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($\alpha$-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 $Ni_2(\beta$-GISA)$(OH)_4$ ($\log_{10} \beta = 30.6 \pm 0.5$) was an order of magnitude bigger than the value for $Ni_2(\alpha$-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] derived from cellulose and xyloisosaccharinic acid (XISA-**3)** [10,11] from the arabinoxylan fraction of plant cell walls, which are the most abundant components of CDP representing up to 80% of the total mass[9,12].

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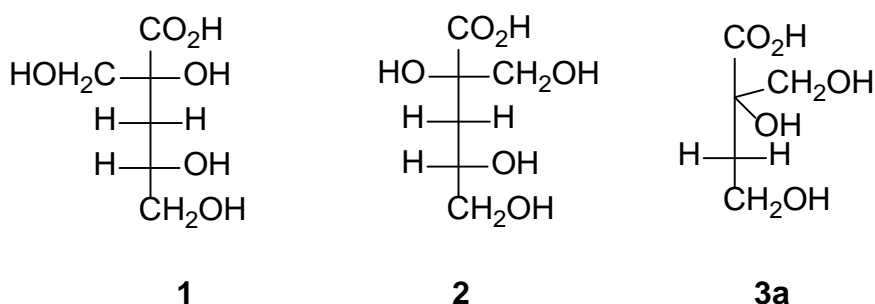
There is growing interest in saccharinic acids for two different reasons: firstly, during the alkaline pulping of wood, in the manufacture of paper and card based products, large amounts of saccharinic acids and other hydroxyl acids are generated as waste products [11,13,14]. Pulp manufacturers would 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 shown that complex formation increases both the aqueous solubility of radionuclides and their mobility within the ground water of a disposal facility[23] [19] [24-26]

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 [28,29 24,25,30,31]. 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 $Ni_2(\alpha\text{-GISA})(OH)_4$ 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).

Bjerrum plot with Glu, α-GISA, β-GISA, XISA

● Glu   ▦ alpha-GISA   ▲ beta-GISA   ◆ X-ISA
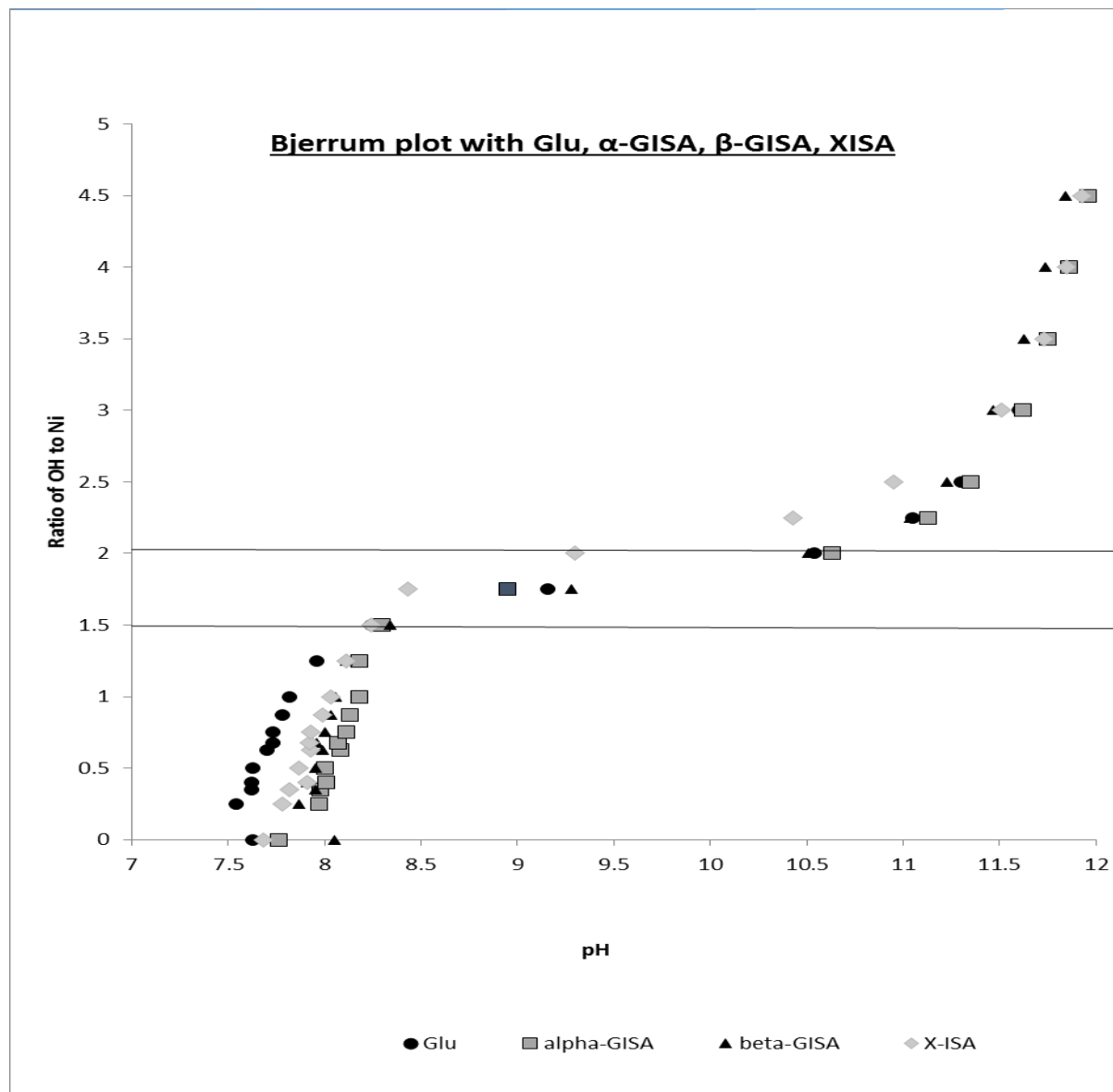
hydroxide ratio was 2:3 ($Ni_2[OH]_3[L]_x$). Further addition of hydroxide increased the solution pH from 8 to 10 and this corresponded to the pH range in which solid precipitated from solution. At higher pHs the complexes become soluble again and a second inflection point was observed close to pH 10.5, 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].

