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# Carbonate and Bicarbonate Complexes of Neodymium and Europium

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The distribution of Eu(III) and Nd(III) between Dowex I-X8 and solutions of $KHCO_3$ and $K_2CO_3$ was studied as a function of salt concentration in order to elucidate their complexing behavior in the presence of these inorganic ligands. Equilibration and chromatographic techniques were employed using radioactive isotopes of Eu and Nd to facilitate the investigation. The distribution of tracer $^{35}S$ in the form of $^{35}SO_4^{2-}$ between Dowex I-X8 and solutions of $KHCO_3$ and $K_2CO_3$ was studied to determine the effect of imbibed electrolyte and changing internal and external activity coefficients. Analysis of the data indicates that imbibement and activity coefficient corrections are negligible over the concentration range that is covered, thus giving an experimental basis for a portion of the data. Distribution coefficients were measured over the concentration range of 0.0010 to 1.00 *m* $K_2CO_3$ and $KHCO_3$. Over this region a logarithmic plot of the distribution coefficient *vs.* the logarithm of salt molality ($KHCO_3$ or $K_2CO_3$) resulted in curves which were analyzed for the complex species that exist in solution and their stepwise formation constants. Computer methods were used to facilitate these calculations. Analysis of the $KHCO_3$ systems indicates the presence of the di-, tetra-, penta-, and heptabicarbonato complexes. A similar analysis of the $K_2CO_3$ systems indicates the presence of the dicarbonato, tricarbonato, and tetracarbonatohydroxo complexes. Inherent weaknesses in the mode of analysis are detailed so that the possibility of error in the interpretation of the data that is presented is understood.

## Introduction

Earlier work by the authors with the rare earths Pr, Nd, Pm, Sm, and Eu[3] has disclosed the existence of stable carbonate complexes of the form $[(CO_3)_4]^{5-}$ in the concentration range 0.3 to 3.0 *M* $K_2CO_3$. This result is consistent with the analysis of a spectrophotometric study of Nd by Poluektov and Konenko[4] in which a tetracarbonate complex was found at 1.0 to 1.5 *M* $K_2CO_3$.

In our earlier study the great stability of this complex species precluded observation of the effect of stepwise addition of carbonate to the metal ion and prevented any thermodynamic analysis of the systems that were investigated. An investigation of the complexing behavior of the rare earths Nd and Eu at lower concentrations of $K_2CO_3$ was, therefore, initiated to facilitate such an analysis. The complexing behavior of these rare earths by bicarbonate ion was also studied over the same concentration range for comparison.

The choice of technique for the study of lanthanon carbonates and bicarbonates is severely limited by their low solubility. Radioactive isotopes of the rare earths at a concentration of $\sim 10^{-10}$ *M* were therefore used to facilitate study of these systems. The affinity of the metal ion for an anion-exchange resin under various experimental conditions was employed to measure the degree of complexing. The effect of electrolyte imbibement and variable solvent activity on activity coefficients in the internal and external phases was tested by studying the exchange of the stable anion, $^{35}SO_4^{2-}$, in trace concentration, as a function of $K_2CO_3$ and $KHCO_3$ concentration.[5] Elution chromatography[6] was used to measure *D*, the distribution of $SO_4^{2-}$ ion between the two phases, in the range $10^{-2}$ to 20. Batch equilibration techniques[7] were employed to measure the higher distribution values of the $Eu^{3+}$, $Nd^{3+}$, and $SO_4^{2-}$ ions.

## Experimental

**Materials.**—The resin Dowex I-X8 200–400 mesh (lot No. 20283) and 20–50 mesh (lot No. 20937), both in the chloride form, were purchased from the J. T. Baker Chemical Company.

Potassium carbonate and bicarbonate solutions were prepared from reagent grade materials.

The nuclides 16-year Eu-152–154, 11.6-day Nd-147, and 87.1-day S-35 were purchased from the Radio Isotopes Division of the Oak Ridge National Laboratories. Carrier free 2.6-year Na-22 was purchased from the Nuclear Science and Engineering Corporation.

**Preparation of Resin Column and Column Operation.**—The column construction, its preparation, and the evaluation of its several parameters (*e.g.*, length and void volume) as well as the method of elution have been described in an earlier report.[3]

**Equilibration Method.**—Prior to beginning equilibrations, the stability of all radioactive solutions was checked by counting aliquot portions over a period of 2–4 days. A disappearance of activity with time in the more dilute carbonate and bicarbonate solutions (less than 0.35 *M*) was noted in both glass and polyethylene vessels due to radiocolloid formation and absorption on the sides of the vessels. This difficulty was eliminated by the addition of nonactive samarium in trace amounts ($10^{-6}$ *M*). Absorption effects are minimized by rare earth dilution. Assay of the radioactivity of solutions containing carrier showed no observable change in activity with time.

Solutions of the appropriate concentration of complexant, with carrier, were then placed in polyethylene bottles. The volume of solution was determined by weighing the bottles before and after addition of solution, density data from the International Critical Tables permitting computation.

