J. Chem. Thermodynamics 114 (2017) 83–92

Contents lists available at ScienceDirect

J. Chem. Thermodynamics

journal homepage: www.elsevier.com/locate/jct

The impact of mixed solvents on the complexation thermodynamics of Eu(III) by simple carboxylate and amino carboxylate ligands

Heather M. Felmy[a,*], Kevin T. Bennett[a,1], Sue B. Clark[a,b]

[a] Department of Chemistry, Washington State University, Pullman, WA 99164, USA
[b] Pacific Northwest National Laboratory, Richland, WA 99354, USA

ARTICLE INFO

Article history:
Received 31 December 2016
Received in revised form 3 May 2017
Accepted 4 May 2017
Available online 12 May 2017

Keywords:
Trivalent f-elements
Methanol
N,N-dimethylformamide
Solvation
HIBA
2-Aminoisobutyric acid

ABSTRACT

To gain insight on the role of mixed solvents on the thermodynamic driving forces for the complexation between trivalent f-elements and organic ligands, solution phase thermodynamic parameters were determined for Eu(III) complexation with 2-hydroxyisobutyric acid (HIBA) and 2-aminoisobutyric acid (AIBA) in mixed methanol (MeOH)-water and N,N-dimethylformamide (DMF)-water solvents. Included in this study were the determination of mixed solvent autoprotolysis constants (pK_s) as well as the thermodynamic formation constants: log β, ΔG, ΔH, and ΔS, for ligand protonation and Eu(III)-ligand complexation utilizing potentiometry and calorimetry techniques. The results presented are conditional thermodynamic values determined at an ionic strength of 1.0 M $NaClO_4$ and a temperature of 298 K. It was found that moving from an aqueous solution to a binary aqueous-organic solvent affected all solution equilibria to some degree and that the extent of change depended on both the type of mixed solvent and the ligand in each study. The ability to understand and predict these changes in thermodynamic values as a function of solvent composition provides important information about the chemistry of the trivalent f-elements.

1. Introduction

A major challenge in the nuclear fuel cycle is the separation of the trivalent lanthanides (Ln(III)s) and the actinides (An(III)s). This is important for both minimizing the volume of highly radioactive waste with the removal of the long lived minor actinides and for reprocessing spent nuclear fuel to recycle useful materials and minimize volumes of waste [1–3]. The removal of neutron poisons, some of which are the Ln(III)s, is needed to reprocess spent nuclear fuel. Future fuel cycles which include partitioning and transmutation also require the separation of the Ln(III)s from the An(III)s. This separation of the Ln(III)s and An(III)s, however, poses a challenge due to their very similar chemical behavior.

In polar solvents such as water, the highly charged trivalent f-elements are known to form extended ordered solvation spheres around the cations [4]. These solvation spheres can be disrupted when the metal cations are complexed by organic ligands, resulting in a favorable entropy gain. This is often the driving force for complex formation. The slight differences in ionic radii between the Ln(III)s and An(III)s, which result in slight differences in charge density, should cause differences in the solvation of the cations. These solvation differences have been used in the extraction of the An(III)s over the Ln(III)s which was accomplished with the use of the Cyanex 301 (bis-(2,4,4-trimethylpentyl)dithiophosphinic acid) extractant, which utilized the difference in hydration number between the An(III) and Ln(III) metal-ligand complexes [5]. In these extractions, the An(III) complexes were extracted with no water molecules while the Ln(III) complexes included one or two water molecules. This could account for the increased affinity for the organic phase of the An(III) complexes resulting in high separation factors between the An(III)s and Ln(III)s of 2000–10,000 [6]. Cyanex 301 is not suited for large scale reprocessing, however, due to its instability in the radiolytic and highly acidic conditions necessary for reprocessing, therefore new separation schemes are needed [1,7,8]. From these results, it is evident that slight differences in solvation between the Ln(III)s and An(III)s can be exploited to improve separations. Mixed aqueous-organic solvents can be used to alter the solvation of the trivalent f-elements and the ability to predict how these solvation changes affect the thermodynamic driving forces for complexation is important in the design of new separation schemes.

When moving from a purely aqueous solution to a mixed aqueous-organic solvent, the solvation sphere around the f-element cations likely changes [9,10]. Studies on the solvation of

---

[*] Corresponding author.
E-mail address: heather.felmy@wsu.edu (H.M. Felmy).
[1] Present Address: Los Alamos National Laboratory, Los Alamos, NM 87545, USA.

http://dx.doi.org/10.1016/j.jct.2017.05.003
0021-9614/

the Eu^{3+} cation in mixed aqueous-organic media indicate less solvation by solvents such as methanol (MeOH) than water [9]. This suggests that the Eu^{3+} cation is preferentially solvated by water in mixed water-MeOH solvents. Conversely, other solvents such as N,N-dimethylformamide (DMF) solvate Eu^{3+} to a greater extent than water indicating a preference for DMF over water in mixed water-DMF solvents.

This solvation by organic solvents can therefore affect the extent of complexation of the f-elements with organic ligands and can affect the thermodynamic driving forces. This has been demonstrated where metal-ligand stability constants changed with a change in solvent composition for mixed aqueous-organic solvents [11–14]. In one study, it was found that the stability constants for Eu(III) and Cm(III) complexed with *n*PR-BTP (2,6- bis(5,6-dipropyl-1,2,4-triazin-3-yl)pyridine) increased with increasing MeOH content of the solvent [11]. In other studies, the stability constants between transition metals such as Cu^{2+}, Ni^{2+}, Co^{2+}, and Fe^{3+} and carboxylate and amino carboxylate ligands were determined in mixed aqueous-organic solvents. It was found that an increase in the concentration of an organic solvent such as MeOH, dioxane, or acetone usually caused an increase in the metal-ligand stability constants. Ligand protonation constants (pK_a values) are also important, as the extent of deprotonation of the ligand will affect the extent of complexation with the metal. The pK_a values have been shown to also generally increase with the addition of these organic solvents to an aqueous solution [12–16]. These stability constants reflect changes in the distribution of species in solution and are therefore important for the study of mixed solvents.

