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Thermodynamic equilibrium constants for important isosaccharinate reactions: A review

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ABSTRACT

Isosaccharinic acid is a cellulose degradation product that can form in low-level nuclear waste repositories and is known to form strong complexes with many elements, including actinides, disposed of in these repositories. We 1) reviewed the available data for deprotonation and lactonisation constants of isosaccharinic acid, and the isosaccharinate binding constants for Ca, Fe(III), Th, U(IV), U(VI), Np(IV), Pu(IV), and Am(III), 2) summarized complexation constant values for predicting actinide behavior in geologic repositories in the presence of isosaccharinate, and 3) outlined additional studies to acquire reliable thermodynamic data where the available data are inadequate.

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1. Introduction

Isosaccharinic acid (HISA(aq)), a cellulose degradation product [1–4], may be produced in significant quantities in low-level nuclear waste repositories [1]. Of the three different forms of HISA(aq) [alpha, (2S,4S)-2,4,5-trihydroxy-2-(hydroxymethyl) pentanoic acid; beta, (2R,4S)-2,4,5-trihydroxy-2-(hydroxymethyl) pentanoic acid; and xylo, 3-deoxy-2-C-hydroxymethyl-D,L-tetronic acid], the alpha form is the most ubiquitous and is the form for which a large quantity of thermodynamic data is available. In the relatively acidic region each of the three forms of HISA(aq), upon losing a water molecule, produces a related cyclic molecule [a lactone, ISL(aq)] that affects the total concentration of HISA(aq) and thus its total complexing ability. In this document HISA(aq) and ISL(aq) refer to the alpha form, unless otherwise identified, which is the focus of this review. The α-HISA(aq), in addition to being known as (2S,4S)-2,4,5-trihydroxy-2-(hydroxy methyl) pentanoic acid, is also known by several other names [3-deoxy-2-C-(hydroxymethyl)-d-erythro-pentanoic acid; d-gluco-isosaccharinic acid; α-d-isosaccharinic acid; isosaccharinic acid; α-d-glucoisosaccharinic acid; α-glucoisosaccharinic acid; α-isosaccharinic acid)] [5]. The structures of α-HISA(aq) and α-ISL (aq) are shown in Fig. 1.

Isosaccharinic acid forms strong complexes with many elements, especially with actinides (Th, U, Np, Pu, Am) that are of major concern in disposing actinide wastes in low-level nuclear waste repositories. Although ISA complexes of major elements (e.g., Na, Ca, Fe)[1] present in geologic environments would not themselves be important from a nuclear waste standpoint, their importance lies in the fact that they compete with radioactive elements for complexation with ISA and thus can modify the final impact of ISA in potentially mobilizing radioactive elements in low-level nuclear waste repositories. Therefore, reliable thermodynamic data for protonation constants of isosaccharinate, lactonisation constants of HISA(aq), isosaccharinate complexes of actinides, and complexes of major elements in geologic environments (e.g., Ca, and Fe) are required to reliably predict actinide behavior in geologic environments containing HISA(aq). The existing data on these various aspects of α-HISA complexes are critiqued in this document. The available thermodynamic data for ISA complexes, especially for actinides, is very limited. A cursory look at the values that we recommend in this article shows that most of the values are based on our publications. This is not by design, but because in most cases they are based on 1) our extensive published critical reviews, and 2) our extensive experimental studies where no other data are available for the given system, or where all of the available reliable

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[1] Sodium does not form strong complexes with ISA$^-$ and thus can be ignored from further consideration of its impact on affecting ISA$^-$ concentration.
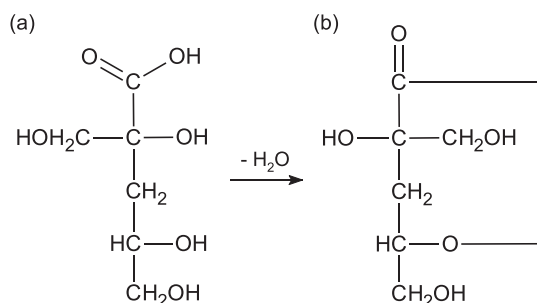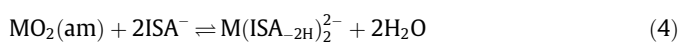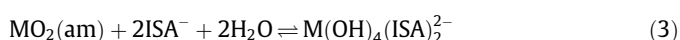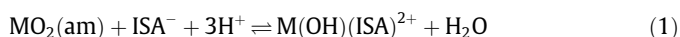
(a)   (b)

Fig. 1. Chemical structures of α-HISA (a) and α-ISL (b) after Hummel et al. [6].

literature data are shown to be consistent with the data presented in our publications.

