COMMUNICATIONS TO THE EDITOR

CHELATION OF THE +3 IONS OF ELEMENTS 95 THROUGH 100 WITH THENOYLTRIFLUOROACETONE

Sir:

Certain reaction properties of the +3 aqueous ions of members of the lanthanide and actinide series of elements appear to correlate with the contraction in ionic radii observed in crystals with increasing atomic number. The usual order of elution by complexing agents from ion exchange columns, namely, in order of decreasing Z, is thus said to be the result of the variation in basicity or charge separation.[1,2]

We have observed some remarkable variations in the extraction equilibria of the thenoyltrifluoroacetonates of the +3 actinides in toluene–aqueous systems (Table I). All equilibrations were conducted to obtain relative extractabilities, *i.e.*, at least two of the elements were present in each of the numerous systems studied to determine the distribution ratios. Trace concentrations of the nuclides Ac^{225}, Am^{241}, Cm^{244}, Bk^{249}, Cf^{252}, 99^{253} and 100^{254} were available for the measurements. Radioactive properties of the newer nuclides have been given in recent publications.[3,4]

TABLE I

DISTRIBUTION RATIOS OF ACTINIDE AND LANTHANIDE IONS

Element	D^a	Element	D^a
Europium	0.82	Berkelium	4.15
Ytterbium	5.59	Californium	2.20
Actinium	0.0001	99	1.60
Americium	.29	100	2.58
Curium	.24		

[a] Concentration ratios (toluene/aqueous, volume basis) at equilibrium in the distribution of the +3 ions between 0.2 *M* thenoyltrifluoroacetone in toluene and 0.088 *M* ammonium monochloroacetate buffer solution, *p*H 3.4, *ca.* 25°.

Equilibrium concentrations in the two phases were determined by α- and β-particle counting, spontaneous fission counting, and α-particle pulse analysis. With the exception of element 100, the dependence of the extraction on acid concentration has been measured for all these elements and found to be inversely proportional to the third power of the acid concentration. These experiments give direct evidence that the stable oxidation state of the new elements berkelium, californium and element 99 is, indeed, the +3 state. The distribution ratios of Table I were determined with the aqueous phase buffered with ammonium monochloroacetate. Other equilibrations of Eu, Am, Cm, Cf and 99 indicate that the +3 states exist as complex ions with one chloroacetate ion per metal ion. The order of extractability appears to be independent of the aqueous phase complexing.

A change in behavior noted in ion exchange studies at the expected position for half-filling of the 5f electron shell is attributed to a discontinuity in ion size.[2] The distribution ratios of Table I also show an abrupt change between Cm and Bk. The distributions in general, however, do not conform to any simple size dependent pattern which might have been anticipated from the trends in crystal radii of these ions.

Radioactive traces of europium and ytterbium were present in a few of the equilibrations, but a general comparison of the properties of the lanthanides and actinides must await adequate thermal data. The comparative study of the two series in this system should be particularly effective for the examination of aqueous phase complexing, polarizability, bonding strengths, and entropy effects.

CHEMISTRY DIVISION
ARGONNE NATIONAL LABORATORY L. B. MAGNUSSON
LEMONT, ILLINOIS M. L. ANDERSON

RECEIVED OCTOBER 23, 1954

---

[1] E. R. Thompkins, J. X. Khym and W. E. Cohn, THIS JOURNAL, **69**, 2769 (1947).

[2] S. G. Thompson, B. B. Cunningham and G. T. Seaborg, *ibid.*, **72**, 2798 (1950).

[3] P. R. Fields, M. H. Studier, J. F. Mech, H. Diamond, A. M. Friedman, L. B. Magnusson and J. R. Huizenga, *Phys. Rev.*, **94**, 209 (1954).

[4] H. Diamond, L. B. Magnusson, J. F. Mech, C. M. Stevens, A. M. Friedman, M. H. Studier, P. R. Fields and J. R. Huizenga, *ibid.*, **94**, 1083 (1954).

THE HYDROLYSIS OF Fe^{3+} ION: MAGNETIC AND SPECTROPHOTOMETRIC STUDIES ON FERRIC PERCHLORATE SOLUTIONS

Sir:

Several workers[1,2] have studied the hydrolysis of Fe^{3+}, or the association of this ion with other ions, employing generally electrochemical or spectrophotometric methods. Most of these workers have considered the following types of equilibria for the study of hydrolysis:

$$Fe^{3+} + H_2O \xrightleftharpoons{K_{1,1}} FeOH^{2+} + H^+ \qquad (1)$$

$$Fe^{3+} + 2H_2O \xrightleftharpoons{K_{1,2}} Fe(OH)_2{}^+ + 2H^+ \qquad (2)$$

Recently Hedström[3] proposed another equilibrium

$$2Fe^{3+} + 2H_2O \xrightleftharpoons{K_{2,2}} Fe_2(OH)_2{}^{4+} + 2H^+ \qquad (3)$$

and from e.m.f. measurements obtained values for the equilibrium constants $K_{1,1}$, $K_{1,2}$, and $K_{2,2}$ at 25°.

From measurements of magnetic susceptibility, over a range of temperature, of 0.04 *M* ferric perchlorate, 3 *M* sodium perchlorate, aqueous solutions of varying acidity, we have found that the species $Fe_2(OH)_2{}^{4+}$, which we shall call the "dimer," is diamagnetic. The forward reaction (3) has been shown to be endothermic, with $\Delta H \simeq$ 9.8 kcal. per mole. Thus, the dimer is more stable at higher temperatures, in the room temperature range.

---

[1] Important references are given by Hedström.[3]

[2] G. A. Gamlen and D. O. Jordan, *J. Chem. Soc.*, 1435 (1953).

[3] B. O. A. Hedström, *Ark. fur Kemi*, **6**, 1 (1953).