An aliquot of the radioactive isotope of the rare earth under investigation was then placed in the solution. After mixing, 2–4 ml. of the radioactive solution was transferred to nitrocellulose test tubes which were weighed empty and with the solution.

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[1] This is an essential portion of a thesis submitted to the Chemistry Department, State University of New York at Buffalo, in partial fulfillment of the requirements of a Doctor of Philosophy degree.

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[3] H. Sherry and J. A. Marinsky, *Inorg. Chem.*, **2**, 957 (1963).

[4] N. S. Poluektov and L. I. Konenko, *Zh. Neorgan. Khim.*, **6**, 1836 (1961).

[5] K. A. Kraus and F. Nelson, "Structure of Electrolyte Solutions," W. J. Hamer, Ed., John Wiley and Sons, Inc., New York, N. Y., 1959, p. 348.

[6] K. A. Kraus and G. E. Moore, *J. Am. Chem. Soc.*, **73**, 9 (1951).

[7] J. Schubert, *J. Phys. Colloid Chem.*, **52**, 340 (1948).

TABLE I

$Eu^{3+}$ DISTRIBUTION COEFFICIENTS AS A FUNCTION OF $K_2CO_3$ CONCENTRATION

| $m$ | $D$ | $m$ | $D$ | $m$ | $D$ |
|---|---|---|---|---|---|
| 1.030 | 2.56 | 0.150 | 703 | 0.0146 | 46,700 |
| 0.708 | 7.47 | 0.100 | 2,080 | 0.00972 | 80,800 |
| 0.708 | 8.85 | 0.100 | 1,860 | 0.00975 | 83,200 |
| 0.502 | 22.8 | 0.0682 | 4,150 | 0.00688 | 138,000 |
| 0.503 | 22.8 | 0.0671 | 4,300 | 0.00678 | 134,700 |
| 0.400 | 45.3 | 0.0486 | 8,020 | 0.00488 | 163,000 |
| 0.400 | 45.3 | 0.0487 | 7,830 | 0.00487 | 182,000 |
| 0.300 | 96.0 | 0.0293 | 18,100 | 0.00294 | 179,400 |
| 0.300 | 111.0 | 0.0293 | 15,000 | 0.00290 | 122,300 |
| 0.200 | 319 | 0.0195 | 37,700 | 0.001976 | 200,000 |
| 0.200 | 322 | 0.0195 | 36,000 | 0.001458 | 281,000 |
| 0.150 | 651 | 0.0146 | 56,300 | 0.001446 | 267,000 |
|  |  |  |  | 0.000975 | 265,000 |

These samples, when assayed, gave the initial radioactivity present in the equilibration vessel.

A portion of the resin (20–50 mesh to facilitate handling), which had been stored in water, was placed in a fritted glass tube and the excess water was removed by centrifugation. The quantity of resin used varied from 0.07 to 8 g. according to the estimated value of the distribution coefficients, large samples being necessary at low values of the distribution coefficients. Sample weights were obtained by weighing the fritted glass tubes before and after removal of the resin. The resin was transferred to the equilibration vessel and the vessel was agitated for 48 to 72 hr.

After attainment of equilibrium, 2–4-ml. samples of the equilibrated solution were removed and the radioactivity of this solution and that of the sample of pre-equilibrated solution were assayed using a standard 1.75 × 2 in. Tl-activated NaI crystal well counter. From these data the distribution coefficient was calculated.

When studying the distribution of $^{35}SO_4^{2-}$, which emits a weak $\beta$-particle (0.167 Mev.), it was necessary to use a different counting technique. A 0.025-ml. drop was placed on a metal planchet, evaporated to dryness, and counted under a Geiger-Mueller tube with a 1.4 mg./cm.$^2$ window. Reproducibility of drop size and geometry was checked by counting three drops from every solution.

**Experimental Errors.**—Measurement of the distribution coefficients by the chromatographic technique was made to within 3%. The greatest error was in the location of the drop number at which the peak appeared. This ranged from 30 to 60 drops and could be located within the limit of ±1 drop.

The low energy $\beta$-particle emitted by $^{35}S$ presented counting problems when measuring $^{35}SO_4^{2-}$ distribution coefficients by the equilibration technique. Reproducible assay of 0.025-ml. samples was shown to be practicable when a 0.025-ml. micropipet was used to deliver three 1-drop samples of each solution. Each 0.025-ml. drop when evaporated to dryness and counted usually agreed within ±10%.

Rare earth distribution coefficients measured by the equilibration technique were characterized by an experimental error which generally ranged from 5 to 10% over most of the concentration range investigated. In very dilute solution ($10^{-3}$ $m$) where $Eu^{3+}$–$CO_3^{2-}$ and $SO_4^{2-}$–$HCO_3^-$ distribution coefficients were on the order of $3 \times 10^5$ and $9 \times 10^5$, respectively, the error increased to as much as 25%. Uptake of tracer by the resin was so great in these dilute solutions that as little as 50 counts/min. above background were present in the solution after equilibration. This difficulty, however, was not encountered in the other systems studied.