There are two potential binding sites for metal ions on isosaccharinic acid, one resulting from the deprotonation of the carboxylate group and the other from deprotonation of one or more alcohol hydroxyl groups. Current experimental techniques (solubility, solvent extraction, adsorption, etc.) used in past studies cannot differentiate between these two types of binding sites. However, if the H^+ and ISA^- dependence of the reactions involving these two types of binding sites that result in similarly charged complex species is the same, then the data can be equivalently modeled. For example, reactions (Eqs. (1) and (2)) can be modeled using one equilibrium constant value and reactions (Eqs. (3) and (4)) with another equilibrium constant value because of their similarity in H^+ and ISA^- dependence of the reactions; they differ primarily in the number of water molecules participating in the overall reaction. In this document we have opted to represent the reactions as if deprotonation of the carboxylate group is the binding site, partly because it is known that deprotonation of the alcoholic OH groups does not occur below pH ∼ 12 [6,7].

$$MO_2(am) + ISA^- + 3H^+ \rightleftharpoons M(OH)(ISA)^{2+} + H_2O \tag{1}$$

$$MO_2(am) + ISA^- + 3H^+ \rightleftharpoons M(ISA_{-H})^{2+} + 2H_2O \tag{2}$$

$$MO_2(am) + 2ISA^- + 2H_2O \rightleftharpoons M(OH)_4(ISA)_2^{2-} \tag{3}$$

$$MO_2(am) + 2ISA^- \rightleftharpoons M(ISA_{-2H})_2^{2-} + 2H_2O \tag{4}$$

2. Results and discussion

Results of our review for deprotonation and lactonisation constants and ISA reactions with Ca, Fe, Th, Np, U, and Am are discussed in the following sections.

2.1. Deprotonation and lactonisation constants of α-HISA(aq) and the Ca-ISA system data

Several investigators [8–16] have reported the deprotonation constants of α-HISA(aq) (Eq. (5)) and $\log_{10}K$ values for this reaction to vary from approximately 3.3 to 4.5. Most of these studies [8,10–16] used potentiometry or electro-migration methods for these investigations, which are incapable of differentiating between different HISA species (i.e. HISA(aq), ISA^-, and ISL(aq)) that are significant in the same acidic pH region, and thus the reported values for Eq. (5) cannot possibly be correct. For this reason, Hummel et al. [6] in their review of these data state that the reported values purportedly for the reaction in Eq. (5) are in reality for the composite reaction (Eq. (6)), with which we agree, and they recommend a $\log_{10}K^0$ value of 4.0 ± 0.5 for this reaction. In contrast to the deprotonation reaction of HISA(aq), only two investigators [7,17] report the $\log_{10}K^0$ values for the lactonisation constant (Eq. (7)). The

reported values are 0.37 ± 0.07 [7] and ∼0.84 ± 0.04 [17]. Reliable values for the reaction in Eq. (5) can be obtained by ^{13}C nuclear magnetic resonance (NMR). However, there are no reliable direct methods of identifying ISL(aq),[2] and thus reliable values for Eqs. (6)–(8) cannot be obtained by direct methods.

