a Dowex-50 column showed the chromium was present as $(H_2O)_5CrSO_4^+$.

trans-Bisethylenediaminediacetatocobalt(III) is reduced more slowly than the tetraammine (increase in ΔF^*), and reduction of the *cis* isomer cannot be observed by the acid-independent path, although this may be due to crowding of the acetate groups together by the bulky ligands, preventing a close approach of the reductant. Bisethylenediaminemaleatocobalt(III), on the other hand, is reduced more rapidly than the corresponding tetraammine, but here a different mechanism has already been proposed.[11] The suggested mechanism involves chromium attack above the chelate ring rather than from the side, so that two of the ligand oxygens can become associated with the reductant.

Variations in rate constant are generally much smaller when V(II) is the reductant: this has been observed for cobalt(III) complexes containing ligands such as nitrate, thiocyanate, and azide[19] and chloride and water.[20] In the past this has led to the suggestion[20] that V(II) reacts by an outer-sphere mechanism in some reductions. On the other hand, the similarities of the ΔS^*–ΔH^* relationships for V(II) and Cr(II) reductions of carboxylato complexes[9] suggest that there V(II) can act through a bridged mechanism. This is further supported by the observation that V(II) can induce the same *cis–trans* isomerism of the pentaamminemaleatocobalt(III) ion as Cr(II).[21] Direct evidence for bridging cannot be obtained because of the substitution-lability of V(III).

Acknowledgment.—The author wishes to thank Professor J. Halpern, University of Chicago, for making available unpublished data.

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Carbonate Complexes of the Lighter Lanthanides

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The distribution of the lighter lanthanides between Dowex I-X8 (carbonate form) and K_2CO_3 solutions has been studied as a function of carbonate concentration in order to elucidate their complexing behavior in the presence of an inorganic ligand. Elution chromatography was employed using radioactive isotopes of Ce, Pr, Nd, Pm, Sm, and Eu to facilitate the investigation. The distribution of tracer ^{35}S in the form of $^{35}SO_4^{-2}$ between Dowex I-X8 and K_2CO_3 solutions was studied to determine the effect on the system 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 covered, thus giving an experimental basis for the theoretical treatment of the data. Distribution coefficients were measured over the concentration range of 0.37 to 2.60 m K_2CO_3. Over this region a logarithmic plot of the distribution coefficient *vs.* K_2CO_3 molality results in straight lines for all the lanthanides that were studied, indicating the presence of stable complex anions in solution. Analysis of these results indicates that the complexes are of the form $[M(CO_3)_4]^{-5}$.

Ion-exchange, potentiometric, and electrophoretic studies of α-hydroxycarboxylate interaction with the lanthanides[3] (and actinides) have shown the presence of negatively charged complexes in solution with four ligands coordinated to the central ion at concentrations greater than 0.1 M. This result also has been obtained with acetate systems.[4] The occurrence of anionic complexes of the rare earths in carbonate solutions also has been demonstrated recently in a qualitative anion-exchange study.[5]

It is felt that the coordination properties of the rare earths in carbonate solutions are of interest for correlation with the acetate and α-hydroxycarboxylate systems. The rare earth–carbonate system is also of interest from a separations point of view. The separation of rare earths into two groups, La, Pr, Nd, Pm and Sm, Eu, Y, has been achieved in practice by digestion with 20% K_2CO_3, the last group being solubilized.[6]

For these reasons it was decided to study the behavior of rare earths in carbonate systems. The choice of technique for study of the system lanthanide–carbonate–water was severely limited by the insolubility of the rare earth carbonates, however, making necessary the use of radioactive isotopes of the rare earths in tracer concentrations of about 10^{-10} M. The affinity of the metal ion for an anion-exchange resin as a function of ligand concentration was used to measure the degree of complexing, ion-exchange column chromatography being selected to facilitate the investigation.[7]

Experimental

Materials.—The resin Dowex I-X8, 200–400 mesh, in the chloride form (lot Number 20283), potassium chloride, and potas-

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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 for a Master of Arts Degree.

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sium carbonate, reagent grade, were purchased from the J. T. Baker Chemical Company. The nuclides 32.5-day Ce-141, the long-lived mixture Eu-152–Eu-154, 11.6-day Nd-147, 2.6-year Pm-147, 13.95-day Pr-143, 47-hr. Sm-153, and 87.1-day S-35 were received 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.—Resin was converted to the carbonate form prior to use, after cycling three or four times in the carbonate and chloride form with 1 *M* K_2CO_3 and 1 *M* KCl, respectively.