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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).

Titration A , α-GISA, β-GISA and X-ISA
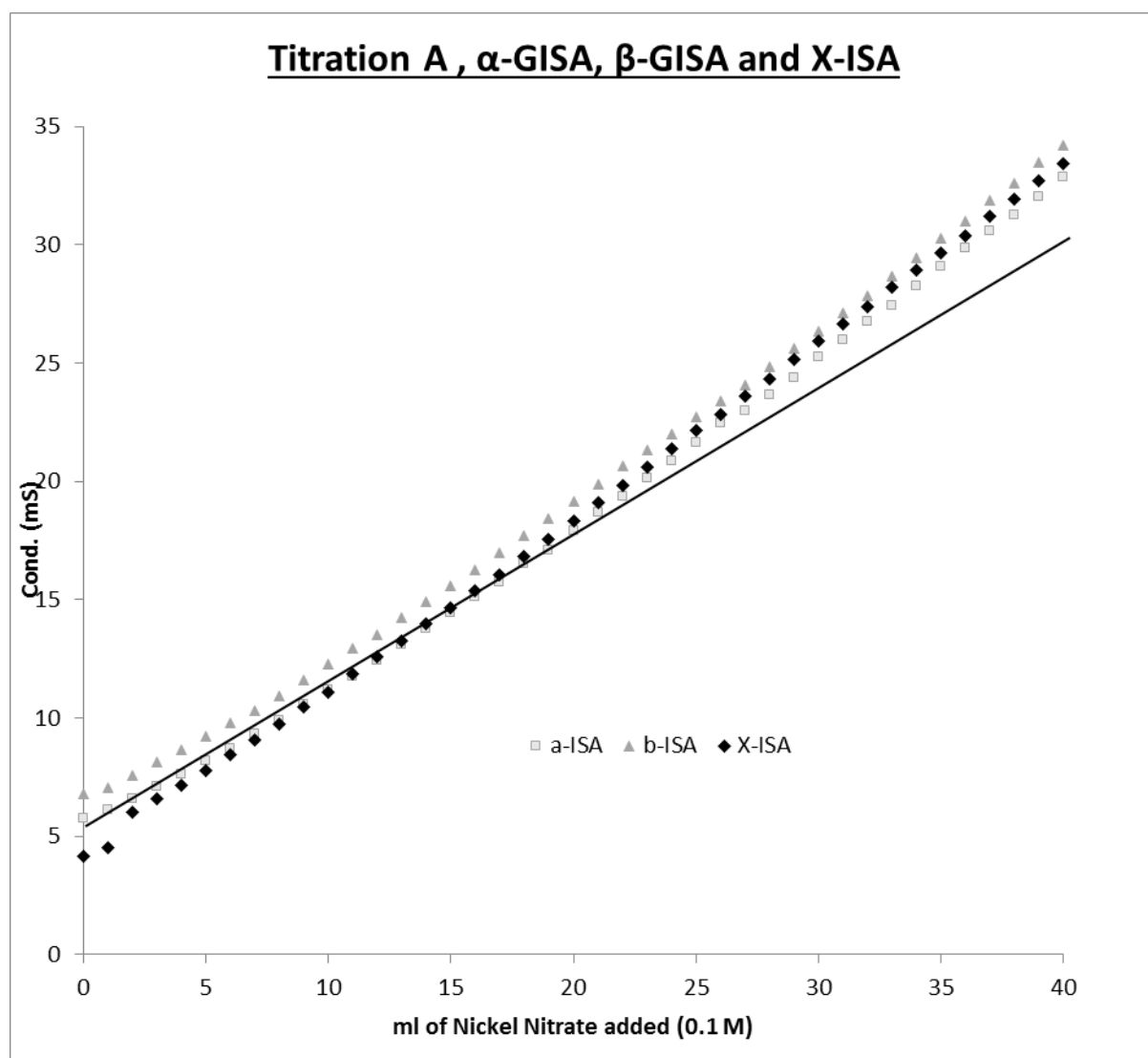
conductance of the solution is due to the formation of the monocationic NiL complex