$$HISA(aq) \rightleftharpoons ISA^- + H^+ \tag{5}$$

$$HISA(aq) + \rightleftharpoons ISL(aq)ISA^- + H^+ \tag{6}$$

$$HISA(aq) \rightleftharpoons ISL(aq) + H_2O \tag{7}$$

Rai and Kitamura [18] conducted a critical review of the thermodynamic data pertaining to this system and report a methodology of obtaining reliable values for deprotonation and lactonisation constants. This methodology involves the use of 1) NMR based reliable data for the deprotonation constant of α-HISA(aq) [9] by taking advantage of the fact that the NMR-based deprotonation values for β-HISA(aq) and X-HISA(aq) [19,20] are similar to the only available value for α-HISA(aq), which provides further confidence in the selected value, 2) extensive Ca(ISA)₂(cr) solubility data[3] [7,15] in the acidic region where the lactonisation constant and the solubility product of Ca(ISA)₂(cr) are simultaneously fitted using a) the SIT model, b) the equilibrium constant value for (CaISA⁺) recommended by Hummel et al. [6] based on studies that included ion exchange and potentiometric studies [21,22] conducted at high pH where the dominant isosaccharinate species is ISA^-, and c) the NMR-based value for the deprotonation constant of α-HISA(aq). Rai and Kitamura [18] recommend $\log K^0$ of −3.27 ± 0.01 for [Eq. (5)], −3.88 ± 0.09 for [Eq. (6)], 0.49 ± 0.09 for [Eq. (7)], −3.76 ± 0.09 for (Eq. (8)), −6.4 ± 0.09 for (Eq. (9)), and 1.70 ± 0.09 for (Eq. (10)), which we accept. Rai and Kitamura's reinterpretation of extensive Ca(ISA)₂(cr) solubility data provides $\log K^0$ values for reactions (Eqs. (9) and (10)) that are consistent with the average of the available values recommended by Hummel et al. [6], which lends credence to the values for other α-HISA reactions reported here.

$$ISL(aq) + H_2O \rightleftharpoons ISA^- + H^+ \tag{8}$$

$$Ca(ISA)_2(cr) \rightleftharpoons Ca^{2+} + 2ISA^- \tag{9}$$

$$Ca^{2+} + ISA^- \rightleftharpoons CaISA^+ \tag{10}$$

2.2. Iron

Only two studies [16,23] report the equilibrium constant values for the formation of ISA complexes of Fe. Based on potentiometric titrations in the presence of 1.05 mol.kg⁻¹ $NaClO_4$ acidic (−$\log_{10}H^+$ concentrations varying from 1.5 to 4.5) solutions, Rao et al. [16] reported respective $\log_{10}K$ values of 5.06 ± 0.17, 8.51 ± 0.15, 11.0 ± 0.16, and 12.99 ± 0.17 for the formation of Fe(ISA)ₙ³⁻ⁿ as n varies from 1 to 4 (Eqs. (11)–(14)). Using the SIT model[4] [24] to

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[2] Although NMR can identify ISL(aq) species, the NMR-based lactonisation constant values show significant dependence on pH [18], which is not correct. We surmise the pH dependence may be due to the fact that the lactonisation reaction is relatively slow. This is one of the reasons Rai and Kitamura [18], discussed in the following paragraph, preferred to calculate this value from the solubility data so the experiments can be conducted over longer equilibration periods to be certain that equilibrium is achieved.

[3] Ca(ISA)₂(cr) solubility was determined as a function of 1) pH ranging from 1 to 14, 2) pH ranging from about 2.9 to 11 and at fixed 0.036 mol.kg⁻¹ $CaCl_2$, 3) $CaCl_2$ concentrations ranging from 0.03 to 0.52 and at a fixed pH value of approximately 8, and 4) ISA concentrations ranging from 0.01 to 0.19 and at a fixed pH value of approximately 8.2.

[4] That included ε(Na⁺, ClO_4^-) = 0.01, ε(Na⁺, ISA^-) = −0.07, and ε(Fe³⁺, ClO_4^-) = 0.56 from Hummel et al. [6]; ε(FeISA²⁺, ClO_4^-) = 0.4 and (Fe(ISA)₂⁺, ClO_4^-) = 0.27 based on average of M²⁺ or M⁺ with ClO_4^- reported in Rand et al. [24]; (Fe(ISA)₃⁰, ClO_4^-) = 0.00 based on convention; and assuming (Fe(ISA)₄⁻, ClO_4^-) = ε(Na⁺, ISA^-) = −0.07.