In concentrated solution, where small values of the distribution were encountered, the amount of radioactive tracer present in the equilibrated solutions was practically the same as in the pre-equilibrated solutions. This necessitated calculating the distribution from a small difference between two large numbers, leading to a large experimental error.

TABLE II

Nd DISTRIBUTION COEFFICIENTS AS A FUNCTION OF $K_2CO_3$ CONCENTRATION

| $m$ | $D$ | $m$ | $D$ |
|---|---|---|---|
| 0.705 | 3.10 | 0.0300 | 5,480 |
| 0.503 | 7.62 | 0.0199 | 11,820 |
| 0.401 | 14.85 | 0.0149 | 17,370 |
| 0.300 | 33.4 | 0.0100 | 28,800 |
| 0.201 | 115.0 | 0.0701 | 39,500 |
| 0.1489 | 230 | 0.0499 | 53,500 |
| 0.100 | 596 | 0.0400 | 72,700 |
| 0.0700 | 1200 | 0.0299 | 68,500 |
| 0.0599 | 1708 | 0.0167 | 92,500 |
| 0.0500 | 2260 | 0.0147 | 97,800 |
| 0.0400 | 3430 | 0.000978 | 116,500 |

TABLE III

$Eu^{3+}$ DISTRIBUTION COEFFICIENTS AS A FUNCTION OF $KHCO_3$ CONCENTRATION

| $m$ | $D$ | $m$ | $D$ |
|---|---|---|---|
| 0.926 | 0.402 | 0.0300 | 12,560 |
| 0.703 | 1.181 | 0.0200 | 22,000 |
| 0.505 | 4.81 | 0.0151 | 21,500 |
| 0.402 | 10.52 | 0.0100 | 31,600 |
| 0.301 | 30.5 | 0.00700 | 35,500 |
| 0.199 | 133.4 | 0.00501 | 35,500 |
| 0.150 | 290 | 0.00401 | 30,400 |
| 0.100 | 938 | 0.00300 | 27,900 |
| 0.0798 | 1494 | 0.0020 | 29,000 |
| 0.0700 | 2120 | 0.00150 | 23,100 |
| 0.0500 | 5600 | 0.00100 | 20,300 |
| 0.0400 | 7170 | 0.000700 | 14,270 |

## Results

The distribution of Eu and Nd between resin and solution as a function of $K_2CO_3$ concentration was measured by the equilibration method over the concentration range of 1.03 to 0.0010 $m$. The results are presented in Tables I and II for $Eu^{3+}$ and $Nd^{3+}$, respectively.

The concentration range of $K_2CO_3$ that was employed was limited by the values of the distribution coefficients that were encountered. In dilute solution the distribution coefficients were of the order of $3 \times 10^5$, leaving little activity in solution to be measured. At high concentrations the distribution coefficients were so low that there was little difference in activity between equilibrated and pre-equilibrated solutions.

The distribution coefficients, measured in $KHCO_3$ by equilibration over the concentration range 1.03 to 0.00070 $m$, are presented in Tables III and IV for $Eu^{3+}$ and $Nd^{3+}$, respectively.

Distribution data for the $*SO_4^{2-}$–$CO_3^{2-}$ and $*SO_4^{2-}$–$HCO_3^-$ systems measured by equilibration and chromatographic techniques are listed in Table V.

A modification of the equation of Marcus and Coryell[8] has been employed to analyze the above data and is given below.

$$\log D = \log K_r + p_r F_m + \frac{m}{l} \log x - \log \sum_{n=0}^{n=N} \beta_n{}^* x^n \quad (1)$$

In this equation $K_r$ is proposed as a constant term which includes the thermodynamic constant $K$ for the ex-

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[8] Y. Marcus and C. D. Coryell, *Bull. Res. Council Israel*, **A8**, 1 (1959).

TABLE IV

$Nd^{3+}$ DISTRIBUTION COEFFICIENTS AS A FUNCTION OF $KHCO_3$ CONCENTRATION

| *m* | *D* | *m* | *D* |
|---|---|---|---|
| 1.03 | 0.463 | 0.0200 | 7,610 |
| 0.722 | 1.326 | 0.0151 | 9,120 |
| 0.509 | 3.86 | 0.0100 | 11,010 |
| 0.303 | 23.4 | 0.00700 | 11,640 |
| 0.201 | 78.1 | 0.00500 | 10,660 |
| 0.151 | 247 | 0.00400 | 11,810 |
| 0.1005 | 535 | 0.00300 | 11,800 |
| 0.0700 | 1380 | 0.00200 | 10,250 |
| 0.0500 | 2410 | 0.00149 | 8,080 |
| 0.0301 | 4790 | 0.00100 | 6,180 |

