BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 49 (8), 2327—2328 (1976)

Stability Constants of the Rare Earth Complexes with 2-Ethyl-2-hydroxy-3-methylbutyric Acid*

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(Received March 23, 1976)

Synopsis. The stability constants of the rare-earth complexes with 2-ethyl-2-hydroxy-3-methylbutyric acid have been determined potentiometrically at 25.0 °C and at an ionic strength of 0.10, with sodium perchlorate as the supporting electrolyte.

The stability constants of the rare-earth complexes with some 2-hydroxymonocarboxylic acids have previously been determined by the authors and their coworkers.[1-3] The complexing agent employed in this study, 2-ethyl-2-hydroxy-3-methylbutyric acid, which will be abbreviated as Hehmb hereafter, was first prepared by Darzens.[4] This acid was expected to have properties similar to those of 2-hydroxyisobutyric or glycolic acids, though it has an apparently lower solubility in water. The stability constants of the rare earth-ehmb complexes were determined by pH measurements, and a comparison with those of the analogous acid complexes will be presented.

Experimental

Reagents and Apparatus. The rare-earth perchlorate solutions were prepared from the respective oxides with a purity of 99.9% or higher, supplied by the Ames Laboratory of the U. S. Atomic Energy Commission. The Hehmb used in this work was also prepared in the Ames Laboratory; it had a melting point of 75.0—75.5 °C, which agreed sufficiently well with Darzens' result, *e.g.*, 76 °C. The solubility of Hehmb in water is 8.11 g/100 g H_2O at 25.0 °C, which allows us to make a saturated solution of 0.56 mol/dm^3. A Beckman model 76 pH meter was used, with its expanded scale, throughout the work, together with Beckman 41263 glass and 39170 reference electrodes.

Procedures. The experimental procedures were similar to those used in the previous work.[3]

Results and Discussion

The acid dissociation constant of Hehmb at 25.0 °C and at an ionic strength of 0.10 with sodium perchlorate was determined to be 2.557×10^{-4}.

The ligand number, $\bar{n}$, and the free-ligand-ion concentration, $[A^-]$, were derived from the hydrogen-ion concentration previously determined and from the known stoichiometry of the solutions. Since the ligand number did not exceed 2 throughout the measurements, only the following two equilibria were considered here:

$$R^{3+} + A^- \rightleftharpoons RA^{2+}, \quad K_1 = [RA^{2+}]/[R^{3+}][A^-];$$

$$RA^{2+} + A^- \rightleftharpoons RA_2^{+}, \quad K_2 = [RA_2^{+}]/[RA^{2+}][A^-];$$

where R^{3+} denotes a trivalent rare-earth cation. The stability constants were computed on an IBM 7044 computer at the Tokai Research Establishment, Japan Atomic Energy Research Institute, Tokai-mura, Ibaraki. The computational programs used were the weighted least-squares ones originally patterned by Sullivan, *et al.*[5] and by Stagg and Powell,[1] adopted to the IBM 7044 computer. The constants thus obtained are shown in Table 1.

The stability constants of the lanthanum ehmb complexes are appreciably lower than those of the corresponding lanthanum complexes, such as 2-hydroxyisobutyrates or lactates. The increase in the constants with the descending periodic sequence down to gadolinium is far more remarkable compared with that in the case of the complexes of the analogous acids, but the subsequent increase in the constants along with the heavier rare earth elements is considerably reduced. The latter trend may be due to the steric effect of the relatively large molecules of the ligand on the cations of a smaller size. These facts indicate that Hehmb may be favorably used for separating lighter rare earths from each other.

Besides the gadolinium break, two more breaks are

TABLE 1. STABILITY CONSTANTS OF THE RARE EARTH COMPLEXES WITH 2-ETHYL-2-HYDROXY-3-METHYLBUTYRIC ACID AT 25.0 °C AND AT $I=0.10$ ($NaClO_4$)[a]

Metal	β_1 $(=K_1)$	$\log\beta_1$	$\log\beta_2$
La	56.8	1.75	2.97
Ce	81.4	1.91	3.02
Pr	92.7	1.97	3.17
Nd	121	2.08	3.54
Pm	—	—	—
Sm	275	2.44	4.17
Eu	419	2.62	4.27
Gd	478	2.68	4.38
Tb	653	2.81	4.60
Dy	723	2.86	4.68
Ho	734	2.87	4.73
Er	886	2.95	4.81
Tm	968	2.99	4.88
Yb	1040	3.02	4.92
Lu	1070	3.03	4.86
Y	608	2.78	4.52

a) The values given in this table are subject to absolute errors of as much as ±5% in the case of K_1, and ±10% in the case of K_2. The values of K_1, however, can be compared with those for the adjacent rare earths with greater confidence.

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* The work was performed at the Institute for Atomic Research and Department of Chemistry, Iowa State University, Ames, Iowa.

apparently observed: one is located between neodymium and samarium, and the other, between holmium and erbium. This result coincides with the observations of some other rare earth chelates, such as ethylenediaminetetraacetates,⁽⁶⁾ picolinates,⁽⁷⁾ and *N'*-methylethylenediamine-*N*,*N*,*N'*-triacetates.⁽⁸⁾ The reason for the fine structure of the stability trend remains to be considered, together with the tetrad effect.⁽⁹,¹⁰⁾

The authors wish to express their gratitude to Mr. J. L. Farrell of the Institute for Atomic Research, Iowa State University, for preparing the Hehmb used in the experiment, and to Mr. T. Tsutsui of the Computational Center, Tokai Research Establishment, Japan Atomic Energy Research Institute.

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