The goal of this study is to gain further insight on the role of mixed solvents on the thermodynamic driving forces of trivalent f-element complexation. This will allow for better predictions of changes in complexation thermodynamics which will aid in the design of better separation schemes for the Ln(III)s and An(III)s. To accomplish this goal, two binary solvent systems with different solvation characteristics were studied: MeOH-water solvents and DMF-water solvents. For this study, the complexation of Eu(III) with two ligands, 2-hydroxyisobutyric acid (HIBA) and 2-aminoisobutyric acid (AIBA), was studied using potentiometry and calorimetry to determine the ligand protonation stability constants (pK_a values), the metal-ligand complexation stability constants (log β values), as well as each corresponding reaction free energy (ΔG), enthalpy (ΔH), and entropy (ΔS). The structures of these two ligands are shown in Fig. 1 in the primary protonation state for this study.

HIBA has been used extensively in chromatographic separations and has been used to separate the lanthanides from one another, making for a good comparison for our aqueous solution results [17–19]. AIBA was chosen as the second ligand for this study due to its similar structure to HIBA; the only difference between the two ligands being the hydroxyl group on the alpha carbon of HIBA and the primary amine on the alpha carbon of AIBA. Previous studies on similar ligands indicate that the hydroxyl group increases the metal-ligand stability constants and the protonated amine decreases the stability constants with the Ln(III)s, compared to ligands without these functional groups on the alpha carbon [20]. The enthalpy values were also more exothermic and the entropy values were less favorable for the alpha hydroxy ligands, leading to a model of ligand coordination to the metal center through the carboxylate group, with hydrogen bonding through the alpha hydroxy group and a second-sphere water molecule, causing a smaller entropy gain [21–28]. This model explains the larger stability constants for alpha hydroxy ligands due to the more favorable enthalpy from the stabilization of the structure. Spectroscopic evidence, however, has led to differing conclusions as to whether or not the alpha hydroxy group of the ligand is actually directly coordinated to the metal cation [29–32]. By comparing the thermodynamic data for ligands differing only in alpha functional groups, including HIBA and AIBA in this study and previous results on isobutyric acid, we are able to draw conclusions about the role of the alpha group of the ligand on the complexation with Eu(III).

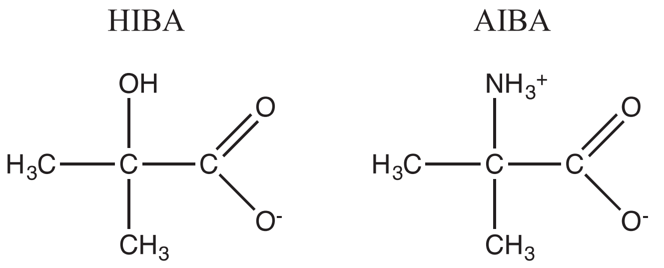

Fig. 1. Chemical structures of 2-hydroxyisobutyric acid (HIBA) in the deprotonated L^- form of the ligand and 2-aminoisobutyric acid (AIBA) in the HL form of the ligand.

2. Experimental

2.1. Chemicals

All chemicals were used without further purification. All solutions were prepared using boiled 18 MΩ water and controlled to an ionic strength of 1.0 M with $NaClO_4$. All NaOH solutions were prepared from a 1 M standard solution and the concentration was determined through titration with potassium hydrogen phthalate using a phenolphthalein indicator. The $HClO_4$ solutions were prepared from a 70% concentrated stock solution and the concentration of each working solution was determined through titration with NaOH with the use of a phenolphthalein indicator. A stock solution of $Eu(ClO_4)_3$ was prepared by dissolving Eu_2O_3 in enough $HClO_4$ to reach a final pH of about 1.5. The concentration of the metal was determined by titration with EDTA using a xylenol orange indicator with an acetate buffer to maintain a pH of 4.5. The concentration of $HClO_4$ in the $Eu(ClO_4)_3$ solution was determined by titration with NaOH using an Orion 8102 BNUWP Ross Ultra Combination pH electrode to determine the endpoint. Solutions of HIBA were prepared by neutralizing the solid acid form of the ligand in enough NaOH to obtain solutions of 50–80% neutralized HIBA. Solutions of AIBA were dissolved as the zwitterion form of the ligand and partially acidified (10–50%) with $HClO_4$ to lower the pH in order to minimize the formation of hydrolysis products of Eu(III). All working solutions were prepared in each percent by volume (% (v/v)) mixed organic-aqueous solvent by adding the appropriate amount of MeOH or DMF using an 865 Dosimat plus (Metrohm) to give the correct final percent MeOH or DMF of the total volume of solution. Solutions of $HClO_4$ and NaOH for the DMF-water mixed solvent systems (used in the calibration of the pH electrodes and in the pK_a titrations) were kept aqueous to avoid the hydrolysis of DMF by strong acids and bases.

2.2. Potentiometry

Potentiometry was used to determine all stability constants in this study and all experiments were performed using a Mettler Toledo DL50 Graphix autotitrator. The temperature was controlled to 298.2 ± 0.1 K with a water bath connected to a water-jacketed titration vessel. The solutions were stirred continuously using a stir plate and Teflon stir bar. The solutions were blanketed with argon to prevent carbonate contamination during the titrations. The inner solution of each electrode was replaced with 1.1 M NaCl in the appropriate solvent. All experiments were done using either