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 $Ni_2(Ligand)(OH)_4$ and this is also in agreement with the stoichiometry determined by Warwick *et al*[32] for α-GISA.
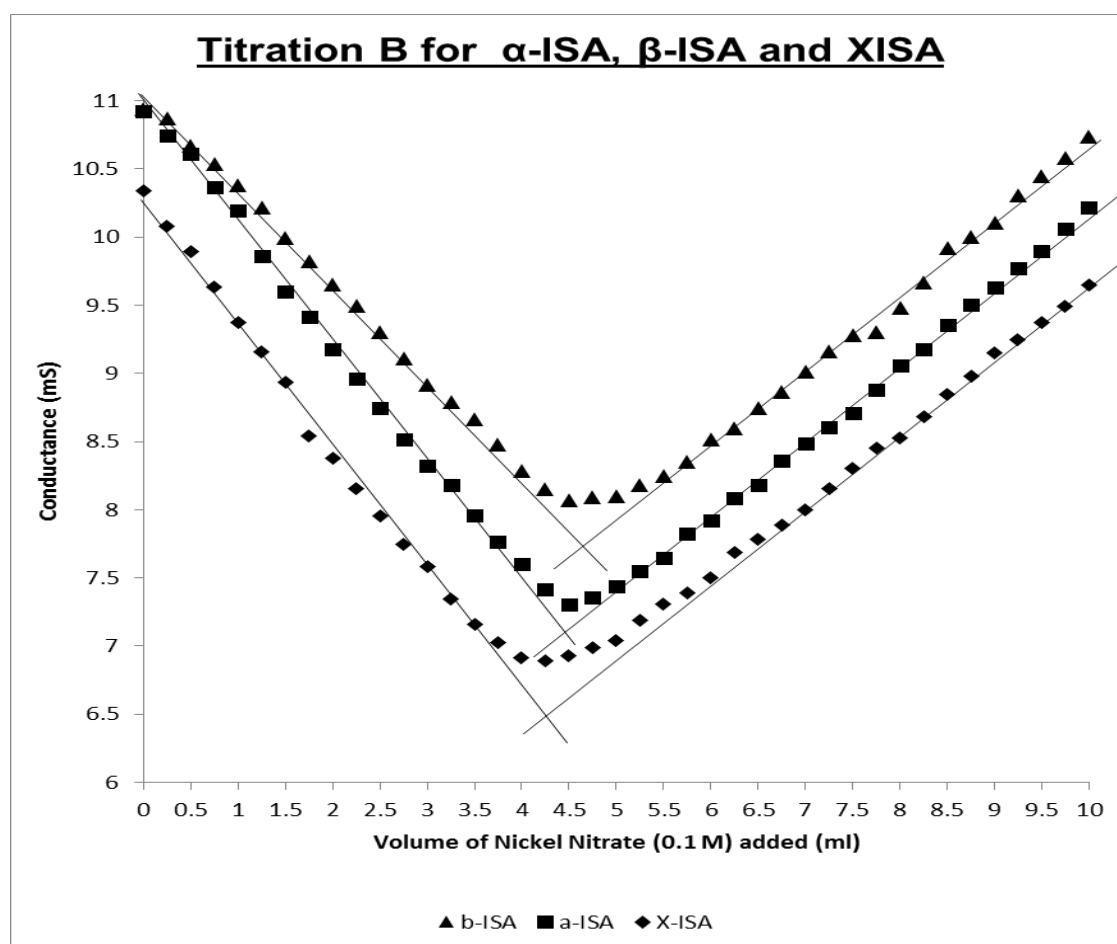

Figure 3. Titration B**,** plot of the changing conductance of an alkaline solution (pH 13) containing ligand (15 mL, 0.1M; diamonds: sodium xyloisosaccharinate;

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triangles: sodium beta-glucoisosaccharinate and squares: sodium alpha-glucoisosaccharinate) on the addition of aliquots of nickel nitrate (0.1M).