TABLE V

$^{35}SO_4^{2-}$ DISTRIBUTION COEFFICIENTS AS A FUNCTION OF $KHCO_3$ AND $K_2CO_3$ CONCENTRATION

| $*SO_4^{2-}$–$HCO_3^-$ | | | | $*SO_4^{2-}$–$CO_3^{2-}$ | |
|---|---|---|---|---|---|
| *m* | *D* | *m* | *D* | *m* | *D* |
| 1.02 | 0.801 | 0.221 | 16.2 | 0.101 | 43.6 |
| 0.910 | 0.880 | 0.101 | 80.3 | 0.0502 | 78.3 |
| 0.778 | 1.18 | 0.0502 | 325 | 0.0301 | 104 |
| 0.690 | 1.63 | 0.0300 | 781 | 0.0100 | 322 |
| 0.601 | 2.32 | 0.0100 | 8,900 | 0.00503 | 940 |
| 0.501 | 3.49 | 0.00500 | 20,500 | 0.00301 | 1330 |
| 0.402 | 5.62 | 0.00300 | 78,900 | 0.00200 | 2000 |
| 0.302 | 8.92 | 0.00200 | 190,600 | 0.00100 | 5000 |
| | | 0.00100 | 930,000 | | |

change reaction between the ligand and the principal complex in the resin, $\beta_n^*$ is an over-all association constant for the formation of the indicated complex, $x$ is the molality of the ligand, $n$ is the ligand number, $N$ is the maximum number of ligands coordinated to the metal ion, $m$ is the charge in the uncomplexed metal ion, $l$ is the charge of the ligand, and $p$ is the number of ligands in excess of $m/l$ in the principal complex MLq which is assumed to be in the resin phase. The function ${}_{\mathrm{r}}F_{\mathrm{m}}$ is a measure of the influence on $D$ of imbibement of electrolyte by the resin giving rise to a change in resin phase activity coefficients and the molality of the ligand in the exchanger.

In the case of the exchange of a stable anion in trace concentration eq. 1 reduces to

$$\log D = \log K_{\mathrm{r}} + m/l \log x + p_{\mathrm{r}}F_{\mathrm{m}} \qquad (2)$$

The slopes of the straight lines that are obtained from a log $D$ *vs.* $x$ plot of the $^{35}SO_4^{2-}$ data are −2 and −1 in bicarbonate and carbonate, respectively. This result indicates that negligible deviation of these systems from "ideal" behavior occurs, even though electrolyte imbibement and changing internal and external activity coefficients may not be negligible and $F_{\mathrm{m}} \approx 0$. By assuming that this result also applies to the rare earth systems, the working equation for analysis of the rare earth distribution data becomes

$$\log D = \log K_{\mathrm{r}} + \frac{m}{l} \log x - \log \sum_{n=0}^{n=N} \beta_n^* x^n \qquad (3a)$$

or

$$D = \frac{K_r x^{m/l}}{\sum\limits_{n=0}^{n=N} \beta_n^* x^n} \qquad (3b)$$

Differentiation of eq. 3a with respect to log $x$ yields

$$\frac{\mathrm{d} \log D}{\mathrm{d} \log x} = \frac{m}{l} - \frac{\sum\limits_{n=0}^{n=N} n\beta_n^* x^n}{\sum\limits_{n=0}^{n=N} \beta_n^* x^n} \qquad (4)$$

or

$$\frac{\mathrm{d} \log D}{\mathrm{d} \log x} = \frac{m}{l} - \bar{n} \qquad (5)$$

where $\bar{n}$, the average ligand number of all the complex ions in solution, is defined by Bjerrum[9] as

$$\bar{n} = \frac{\sum\limits_{n=0}^{n=N} n\beta_n^* x^n}{\sum\limits_{n=0}^{n=N} \beta_n^* x^n} \qquad (6)$$

Thus the slope at any point on a plot of log $D$ *vs.* log $x$ gives the average ligand number of the mixture of complexes which is present at that point, if the equation, as employed, is thermodynamically correct.

A slope analysis of the rare earth carbonate data, plotted in Fig. 1, shows that the maximum slopes obtained at high concentration are −3 for the europium and −2.9 for neodymium. (These graphs include data previously reported.[3]) This corresponds to an average ligand number of 4.5. It should be noted that the slope of 3.0 is constant from 0.300 to 3.00 *m* for europium and is interpreted as corresponding to a stable complex ion with a ligand number of 4.5.

A half-integral coordination number can be explained by assuming the presence of a hydroxo group in the complex at high concentrations which leads to a complex of the type $[M(OH)(CO_3)_4]^{6-}$. There is an appreciable quantity of hydroxide ion at high concentrations of $K_2CO_3$ (pH 11.5–12) to justify this estimate. The slopes at low concentrations indicate the presence of complexes of the type $[M(CO_3)_2]^-$.