The columns employed consisted of soft glass tubing, approximately 3 mm. i.d. and 1–50 cm. long, depending on the value of the distribution. A side arm at the top facilitated control. The column tip was drawn out to give a drop volume of about 0.030 ml., enabling the peak of a chromatographic wave to be located accurately.

The average cross section of a column was determined with an accuracy of ±0.4% by correlating the weight of three separate samples of water that were delivered from the column with the linear movement of the water down the column. A small bed of pulped filter paper, with minimal volume displacement and no apparent sorption properties, served as the resin support.

Reproducible packing of the resin bed was achieved by use of a doorbell-vibrator. The bed height of each column was measured, a cathetometer being employed for the shorter beds to facilitate a ±0.3% accuracy in the measurement. Since the resin bed was packed in water, a portion of the potassium carbonate eluent which was to be used subsequently was passed through the column for a suitable length of time to convert any hydrolyzed portion of the resin to the carbonate form.

When the specific gravity of the (concentrated K_2CO_3) eluent was greater than that of the resin beads, it was necessary to settle some pulped paper on top of the resin bed to restrain the resin during passage of eluent through the bed.

Column Operation.—The experimental procedure was similar to that of Thompson, *et al.*[8] Eluent flow rates, controlled by adjusting the height of a constant-head funnel above the column, were kept below 0.427 ml./cm.^{2} min. Below this flow rate the shape and position of an elution peak were unaffected. Eluent drops were continuously collected on a traveling strip of 6-in. wide chart paper which was driven by an Esterline-Angus Model AW synchronous chart drive. The rate of travel was adjusted to maintain a reasonable spacing of drops. Radioactive content of the drops was assayed by passing them under an infrared lamp for drying and then under a Model D-34 Geiger Mueller tube manufactured by the Nuclear-Chicago Corporation. The detector was shielded from β-radiation by placing it in a cast-iron cylinder with a plate at the bottom containing a 1-in. diameter orifice in the center. The window of the detector was placed directly above the orifice. This arrangement was necessary to screen, at least partially, the drop being monitored from those drops preceding and following it.

The signal from the detector was transmitted to the amplification section of a Model 49–50 scaler and then fed into a Model 35–4 count rate meter, both manufactured by the Radiation Instrument Development Laboratory. Finally the signal was fed into a Minneapolis-Honeywell "Electronik" high speed strip chart recorder.

When two or more rare earth isotopes were eluted simultaneously, the radioactivity in the dried drops was remeasured under the thin window of a gas flow proportional counter with and without an aluminum absorber covering the particular sample. This procedure, for example, allowed Pm-147 to be differentiated from Eu-152, 154.

Several experiments were run with the 282-day Ce-144 (present as an impurity in Ce-141) in secular equilibrium with 17.5-month Pr-144. After the separated Pr-144 had decayed for at least five half-lives and had regrown into the separated cerium, the samples were remeasured to obtain the elution curve for cerium alone. The praseodymium elution pattern could then be resolved by appropriate subtraction of the cerium curve.

Drop volume determinations were made following each run by weighing three drops of eluent. Constancy of experimental conditions was checked during a number of runs by this technique.

Results

Void volumes, measured as a function of K_2CO_3 concentration by determining the volume of eluent required to elute $^{22}Na^+$, a nonexchangeable ion,[9] are shown in Table I. An apparent significant upward drift in the void volume with K_2CO_3 concentration is attributed to increasing invasion of the resin by the mixed electrolyte as K_2CO_3 concentrations are increased beyond 1 *m*. Constancy of the value that is obtained at the lower molalities is believed to indicate that electrolyte invasion is insufficient to be noticeable. The value of 0.352 thus provides an accurate estimate of void volume and is used in calculating distribution coefficients.

TABLE I

VOID VOLUME AS A FUNCTION OF K_2CO_3 CONCENTRATION

Molality	Void vol., fraction of bed vol.
0.371	0.352
0.508	.352
1.023	.354
1.57	.421
2.12	.416
3.26	.454

Distribution coefficients that were measured for several rare earths and $^{35}SO_4^{-2}$ as a function of K_2CO_3 molality are presented in Tables II and III.

