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STRUCTURE AND AQUEOUS SOLUBILITY OF SODIUM ISOSACCHARINATE

Ranko P. Bontchev, Robert Moore, Mark Tucker and Kathleen Holt
Sandia National Laboratories, P.O. Box 5800, MS-0779,
Albuquerque, NM 87185
rcmoore@sandia.gov

INTRODUCTION

It has been recently shown that Isosaccharinic acid, $C_6H_{12}O_6$ (ISA), and its derivatives have potential applications in decontamination and remediation processes for materials and sites contaminated with actinides. ISA forms strong complexes with actinides in the IV oxidation state in the acidic and basic pH regions[1-3]. The use of ISA as a chelating agent in decontamination formulations has recently been proposed[4,5]. The most widely studied form of ISA, calcium ISA (Ca ISA), has a low aqueous solubility that makes it less than ideal for use in water-based decontamination formulations. Sodium ISA (Na ISA) is reported to have a relatively high aqueous solubility[2,3]. However, the reported information on sodium ISA solubility is qualitative with no specific values reported. In a recent investigation[6] we reported on the crystal structure of Na ISA and its significant differences from the calcium form. In this work, we report the solubility of Na ISA as a function of pH and examined the differences in crystal structure of Na ISA and Ca ISA. The results from our previous work[6] can be used to explain the difference in aqueous solubility between the sodium and calcium forms.

EXPERIMENTAL

Calcium ISA was prepared using the procedure described by Whistler and BeMiller[7]. Sodium ISA was prepared from the calcium form by dissolving 10.0g Ca ISA in 1 L of D.I. water at 100°C. A stoichiometric amount of NaOH was added and mixture was allowed to cool and shaken for 3 days. Precipitated calcium hydroxide and excess Ca ISA were removed by centrifugation. Na ISA was isolated by evaporation of the water in

a 60°C thermostated vacuum oven. The purity of the Na ISA was verified by XRD and FT-IR.

Solubility experiments were performed by mixing excess Na ISA in 25 mL of D. water in 50 mL Oak Ridge centrifuge tubes at 22°C. HCl and NaOH were used to adjust solution pH. The pH of each solution was constant after 3 days and the mixtures were shaken for a total of 7 days. The solubility of Na ISA was determined gravimetrically by separating the solids by centrifugation followed by sampling of the solution phase and filtration through 0.2 µm syringe filters. The solution samples were weighed and the amount of Na ISA in solution determined by evaporating the water in a 60°C thermostated vacuum oven for 2 days. The solids were then ashed at 800°C and a material balance was performed to correct for the addition of HCl and NaOH for pH adjustment and to verify the purity of the Na ISA.

RESULTS

The results of solubility experiments are given in Figure 1. The solubility of Na ISA was determined to be 1.18 to 1.23 M and shows no effect of pH between pH 5 to 10. The error bars represent the average of two measurements per pH value, the uncertainty in the gravimetric method and results from calculations from ashing the solids. The solubility of Ca ISA is reported to be at the millimolar level[1-3].

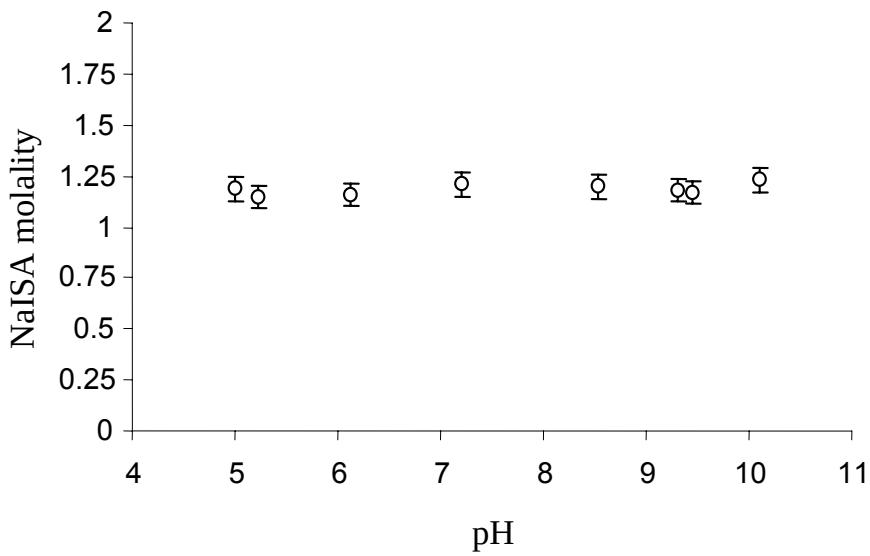

Figure 1. Solubility of sodium ISA in water at 22°C between pH 5 to 10. Values were determined gravimetrically and corrected for added HCl and NaOH for pH adjustment.

There are several significant structural differences between the sodium and calcium form of ISA. The solid Na-ISA crystallizes with one water molecule per formula unit, $NaC_6H_{11}O_6 \cdot H_2O$. In the structure the water molecules, together with the Na^+ cations, are arranged in separate layers between the ISA species. In turn this accounts for an enhanced $(H_2O, Na^+)_{solid} \leftrightarrow (H_2O)_{solvent}$ exchange and hence for increased solubility. In

comparison, there are no solvent (H_2O) molecules in the structure of Ca-ISA. Another factor affecting the solubility properties is the type of hydrogen-bonding in both structures. As noted above, in Na-ISA the (O-H**...**O) hydrogen bonds result only in $(ISA)^-/H_2O$ layers, the connectivity in the third direction provided by O_{ISA}–Na–O_{ISA} bonding. In Ca(Sr)-ISA there is a (O-H**...**O) network expanding in all three directions together with a set of O_{ISA}–Ca/Sr–O_{ISA} bonds. The final difference between Na-and Ca-ISA concerns the metal coordination. In both cases the metal atoms are coordinated by four $(ISA)^-$ species. In Na-ISA, however, each ISA acts as a monodentate ligand, while in Ca-ISA the organic species act as bidentate ligands. As a result, each sodium atom is coordinated by five oxygen atoms ($4O_{ISA}$ + $1O_w$), while each calcium atom is coordinated by eight oxygen atoms ($8O_{ISA}$). Clearly, the Ca-coordination is much stronger compared to that of Na form[6]. All of the above structural differences between Na- and Ca(Sr)-ISA act in accord and contribute to the higher solubility of Na-ISA in water.

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LITERATURE CITED

1. Rai, D.P., L.F. Rao and Y.X. Xia, 1998. Solubility of crystalline calcium isosaccharinate. *Journal of Solution Chemistry* **27**(12), 1109-1122.
2. Rai, D., L. Rao and D.A. Moore, 1998. The influence of isosaccharinic acid on the solubility of Np(IV) hydrous oxide. Radiochim. Acta **89** 3-13.
3. Xia, Y.X., Rao, L.F. and Rai, D., 1998, Complexation of neptunium (IV) with isosaccharinate at different ionic strengths. **216**(2), p.97.
4. Holt, K., R.C. Moore, M. Tucker and F. Salas, 2002, Gel for decontamination of actinide contaminated surfaces, Proceedings of the American Chemical Society, Albuquerque, NM.
5. Moore, R.C, D. Rai and M. Tucker. (2003) The use of ISA in Decontamination Formulations . U.S. Patent Application, patent pending.
6. Bontchev, R.P. and R.C. Moore, 2003, Crystal structure of Na-ISA, submitted to Carbohydrate Research.
7. Whistler, R.L. and J.N. BeMiller, 1958, In Carbohydrate Chemistry, α–D-Isosaccharino-1,4-lactone.