By rearranging eq. 3b and setting the upper and lower limits of $n$ to 2 and 4.5, respectively, the following equation is obtained

$$x^{1.5}/D = \beta_2' x^2 + \beta_3' x^3 + \beta_4' x^4 + \beta_5' x^{4.5} \qquad (7)$$

where $\beta_n' = \beta_n^*/K_{\mathrm{r}}$. This equation corresponds to the occurrence of the following reactions over the concentration range studied.

$$[M(CO_3)_2]^- + CO_3^{2-} \xrightleftharpoons{k_3} [M(CO_3)_3]^{3-}$$

$$[M(CO_3)_3]^{3-} + CO_3^{2-} \xrightleftharpoons{k_4} [M(CO_3)_4]^{5-}$$

$$[M(CO_3)_4]^{5-} + OH^- \xrightleftharpoons{k_5} [M(OH)(CO_3)_4]^{6-}$$

A 4.5-power dependence of $x$ during the formation of the species $[M(CO_3)_4(OH)]^{6-}$ is reasonable since the hydroxide ion is proportional to the square root of the carbonate ion concentration above 0.01 *m* $K_2CO_3$.

Analysis of the data by the method of Sillén,[10] and by the method of least squares,[11,12] indicates that, for

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[9] J. Bjerrum, "Metal Ammine Formation in Aqueous Solution," P. Haase and Son, Copenhagen, 1941.

[10] L. G. Sillén, *Acta Chem. Scand.*, **10**, 186 (1956).

[11] L. G. Sillén, *ibid.*, **16**, 159 (1962).

[12] J. C. Sullivan, J. Rydberg, and W. F. Miller, *ibid.*, **13**, 2023 (1959).

TABLE VI

CONSTANTS FOR THE $Eu^{3+}$– AND $Nd^{3+}$–$CO_3^{2-}$ SYSTEMS

| | $Eu^{3+}$ | $Nd^{3+}$ |
|---|---|---|
| $\beta_2'$ | $6.65 \times 10^{-5} \pm 0.80$ | $2.42 \times 10^{-4} \pm 0.14$ |
| $\beta_3'$ | $5.84 \times 10^{-3} \pm 0.30$ | $1.90 \times 10^{-2} \pm 0.10$ |
| $\beta_{4.5}'$ | $0.328 \pm 0.01$ | $0.909 \pm 0.03$ |
| $\beta_3'/\beta_2'$ | 87.8 | 78.5 |
| $\beta_{4.5}'/\beta_3'$ | 56.2 | 47.8 |

TABLE VII

CONSTANTS FOR THE $Nd^{3+}$–$HCO_3^-$ SYSTEM

| | |
|---|---|
| $\beta_2'$ | $9.78 \times 10^{-8} \pm 0.7 \times 10^{-8}$ |
| $\beta_3'$ | $4.98 \times 10^{-5} \pm 0.25 \times 10^{-5}$ |
| $\beta_4'$ | $3.12 \times 10^{-3} \pm 0.1 \times 10^{-3}$ |
| $\beta_6'$ | $1.501 \pm 0.04$ |
| $\beta_3'/\beta_2'$ | 510 |
| $\beta_4'/\beta_3'$ | 62.7 |
| $\beta_6'/\beta_4'$ | 481 |

the Eu– and Nd–carbonate systems, the curve $D$ *vs.* $x$ is best described by the equation

$$x^{1.5}/D = \beta_2'x^2 + \beta_3'x^3 + \beta_{4.5}'x^{4.5} \tag{8}$$

presuming that the thermodynamic behavior of the system is appropriately handled. Curve fitting by means of eq. 7 leads to negative constants which are inadmissable.

The absence of the term $\beta_4'x^4$ indicates that the species $[M(CO_3)_4]^{5-}$ is not present over an appreciable concentration range and cannot be detected within the limits of experimental error. The reactions that can be detected are

$$[M(CO_3)_2]^- + CO_3^{2-} \rightleftharpoons k_3 \rightleftharpoons [M(CO_3)_3]^{3-}$$

$$[M(CO_3)_3]^{3-} + OH^- + CO_3^{2-} \rightleftharpoons k_4k_5 \rightleftharpoons [M(OH)(CO_3)_4]^{6-}$$

The constants in the equation, calculated by the method of least squares on a Burroughs Datation computer, are tabulated in Table VI. These constants are ratios of the over-all formation constant $\beta_n'$ to the exchange constant $K_r$. The more significant constants $k_3$ and $(k_4k_5)$, which are equilibrium constants for the reactions shown above, are obtained by taking the ratios $\beta_3'/\beta_2'$ and $\beta_{4.5}'/\beta_3'$, respectively.