TABLE II

THE DISTRIBUTION COEFFICIENTS OF SOME RARE EARTHS

	D_{RE}					
$m_{K_2CO_3}$	Ce(IV)	Pr(III)	Nd(III)	Pm(III)	Sm(III)	Eu(III)
0.371	18.5	5.25	6.25	9.00	16.0	24.0
.508	5.17	2.18	2.90	4.77	6.5	10.7
.712	1.30	0.831	1.14	1.62	2.35	3.28
1.023	0.500	.338	0.405	0.675	0.860	1.51
1.55				.0984	.166	0.374
2.11				.105		.168
2.58						.0946
2.60				.0841		

TABLE III

THE DISTRIBUTION OF $^{35}SO_4^{-2}$

$m_{K_2CO_3}$	$D_{SO_4^{-2}}$
0.100	22.9
.200	11.3
.371	6.21
.508	4.23
.712	2.97
1.023	2.03
1.57	1.20
2.12	0.714

The slopes of the straight lines that are obtained from a log *D* *vs.* log $m_{CO_3^{-2}}$ plot of the rare earth data are −2.5 to −3 for each of the rare earths except Ce. The slope of the straight line due to Ce is −4. This anomalous result is believed to be due to the trans-

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formation of the radioactive Ce to its tetravalent state on standing in carbonate solution. Support for this explanation of the results with Ce was obtained in experiments that were conducted in the presence of hydroxylamine. The behavior of Ce, in this environment, approaches the behavior of Pr, which is not affected. A slope of -1 is observed for the $^{35}SO_4^{-2}$–CO_3^{-2} system.

The $^{35}SO_4^{-2}$–CO_3^{-2} system was employed to determine the effect of imbibed electrolyte and changing internal and external activity coefficients. The observed result indicates that deviations from ideality due to these effects are negligible for this system in the concentration range that was studied. By assuming that this result also applies to the several rare earth–carbonate systems, the straight line relationship between log D_{RE} and log $m_{CO_3^{-2}}$ that is observed for all of the lanthanides indicates the presence of stable anion complexes with a charge of -5; *i.e.*, a rare earth complex of the form $[RE(CO_3)_4]^{-5}$. If tetravalent properties are attributed to the Ce, six carbonato ligands appear to be coordinated with it.

The formation constants for these complexes cannot be determined in this system because the change in distribution coefficient with change in ligand concentration is not a function of the degree of complexing. The only constants which can be measured are the exchange constants K_r (see next section) and these are tabulated in Table IV.

TABLE IV

RARE EARTH EXCHANGE CONSTANTS

	K_r
Pr(III)	0.390
Nd(III)	.448
Pm(III)	.751
Sm(III)	.861
Eu(III)	1.47
Ce(IV)	0.355

Discussion

The logarithmic relation, $\log D = \log K_r + p \log m_L$, that has been used to correlate the data as described above is similar to expressions that have been employed by a number of authors for the same purpose.[3,10,11]

In this equation p is the charge of the complex ion in units of l, the charge of the ligand, and K_r is proposed as a constant term which includes the thermodynamic constant, K, for the exchange reaction between the ligand and the stable ionic species of the trace metal component in the resin and solution phases. To obtain a linear relation between log D and log m_L, K is multiplied by the ratio of the activity coefficients of each species involved in the exchange reaction and the resin phase molality of the ligand.

Failure of the approximations that are made in assigning constancy to K_r is always a potential source of confusion in the analysis of distribution data by this equation. Our attempt, in this investigation, to circumvent this difficulty by demonstrating the utility of the expression for predicting correctly the charge of the known stable ion, $^{35}SO_4^{-2}$, in the presence of the eluting ion over the concentration range employed in the study of the rare earths does not unambiguously prove the applicability of this method of charge analysis to the system of interest. It has been pointed out correctly by one of the referees that the added assumption that this judgment implies is that exchange reactions involving ions of different charge behave similarly. Some justification for this additional assumption, however, is the ideal behavior of the $^{35}SO_4^{-2}$–HCO_3^- exchange, in the same concentration range, that has been observed by us in the study of rare earth–bicarbonate systems.[12] Additional support for our interpretation of the data is the corroboration that is found in the published results of Poluektov and Konenko,[13] who identified the complex ionic species $[Nd(CO_3)_4]^{-5}$ in ultraviolet spectral studies, and Golovnya and Pospelova,[14] who identified, in solubility studies, the Ce(IV) compounds $[Ce(CO_3)_x \cdot (H_2O)_y]^{-n}$, where $x = 4$, 5, and 6 and $y = 0$, 1, and 2.

The high charges on the carbonate complexes are not unusual for the rare earths. Giesbrecht[15] has shown that (Ce(III)–polyphosphate complexes of the form $[Ce(P_3O_{10})_2]^{-7}$ exist. Tetravalent actinides have been shown to form HPO_4^{-2} complexes with up to five ligands coordinated to the central ion.[16] Evidently it is possible for lanthanides and actinides to form highly charged complex ions.

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