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C. E. Lang
Loras College

G. J. Schrobilgen

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Stability Trends for the Lanthanides on Dowex A-1 Chelating Resin

C. E. LANG¹ AND G. J. SCHROBILGEN

Abstract. Distribution coefficients have been determined for a number of trivalent lanthanide ions on an ion exchange resin containing N-benzyliminodiacetic acid groups. At pH 2.00, $\mu=0.100$ and 25.00°C. the relative stability trends for lanthanum through neodymium were found to be in agreement with trends previously observed with iminodiacetic acid N-methyliminodiacetic acid and N-benzyliminodiacetic acid. Beyond neodymium the distribution coefficient sequence of lanthanide-resin chelates is inverted. On the basis of the distribution coefficients, the inverted elution sequences previously reported in the literature for lanthanum and lutetium on the resin can be explained.

A number of plausible explanations for the trends observed can be offered, among which are steric effects, changes in coordination number and electrostatic repulsive effects. Infrared spectral data indicate the existence of a zwitterionic lanthanide chelate species which may contribute to the latter effect.

Dowex A-1, a chelating resin with iminodiacetic acid groups attached to a styrene-divinylbenzene copolymer matrix, is, to our knowledge, the first commercially available material of this type. Since hitherto no literature data concerning the distribution coefficients of trivalent lanthanide ions on this resin are known to the authors, it seemed interesting to extend studies to this region.

Christell, Forberg and Westermarck¹ have investigated the elution sequence of La^{+3} and Lu^{+3} with 0.1 N hydrochloric acid on a column of the resin in calcium form. Their tracer experiments demonstrated Lu^{+3} was eluted first, indicating that the lanthanum chelate is inherently more stable than the lutetium chelate. Trends found in the formation constants for related aminedicarboxylate chelates, namely iminodiacetate,² N-methyliminodiacetate³ and N-benzyliminodiacetate,³ are just the opposite of the stability sequence observed for La^{+3} and Lu^{+3} on the resin.

This paper reports a study of the stability trends observed for La^{+3} , Pr^{+3} , Nd^{+3} , Sm^{+3} , Gd^{+3} , Tb^{+3} , Dy^{+3} and Yb^{+3} on the resin in acidic media. The results further substantiate the relative elution sequence observed for La^{+3} and Lu^{+3} on the resin and indicate several possible explanations for the observed trends.

EXPERIMENTAL

Distribution Coefficients

Standard lanthanide stock solutions were prepared by dissolving a weighed amount of the oxide (99.9% pure) in an excess of

¹Loras College, Dubuque, Iowa.

3 N hydrochloric acid and evaporating to dryness on a steam bath. The chlorides were redissolved and diluted to volume to give solutions 0.005000 M in the respective lanthanides.

The Dowex A-1 resin (50-100 mesh) was converted to the H⁺ form by treating the Na⁺ form with 20 volumes of 2 N hydrochloric acid in a Büchner funnel followed by rinsing with deionized water until the effluent was neutral to litmus. The treated resin was air-dried until free-flowing and stored for use.

The exchange capacity of the air-dried resin was determined by allowing weighed portions of the resin to stand in contact with 1 M [Cu(NH₃)₆]⁺² for four days with frequent agitation. The Cu⁺² ion was eluted from the resin with 1 N sulfuric acid and determined electroanalytically. The exchange capacity was found to be 3.314 ± 0.004 moles N-benzyliminodiacetate groups/g. air-dried resin.

Distribution coefficients were determined by a batch procedure. In each case 1.000 g. of air-dried resin was equilibrated with 100.0 ml. of diluted lanthanide stock solution 0.001000 M in Ln⁺³ and 0.01000 M in H⁺ for 16 hours with constant stirring at 25.00 ± 0.02°C and μ = 0.100 (adjusted with NaCl). Sides and Kenner⁴ concluded, in the case of the alkaline earths, that six hours was sufficient to give a constant distribution coefficient.

At the end of the stirring time the pH was measured *in situ* with a combination glass-calomel electrode and aliquots of the solution were withdrawn for analysis. Values of pH were converted to concentration values using a correction factor of -0.07 pH unit found for a 0.01000 M hydrochloric acid solution at 25.0°C and μ = 0.100 (NaCl). In no case did the final pH value deviate by more than ± 0.02 pH unit from the initial value. Lanthanide concentrations were determined spectrophotometrically as the Xylenol Orange complexes. A 10⁻³ M Xylenol Orange solution was freshly prepared in water from the tetrasodium salt. To an aliquot of the solution containing lanthanide ion was added 10.0 ml. of pH 6.1 ammonium acetate buffer and 3.00 ml. of 10⁻³ M Xylenol Orange solution and the volume adjusted to 25.00 ml. with water. The absorbances of the unknowns were measured against identical reagent blanks at 576 mμ on a Beckman DU Spectrophotometer employing 1.000 cm. quartz cells. Concentrations were determined from standard lanthanide stock solutions.