Slope analysis and curve fitting by the method of least squares of the data for the Nd–$HCO_3$ system (Fig. 2) leads to the equation

$$\frac{x^3}{D} = \beta_2'x^2 + \beta_3'x^3 + \beta_4'x^4 + \beta_6'x^6 \tag{9}$$

This equation corresponds to the reactions

$$[M(HCO_3)_2]^+ + HCO_3^- \rightleftharpoons k_3 \rightleftharpoons [M(HCO_3)_3]$$

$$[M(HCO_3)_2] + HCO_3^- \rightleftharpoons k_4 \rightleftharpoons [M(HCO_3)_4]^-$$

$$[M(HCO_3)_4]^- + 2HCO_3^- \rightleftharpoons k_4k_5 \rightleftharpoons [M(HCO_3)_6]^{3-}$$

The data are not capable of resolving the species $[M(HCO_3)_5]^{2-}$, thereby accounting for the absence of a term $(\beta_5'x^5)$ in eq. 9. The constants for eq. 9 are listed in Table VII.

The plot of log $D$ *vs.* log $x$ for the Eu–$HCO_3$ system, Fig. 2, differs markedly from that for the Nd–$HCO_3$ system. The two curves are parallel at low concentrations of $KHCO_3$ (low $x$) and then the slope of the $Eu^{3+}$ curve becomes steeper until finally at high concentrations it crosses the curve for $Nd^{3+}$. The $Eu^{3+}$ curve is linear and has a slope of −4, which corresponds to an average ligand number, $\bar{n}$, of 7 (eq. 4). The slope at low concentrations approaches +1, which is indicative of an average ligand number of 2.

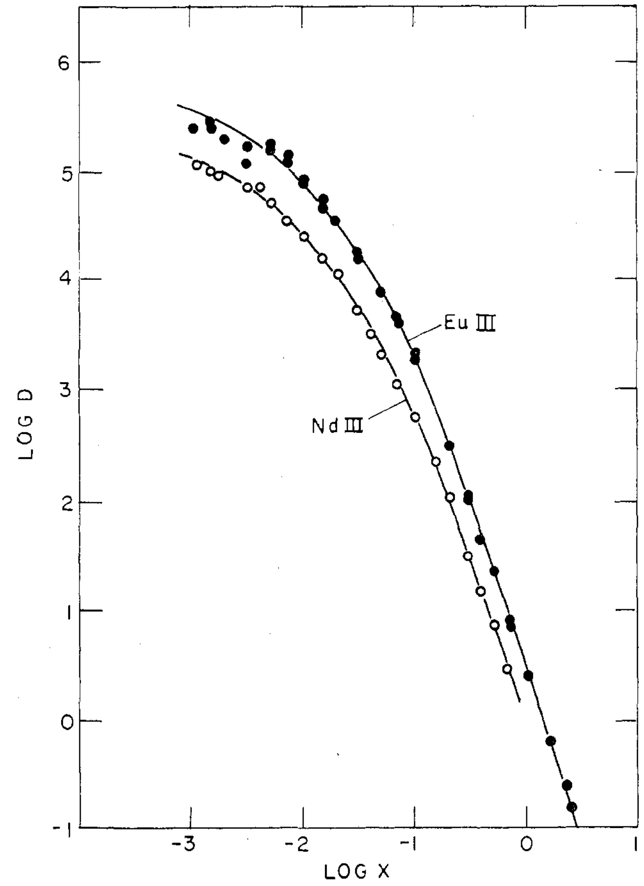

Fig. 1.—Distribution coefficients of Eu(III) and Nd(III) as a function of $K_2CO_3$ concentration.

TABLE VIII

CONSTANTS FOR THE $Eu^{3+}$–$HCO_3^-$ SYSTEM

| | |
|---|---|
| $\beta_2'$ | $5.71 \times 10^{-8} \pm 0.5 \times 10^{-8}$ |
| $\beta_4'$ | $2.01 \times 10^{-3} \pm 0.15 \times 10^{-3}$ |
| $\beta_5'$ | $3.47 \times 10^{-2} \pm 0.12 \times 10^{-2}$ |
| $\beta_7'$ | $3.51 \pm 0.20$ |
| $\beta_4'/\beta_2'$ | $3.52 \times 10^4$ |
| $\beta_5'/\beta_4'$ | 17.3 |
| $\beta_7'/\beta_5'$ | 101 |

Slope and least square analysis leads to the four-term equation

$$x/D = \beta_2'x^2 + \beta_4'x^4 + \beta_5'x^5 + \beta_7'x^7 \tag{10}$$

The calculated constants are listed in Table VIII.

