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A study of the metal binding capacity of saccharinic acids formed during the alkali catalysed decomposition of cellulosic materials: nickel complexation by glucoisosaccharinic acids and xyloisosaccharinic acids

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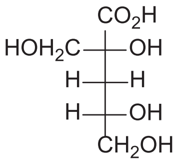
ABSTRACT

The stoichiometry of the metal complexes formed between nickel and the ligand β-glucoisosaccharinic acid (β-GISA) and a racemic mixture of enantiomers of xyloisosaccharinic acid (XISA) has been determined at both neutral and alkaline pHs. Bjerrum plots, Job's plots and conductance measurements indicated that for each of the systems one to one Ni(ligand) complexes were formed at near neutral pHs (<7.5). At intermediate alkaline pHs (7.5–13) there is evidence to support the formation and precipitation of $Ni_2(ligand)(OH)_3$ complexes, finally, at high pH (>13) sparingly soluble $Ni_2(ligand)(OH)_4$ complexes were formed. The stability constants for the Ni(β-GISA), Ni(α-GISA) and Ni(XISA) complexes formed at neutral pH were determined under identical conditions using polarographic studies. The measured stability constants for Ni(β-GISA) ($\log_{10} \beta = 1.94 \pm 0.15$) and for Ni(α-GISA)($\log_{10} \beta = 2.07 \pm 0.13$) are very similar; the value measured for the Ni(XISA) complex ($\log_{10} \beta = 0.83$) was an order of magnitude smaller. The stability constants for the $Ni_2(Ligand)(OH)_4$ complexes formed at highly alkaline pHs were determined using the Schubert method. The measured stability constant for Ni_2(β-GISA)$(OH)_4$ ($\log_{10} \beta = 30.6 \pm 0.5$) was an order of magnitude bigger than the value for Ni_2(α-GISA)$(OH)_4$ ($\log_{10} \beta = 29.0 \pm 0.5$) measured under identical conditions. Attempts to measure the stability constant for $Ni_2(XISA)(OH)_4$ were unsuccessful; $Ni_2(XISA)(OH)_4$ complexes were not present in significant amounts at high pH to allow the $\log_{10}\beta$ value to be determined by the Schubert method.

1. Introduction

Under alkaline conditions cellulosic and hemicellulosic materials undergo partial depolymerisation by the 'peeling' reaction[1–3] to generate a wide variety of 'cellulose degradation products'[4–6] (CDP). In aqueous alkaline solutions and at low temperatures saccharinic acids,[7,8] α- and β-glucoisosaccharinic acids (α-GISAs **1** and β-GISA **2**),[9] which are derived from cellulose and xyloisosaccharinic acid (XISA-**3**)[10,11] from the arabinoxylan fraction of plant cell walls, are the most abundant components of CDP representing up to 80% of the total mass.[9,12]



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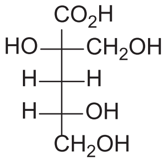

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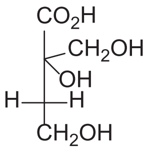

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There is growing interest in saccharinic acids for two different reasons: firstly, during the alkaline pulping of wood, in the manufacture of paper and card based products, large amounts of saccharinic acids and other hydroxyl acids are generated as waste products.[11,13,14] Pulp manufacturers would like to be able to isolate saccharinic acids and to develop commercial uses for them. The second reason why saccharinic acids are of interest is related to the influence that CDP have on the safe disposal of intermediate level radioactive waste.[15–19] It has been recognised for a number of years that the saccharinic acids generated during the depolymerisation of the cellulose and hemicelluloses present in waste storage facilities have the potential to complex with radionuclides.[20–22] It has been

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shown that complex formation increases both the aqueous solubility of radionuclides and their mobility within the ground water of a disposal facility.[19,23–26]

Supplies of α-GISA are available through the treatment of lactose with a saturated solution of calcium hydroxide[27] and material synthesised using this method have been used to determine the complexation ability of α-GISA with a large number of different metals.[24,25,28–31] Warwick et al. have reported the stoichiometry and stability constants for the formation of nickel α-GISA complexes[32] and the complexes formed with uranium.[30] Evans et al. have studied α-GISA complexes with europium, cobalt and strontium.[24] Vercammen et al. have studied the complexes of α-GISA with europium and thorium[29] and Rojo et al. have studied α-GISA complexation with Pu(IV) and Tc(IV).[33] Rai et al. have studied the thermodynamics and reactions of GISAs with calcium, thorium and neptunium.[34,35]

To date, similar studies of the complexes formed by β-GISA and XISA have not been performed. In this paper we report the results of our investigation of the stoichiometry of the complexes formed between nickel and the three ligands α-GISA, β-GISA and XISA, at both neutral and alkaline pHs, and the measurement of the stability constants of the corresponding nickel complexes.