Binding Studies

Infrared spectral data may indicate the existence of a zwitterionic lanthanide chelate species. A quantity of the lanthanum-resin chelate was prepared by equilibrating approximately 0.5

g. of I^+ form of the resin with 25ml. of 3 M $LaCl_3$ in 0.1 M ammonium acetate buffer for one week at pH 5.0. The resin was removed by filtration and washed with 50 volumes of water. Half of the washed resin sample was equilibrated with 28% ammonia (\sim pH 12) for 24 hours. The ammonia treated portion was filtered off and washed with 20 volumes of ethanol to prevent hydrolysis while removing excess ammonia from the resin. After drying both portions of the resin for five days at $110^\circ C$, their infrared spectra were recorded using the KBr disk method (1 mg. resin/0.4 g. KBr). Both spectra were identical except in the 1000-1100 cm^{-1} region. The absorptions in this region are summarized in Table 1 (Na^+ and H^+ forms are included for comparison).

Table 1. Principal Absorption Bands in the 1000-1100 cm^{-1} Region for Zwitterionic and Non-zwitterionic Forms of Dowex A-1

| H_2X | La^{+3} (zwitterionic) | Na_2X | La^{+3} |
|--------|--------------------------|---------|-----------|
| 1070 | 1085 | 1100 | 1085 |
| | | 1050 | 1045 |
| 1015 | 1015 | 1015 | 1015 |

The appearance of the 1045-1050 cm^{-1} absorption band upon treatment of the chelate with concentrated ammonia corresponds to the C-N stretch frequency of the t-amine group formed upon removal of the hydrogen.⁵

The binding ratio for H^+ was determined from the infrared spectra. Ratios of the absorption corresponding to the position of the t-amine absorption and the 810 cm^{-1} absorption (internal standard) were set equal to 0% and 100% for the H^+ and La^{+3} (ammonia treated) forms, respectively. The ratio of the 1045 and 810 cm^{-1} absorbances was likewise determined for the zwitterionic form of the resin. The binding ratio determined in this manner was $H^+ : N\text{-benzyliminodiacetate groups} = 0.32 \pm 0.03$ or 1:3.

A weighed quantity of the La^{+3} (ammonia treated) form of the resin was treated with 0.5 M hydrochloric acid to remove the sorbed lanthanum ion, followed by 50 volumes of water, dried to constant weight at $110^\circ C$ and reweighed as the H^+ form. The ratio determined by this method was $La^{+3} : N\text{-benzyliminodiacetate groups} = 0.64 \pm 0.02$ or 2:3.

RESULTS AND DISCUSSION

Variation of the Distribution Coefficients with Ionic Potential

The distribution coefficient is defined by the equation

$$D = \frac{x_{Ln^{+3}resin}}{x_{Ln^{+3}aqueous}} \quad (1)$$

where $x_{Ln^{+3}}$ is the mole fraction of lanthanide ion. Values for D are listed in Table 2.

Table 2. Distribution Coefficients for the Lanthanides on Dowex A-1 Chelating Resin

$t = 25.00^\circ C, pH = 2.00$
 $= 0.100 (NaCl)$

| Metal | D^a |
|------------------|-------|
| La ⁺³ | 0.381 |
| Pr ⁺³ | 0.965 |
| Nd ⁺³ | 1.319 |
| Sm ⁺³ | 0.845 |
| Gd ⁺³ | 0.651 |
| Tb ⁺³ | 0.561 |
| Dy ⁺³ | 0.562 |
| Er ⁺³ | 0.828 |
| Yb ⁺³ | 0.375 |

^a The relative error in the values for the distribution coefficients is estimated to be $\pm 0.7\%$.

It is instructive to consider plots of $\log K$ versus ionic potential, where K is the formation constant for the lanthanide chelate.⁶ However, since the stoichiometry of the lanthanide-resin chelate formation is not known, it becomes impossible to use this approach unless certain assumptions are made. If one assumes a maximum of, say, three N-benzyliminodiacetate groups to be involved in chelation with a single lanthanide ion (only in a few cases is the number of carboxylate ligands that can be crowded about a lanthanide ion suspected to be greater than six), the concentration of the ligand can be shown, on the basis of the experimental conditions employed here, to be essentially constant throughout the lanthanide series. D , then, can be considered directly proportional to K .

For the sake of comparison, the values

$$D = \frac{[LnY^+] + [LnY_2]}{[Ln^{+3}]} \quad (2)$$

where Y^{2-} represents the ligand, have been calculated for iminodiacetate, N-methyliminodiacetate, and N-benzyliminodiacetate complexes from their respective acid dissociation and formation constants^{2,3} at pH 2.00 ($[LnY_2] \approx 0$ at pH 2.00), 25.0°C and $\mu = 0.100$. D values were calculated using 0.001000 M as the initial Ln^{+3} concentration and 0.03314 M for the initial concentration of aminedicarboxylic acid the total concentration of N-benzyliminodiacetate groups present when 1.000 g. of air dried

resin is placed in 100.0 ml. of solution. Calculations were performed on an IBM 1130 Computer using a modified version of the general digital computer program for chemical equilibrium calculations written by Bard and King.⁷ D values calculated for these simple monomeric aminedicarboxylic acids, too, can be said to be directly proportional to K using an argument similar to that used in the case of the resin distribution coefficients.