## Discussion

Our attempt in this investigation to circumvent the difficulties inherent in the analysis of distribution data by proposing that the effect of $CO_3^{2-}$ and $HCO_3^-$ on the principal rare earth complex species in the resin phase, $[M(CO_3)_x]^{(3-2x)-}$ and $[M(HCO_3)_x]^{(3-x)-}$, respectively, exactly parallel their effect on the stable $^{35}SO_4^{2-}$ ion in both phases during the exchange reactions involving these various species is a potential

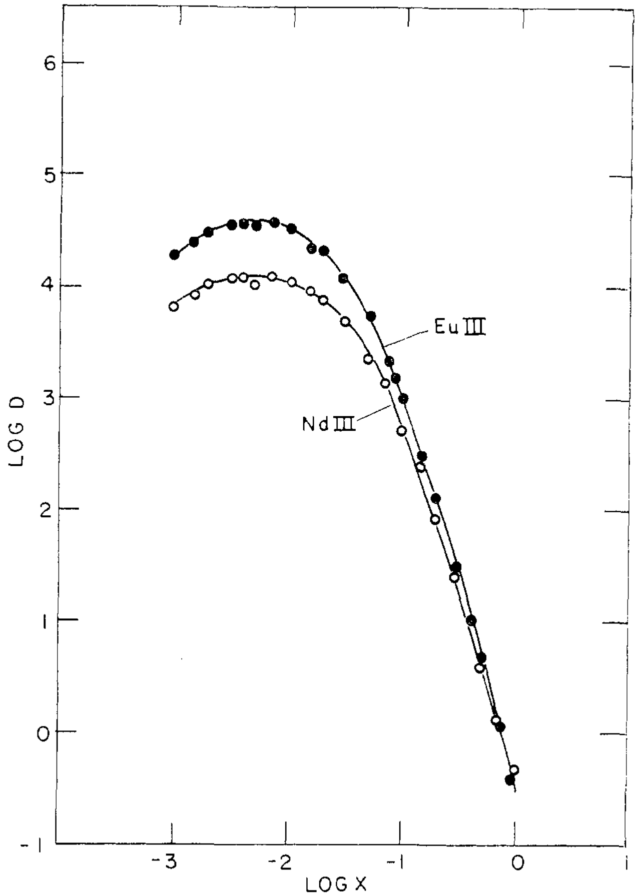

Fig. 2.—Distribution coefficients of Nd(III) and Eu(III) as a function of $KHCO_3$ concentration.

source of error in the analytical treatment. Some justification for this approximation, however, derives from the equivalent behavior of $^{35}SO_4^{2-}$ in the $HCO_3^-$ and $CO_3^{2-}$ systems. Since no deviation from "ideal" behavior of this trace bivalent ion is observable in the presence of a one-one and a one-two electrolyte, the effect of charge is presumably not very important in these ligand systems. Certainly, in the case of the rare earth-bicarbonate system where the maximum charge of the principal species in the resin is probably $-2$ or $-3$ as compared to the $-2$ charge of $^{35}SO_4^{2-}$, the approximation is a reasonable one. Additional support of this treatment in the case of the rare earth-carbonate systems comes from corroboration of our assignment[3] of four carbonates to the stable rare earth complex in 0.3 to 3.0 $M$ $K_2CO_3$ by Poluektov and Konenko,[4] who identified a stable complex species of Nd with $4CO_3^{2-}$ in ultraviolet spectral studies carried out in 1.0 to 1.5 $M$ $K_2CO_3$.

The characterization in this study of the stable rare earth carbonate and bicarbonate species (*e.g.*, $[Eu(OH)(CO_3)_4]^{6-}$, $[Nd(OH)(CO_3)_4]^{6-}$, $[Eu(HCO_3)_7]^{4-}$, and $[Nd(HCO_3)_6]^{3-}$) in the presence of high ligand concentration is believed to have been demonstrated with a high degree of certainty on this basis. The existence of a mixed ligand complex as reported herein is not an unusual phenomenon. Hydrolysis of partially aquated complex ions leading to the presence of a hydroxide group in a complex is not unusual. It has been reported for the Ti(IV)–$H_2SO_4$ system[13] among others. Evidence has been found for the existence of mixed $NO_3^-$–$OH^-$ complexes of Ce(IV).[14] The increase in the tendency of the lanthanide elements to form basic carbonate precipitates, $M(OH)CO_3$, with atomic number has been reported.[15,16] Since the basicity of the rare earths decreases with atomic number, this is not an unusual result.

The constant for the reaction

$$La^{3+} + HOH \rightleftharpoons LaOH^{2+} + H^+$$

has been reported as $10^{-10.1}$.[17] Thus, even at pH 12, $CO_3^{2-}$ should be able to compete successfully with $OH^-$ for the metal ion. Eventually, however, the lower charge of the hydroxide ion may be preferred.

There is no reason to be surprised by the high negative charges found on these complex anions. Giesbrecht[18] has reported Ce(III) forms dipolyphosphate complexes of the type $[Ce(P_3O_{10})_2]^{5-}$, and salts containing the anion $[Ce(CO_3)_6]^{8-}$ have been synthesized.[19] A five-coordinated $HPO_4^{2-}$ complex has been reported for Pu(IV),[20] having a charge of $-6$, and also a tetraoxalato complex of Pu(III),[21] having a charge of $-5$. Evidently the actinides and lanthanides can carry high charges and pack four, five, and six bulky anions around themselves.