2. Results and discussion

2.1. Determination of the stoichiometry of nickel β-GISA and nickel XISA complexes at different pHs and comparison with those for α-GISA

The procedures used to explore the stoichiometry of the complexes formed between nickel and the ligands were the same as those that have been previously employed to study nickel gluconate[36] and nickel α-GISA complexes.[32] For the nickel α-GISA complexes, the stability constants measured by Warwick et al.[32] at neutral pH ($\log_{10}\beta = 2.20–2.58$) indicated relatively weak binding of nickel and the formation of a one to one complex Ni(α-GISA) whilst at high pH (>10) a considerably larger stability constant ($\log_{10}\beta = 29.9$) for the formation of Ni_2(α-GISA)$(OH)_4$ was measured. In order to determine if β-GISA and XISA behave in a similar manner, the effect of the addition of nickel nitrate to solutions containing these ligands and also α-GISA was studied at various pHs. In the first instance, the systems were studied using UV–vis spectroscopy. For all three ligands, addition of nickel nitrate at neutral pH generated soluble green complexes, as the pH was raised above 7.5 crystalline solids precipitated and this precipitate was visible until the pH rose to above 12. At pHs of 13 and higher, when working in dilute solution, a second soluble green complex was formed.

2.1.1. Bjerrum plots[37]

To determine the ratio of nickel to hydroxide in the various different complexes, a series of titrations were performed in which the nickel to hydroxide ratio was varied whilst keeping the nickel to ligand ratio constant. Four separate Bjerrum plots were constructed: one for a solution of nickel and β-GISA, one for a solution of nickel and XISA, one for a solution of nickel and α-GISA and, for comparison purposes, a Bjerrum plot was also produced using identical conditions for the complex formed between nickel and gluconic acid (Fig. 1).

It is clear from the Bjerrum plots that all four ligands behave in a similar manner with the first inflection points in the plots being observed close to pH 8 when the nickel to hydroxide ratio was 2:3 ($Ni_2[OH]_3[L]_x$). Further addition of hydroxide increased the solution pH from 8 to 10 and this corresponded to the pH range in which solid precipitated from solution. At higher pHs the complexes become soluble again and a second inflection point was observed close to pH 10.5, at which point the nickel to hydroxide ratio was 1:2. It has previously been shown that for the gluconate and α-GISA systems the complexes formed at high pH have $Ni_2[OH]_4[L]_x$ stoichiometry.[32]

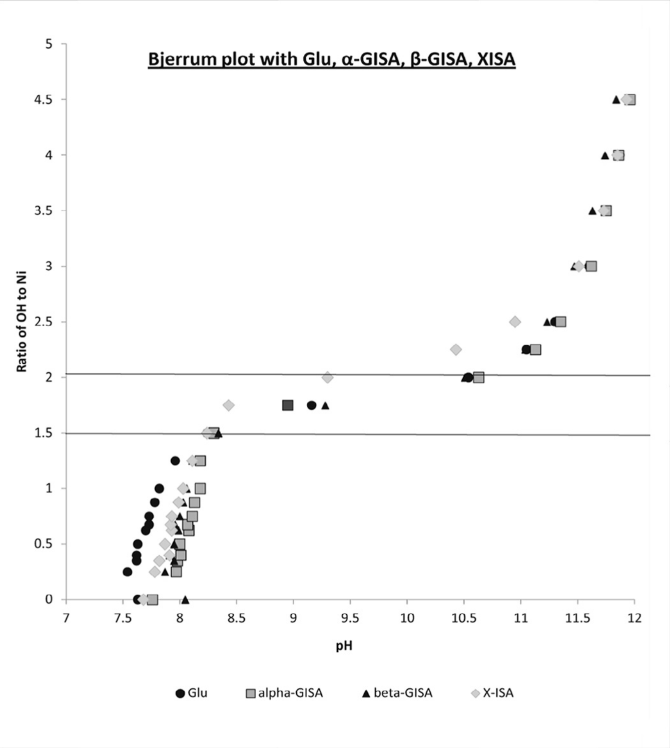

Fig. 1. Bjerrum plots; showing the change in pH on the addition of aliquots of a solution of sodium hydroxide (0.1 M) to a solution containing nickel (0.01 M) and ligand (0.01 M; circles: sodium gluconate; diamonds: sodium xyloisosaccharinate; triangles: sodium beta-glucoisosaccharinate and squares: sodium alpha-glucoisosaccharinate). The change in pH is plotted as a function of the ratio of OH to Nickel.

2.1.2. Conductometric titrations

In order to determine the ratio of nickel to ligand in the complexes formed at neutral pH and to confirm the ratio of nickel to ligand in the complexes formed at alkaline pHs, a range of conductometric titrations were performed in which solutions of ligands were titrated with nickel (at neural and high pH). At neutral pH, all three systems behaved in a similar manner: initial addition of the nickel nitrate to the ligands caused the conductance to increase linearly until one equivalent of nickel had been added (Fig. 2; 0–20 mL); after this point a small increase in the slope of the plot was observed (Fig. 2; 20–40 mL).

The results of the conductivity experiments are indicative of a rapid formation of a one to one complex of ligand with nickel at neutral pH; the initial increase in the conductance of the solution is due to the formation of the monocationic NiL complex and the addition of nitrate anion; once all the free ligand has been consumed the slope increases as additional dicationic nickel and nitrate anions are added.

When the same experiments were repeated starting at a high pH (13), again each of the systems generated similar conductance profiles. At the start, the conductance of the solutions decreased (Fig. 3) as complex formation removed ions from solution. Once the available free ligand had been consumed, further addition of both nickel and nitrate ions caused the conductance to increase (Fig. 3). The minimum in the curve was observed close to the point at which the nickel to ligand ratio was 2:1 and, combining this result with those of the Bjerrum plots, these results suggest that the stoichiometry of the complex being formed at high pH is Ni_2(Ligand)$(OH)_4$