Values for $\log D$ are plotted versus ionic potential, Z^2/r , where r is the ionic radius in Å⁸ and Z is +3, the charge of the lanthanide ion, in figure 1.

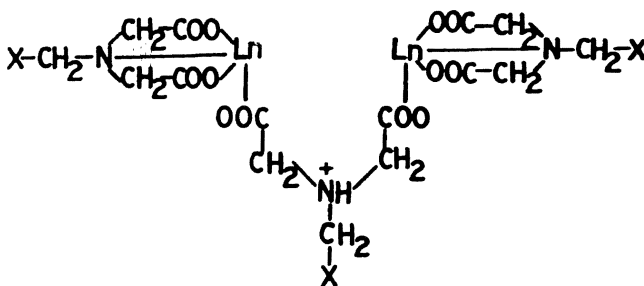


Figure 1. A possible structure for the lanthanide-resin chelate (X represents the copolymer matrix).

Stability trends for lanthanum, praseodymium and neodymium are found to parallel similar trends observed for D values computed for the simple aminedicarboxylate chelates. Since the plot of the $\log D$ vs. Z^2/r exhibits the expected linearly increasing course in the region lanthanum-neodymium, there does not appear to be any pronounced steric hindrance in their chelates.

Inversion of the sequence between neodymium and terbium may arise from a number of factors, chief among which may be increased steric hindrance as the size of the lanthanide ion decreases and/or the presence of increased electrostatic repulsive forces with increasing ionic potential. The results of our binding studies, which are in agreement with a structure proposed by Hering⁹ (see figure 2), seem to indicate that the latter effect might be an important contributing factor.

The presence of increased $\text{Ln}^{+3}\text{-Ln}^{+3}$ and $\text{Ln}^{+3}\text{-H}^+$ Coulombic repulsive forces at high ionic potentials in Hering's structure may help to account for stability trends observed for neodymium-terbium. Even if the protonated N-benzyliminodiacetate group is not coordinated to adjacent lanthanide ions, one would expect, in light of the high concentration (~ 1 M) and restricted freedom of movement of the N-benzyliminodiacetate groups within the inter-

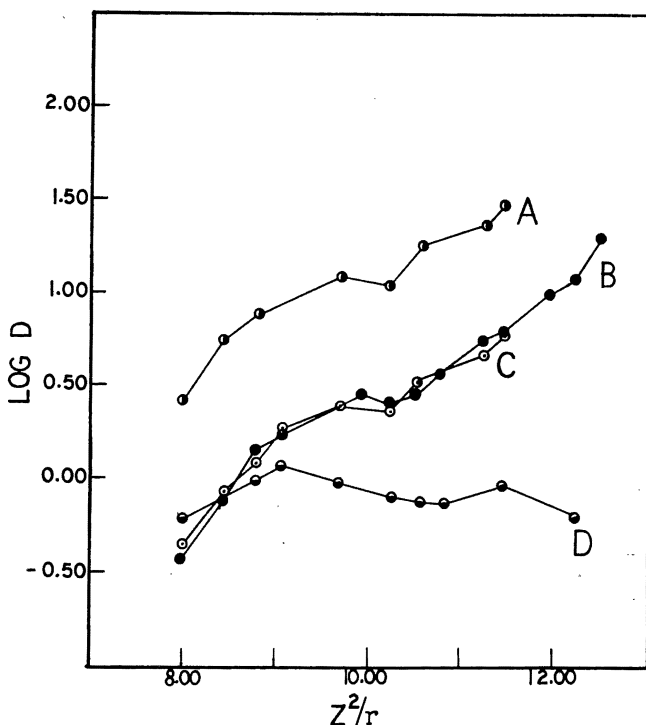


Figure 2. A—N-benzyliminodiacetic acid
 B—iminodiacetic acid
 C—N-methyliminodiacetic acid
 D—Dowex A-1

stices of the resin, that such effects might be a contributing factor.

It is interesting to note that the departure from linearity for neodymium-erbium is very similar to the trends observed by Grenthe and Fernelius for dipicolinate complexes in this region.⁶ In both cases, instead of the expected linearly increasing course, a curve is obtained where only the first part, lanthanum-neodymium, increases linearly, while the second part, samarium-erbium, decreases to terbium, remains essentially constant for terbium-dysprosium and increases to erbium. Because of the many coordination sites available in these ligands, it is possible, as Grenthe and Fernelius point out in the case of dipicolinate chelates, that a change in the number of points of attachment after neodymium may have occurred. Such a change in configuration may be brought about by electrostatic repulsive effects and/or steric effects proposed earlier. That such a change in configuration can indeed occur has been demonstrated in the case of lan-

thanide-EDTA chelates by the infrared studies of Moeller, Moss and Marshall¹⁰ and Kolat and Powell.¹¹

It is difficult to explain the fact that the distribution coefficient for ytterbium is less than that for lanthanum. However, it is sufficient to note, at this time, that a decrease is expected beyond erbium if the stability trend observed by Christell, Forberg, and Westermark for lanthanum and lutetium (i.e. $D_{La}^{+3} > D_{Lu}^{+3}$) is to be borne out.

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