It is not possible to decide whether or not some or all of the carbonate groups in $[M(CO_3)_4OH]^{5-}$ are chelated. There is evidence for carbonate ion chelation in the solid state[22,23] and in solution[19] in the case of the hexacarbonatocerate(IV) ion. In the latter case four of the carbonate ligands could be titrated with HCl and two could not. It is possible that two or more carbonate groups are chelated in the trivalent rare earths studied, thus explaining a maximum of four carbonate ligands in the complex.

The results reported herein—a heptabicarbonato complex of europium and a hexabicarbonato complex of neodymium with a hint of a heptabicarbonato complex—are rather unusual. A coordination number of seven or eight is quite rare, and the fact that it appears generally in the heavier atoms such as zirconium, niobium, tantalum, and iodine leads one to suspect that f orbitals are involved,[24] although structures have been

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deduced which require only s, p, and d orbitals. Rare earth oxides have the well-known $AM_2O_3$ structure[25] in which seven oxygen atoms are coordinated to each metal atom. In this regard, neodymium shows a coordination number of nine in $Nd(H_2O)_9(BrO_3)_3$. Most recently, also, Thompson and Loraas[26] have reported evidence for a coordination number larger than six in the rare earths forming mixed complexes with N-hydroxyethylenediaminetriacetic acid and glycine, ethylenediaminediacetic acid, and N-hydroxyethyliminodiacetic acid.

It is not possible to state whether the heptabicarbonato complex represents the coordinatively saturated species, but evidently coordination numbers greater than six are known for the heavy elements. Future research in this area should be directed toward elucidating the role of f orbitals in these complexes and in determining the dentate character of the ligands.

Even though the comprehensive analysis of the data that has been presented may be somewhat in error, justification for its presentation is believed to derive from the facts that (1) it provides an estimate of the interesting complexing situation of the rare earths in carbonate and bicarbonate systems and (2) it points out real differences between the neodymium and europium sequence of compounds.

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# The Preparation and Some Properties of a Europium Dicarbide Phase

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A previously unreported lanthanon dicarbide, $EuC_2$, has been prepared in a stainless steel bomb by the reaction of the metal with graphite. The lattice parameters, some chemical properties, and a comparison of this phase with other dicarbide phases are presented.

## Introduction

The crystal structure and some chemical properties of several tetragonal rare earth dicarbides have been reported.[1-4] However, no carbide of europium has been mentioned, and, since europium is an element which differs in many ways from its neighbors, it seemed desirable to investigate the europium–carbon system and determine whether or not a dicarbide could be prepared.

## Experimental

Two techniques were used in the preparation of the dicarbide phase. In the first of these, weighed quantities of a powdered mixture of calcined europium sesquioxide (99.8% pure), obtained from the Michigan Chemical Company, St. Louis, Michigan, and spectrographic grade graphite, in the ratio of one mole of the sesquioxide to 7.1 moles of graphite, were placed into a graphite crucible which previously had been outgassed by maintaining it at 1630° by induction heating in the vacuum system until the residual pressure in the system was $4 \times 10^{-6}$ torr or less. No deposit was observed on the walls of the heating assembly when the weight of the crucible remained constant to ±0.5 mg. Temperature was measured by sighting with a Leeds and Northrup disappearing-filament type optical pyrometer through a prism and optical window into a black body hole situated in the bottom of the crucible.

The crucible, charged with the oxide–carbon mixture, was covered with a snug-fitting, outgassed graphite lid through which a 0.040-in. diameter hole had been drilled, and was heated, as described above, to about 1450° until the deposit which effused from the orifice and condensed on the Vycor vacuum jacket began to flake. Care was exercised to ensure that none of the condensed phase was lost. The crucible was subsequently heated until no europium could be detected in the crucible, and from weight differences of the crucible, the weight of the unreacted graphite could be determined. The condensate was immediately hydrolyzed with either 6 *N* hydrochloric or nitric acid, filtered, and analyzed for europium by weighing the calcined oxalate precipitate. The quantity of carbon in the condensate was determined by direct weighing of the residue that remained after the hydrolysis.

In the other technique, europium metal (99% pure), obtained from the Michigan Chemical Company, St. Louis, Michigan, together with graphite in the ratio of 2 moles of carbon to 1 mole of europium was inserted into a small stainless steel bomb machined from 1-in. bar stock. The cavity of the bomb, which was $^3/_8$ in. in diameter and $^5/_8$ in. high, was charged under an atmosphere of dry helium. The bomb was sealed with a platinum gasket and then heated under a flow of helium in a resistance tube furnace for 12 hr. at about 1050° and then cooled slowly. The bomb was opened and the sample removed from the bomb and stored in a glove box filled with purified helium.

Weighed samples of the bomb contents were hydrolyzed in approximately 3 *N* HCl, digested for 2 hr., and then filtered to remove the free graphite, which subsequently was dried and weighed. The europium was precipitated as the oxalate and determined gravimetrically, as described above. Bound carbon was determined by difference. The absence of iron in the dissolved samples was demonstrated by a qualitative iron test.

The gases produced by hydrolysis in some runs were swept

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