{}^*] = 4.16 \times 10^{-7} \qquad (10)$$

$$K_2 = [H^+][CO_3^{2-}]/[HCO_3^-] = 4.84 \times 10^{-11} \qquad (11)$$

From the stoichiometry of the rare-earth carbonate

$$\tfrac{3}{2}[Ln^{3+}] = [C_{CO_2}]_{total} = [H_2CO_3{}^*] + [HCO_3^-] + [CO_3^{2-}] \qquad (12)$$

Both $[HCO_3^-]$ and $[H_2CO_3{}^*]$ can be expressed in terms of $[CO_3^{2-}]$ by using the dissociation equations.

$$\tfrac{3}{2}[Ln^{3+}] = ([CO_3^{2-}]/K_1K_2)([H^+]^2 + K_1[H^+] + K_1K_2) \qquad (13)$$

Equation 12 can be solved for $[CO_3^{2-}]$ and substituted into eq 1.

$$K_{sp} = [Ln^{3+}]^2\left(\frac{\tfrac{3}{2}[Ln^{3+}]K_1K_2}{[H^+]^2 + K_1[H^+] + K_1K_2}\right)^3 \qquad (14)$$

The activity product form of eq 13 is

$$K_{ap} = \frac{\tfrac{27}{8}[Ln^{3+}]^5[f_{Ln^{3+}}]^5[K_1K_2]^3}{([a_{H^+}]^2 + [a_{H^+}]K_1 + K_1K_2)^3} \qquad (15)$$

From the solubility data given in Table I, the activity products were calculated. The ionic strength was measured by using the known perchlorate ion concentration and the determined hydrogen ion and rare-earth cation concentrations. The activity coefficient for a rare-earth cation can be calculated from the extended Debye–Hückel expression (*8*). The activity products were then calculated.

Discussion

The quantitative analysis of the rare-earth cation and hydrogen ion can best be represented in two figures. But the final results are given in one figure. The limiting factor which reduces the overall accuracy is due to several mathematical manipulations, i.e., rare-earth concentration to the fifth power and activity of hydrogen ion to the sixth power, etc. Clearly, any small error in these numbers would be appreciably magnified by the mathematical operation.

The molar solubilities were calculated from the solubility products and are given in Figure 1. In this figure two distinct peaks are obvious. The first peak represents a characteristic solubility behavior of the light rare-earth cations. The second peak, at erbium, shows an anomalous solubility behavior. A "gadolinium break", which represents the half-filled 4f shell, is also present, and the yttrium solubility coincides with the heavy rare-earth solubility.

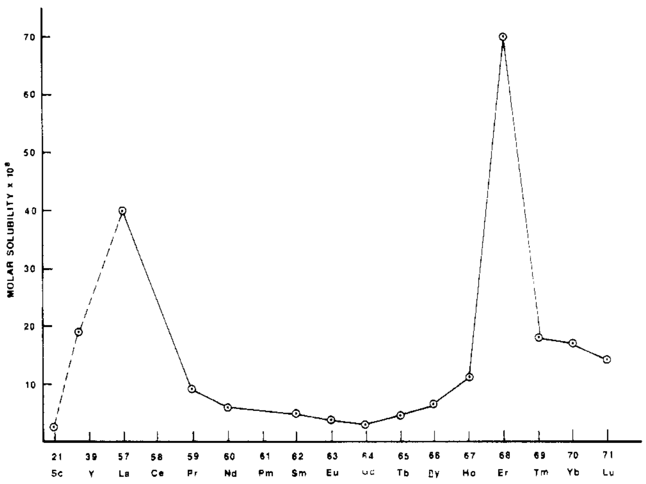

Figure 1. Solubilities of the rare-earth carbonates.

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

rare earth	pK_{sp}	rare earth	pK_{sp}
Sc	35.77 ± 0.25	Gd	35.45 ± 0.05
Y	31.52 ± 0.52	Tb	34.86 ± 0.65
La	29.91 ± 0.05	Dy	33.97 ± 0.19
Pr	33.19 ± 0.26	Ho	32.8 ± 1.2
Nd	34.10 ± 0.48	Er	28.25 ± 0.32
Sm	34.41 ± 0.53	Tm	31.58 ± 0.28
Eu	35.03 ± 0.25	Yb	31.67 ± 0.78
		Lu	32.16 ± 0.24

The saturated solution of lanthanide carbonates in pure water is approaching infinite dilution, about 10^{-7}–10^{-8} M. This means that the activity product and solubility product are essentially the same. These values are given in Table II.

The high solubility of erbium carbonate is unexpected. Normally the solubility of the rare earth compounds forms a fairly smooth relationship. These values were redetermined and the anomaly appears to be real. X-ray analysis of the erbium carbonate and holmium carbonate showed their crystal structures are very similar. So a modification in crystal structure does not explain the difference.

Even though the solubility differences between the erbium carbonate and holmium carbonate is not explained, the difference is large enough that it may provide a good separation of these two elements, as well as a separation between erbium and thulium.

Acknowledgment

We thank Dr. Paul D. Robinson, Southern Illinois University at Carbondale, for the X-ray analysis.

Literature Cited

(1) Gordon, L.; Salutsky, M. L.; Willard, H. H. "Precipitation From Homogeneous Solution"; Wiley: New York, 1959; pp 104, 149.
(2) Firsching, F. H.; Cuca, R. C. *J. Chem. Eng. Data* **1981**, *26*, 116.
(3) Stewart, D. C.; Kato, D. *Anal. Chem.* **1958**, *30*, 164.
(4) Stumm, W.; Morgan, J. J. "Aquatic Chemistry"; Wiley: New York, 1970; pp 118–122.
(5) Wissbrun, K. F.; French, D. M.; Patterson, A. *J. Phys. Chem.* **1954**, *58*, 693.
(6) Kern, D. M. *J. Chem. Educ.* **1960**, *37*, 14.
(7) Sillen, L. G.; Martell, A. E. "Stability Constants"; The Chemistry Society: Burlington House, London, 1964; p 133.
(8) Laitinen, H. "Chemical Analysis"; McGraw-Hill: New York, 1960; pp 19, 26.

Received for review January 22, 1985. Revised manuscript received June 16, 1985. Accepted July 30, 1985.