There is a small variation in the position of the minima in the titration curves carried out at high initial pH, this is likely to be a consequence of the drop in the pH of the system as the experiments were performed (data not shown) and a shift in the speciation of the metal to the mono-nickel species as the pH moves considerably below 13.
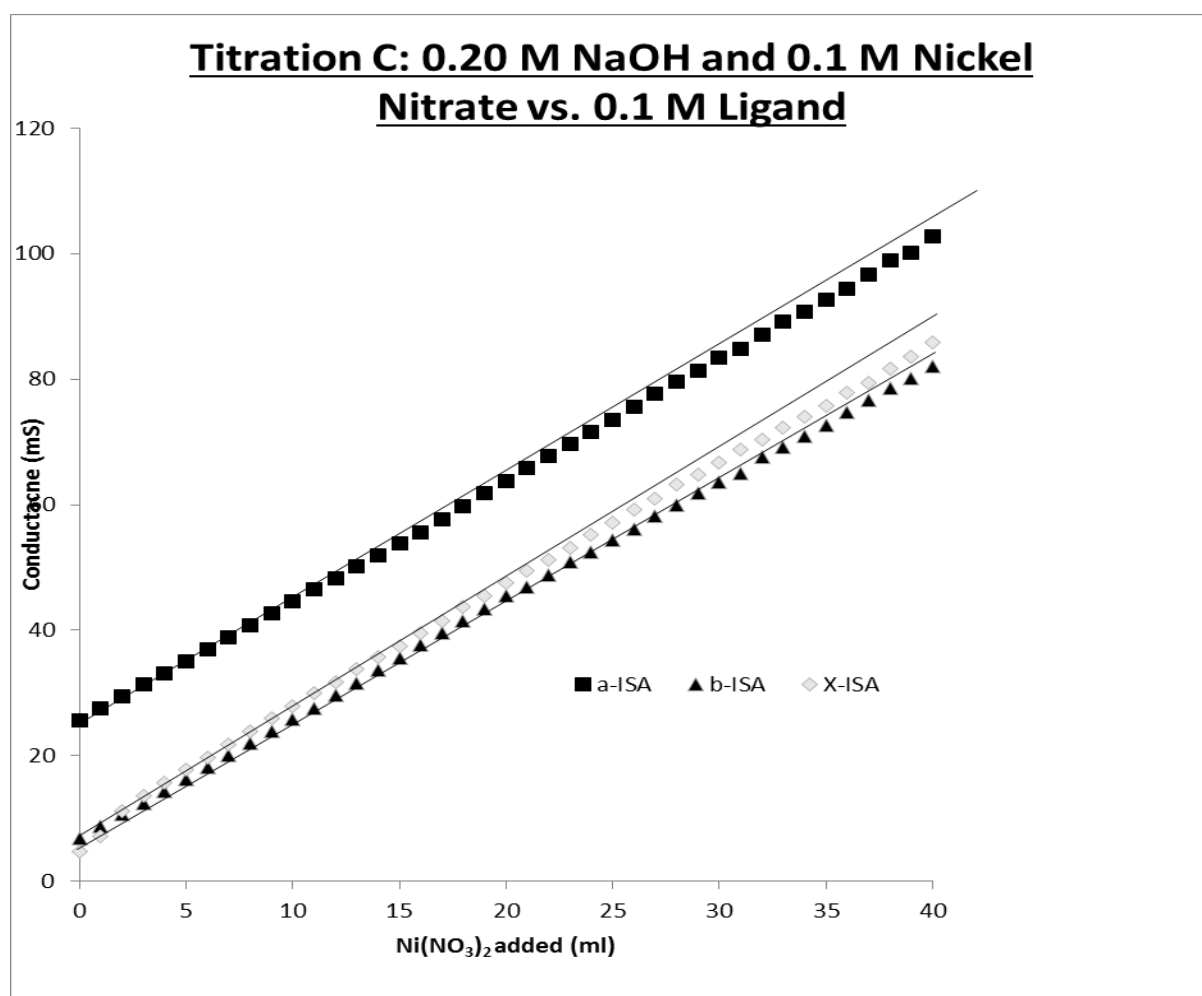

Figure 4. Titration C, plot of the changing conductance of an alkaline solution (pH 13) containing ligand (10 mL, 0.1M; diamonds: sodium xyloisosaccharinate; triangles: sodium beta-glucoisosaccharinate and squares: sodium alpha-glucoisosaccharinate) on the simultaneous addition of equal volumes of nickel nitrate (0.1M) and sodium hydroxide (0.2M).

The pH drops as hydroxide ion is removed in the formation of $M_2(L)(OH)_4$ and $M(OH)_n$ complexes. In order to avoid any changes in pH, an additional set of conductance measurements was made in which the ligand was titrated with a mixture of nickel and hydroxide in the ratio of 1:2; the value was chosen to represent the ratio of nickel to hydroxide in the complex formed at high pH, as determined in the Bjerrum plots. The new conductance profiles (Fig. 4) for the three ligands are very similar but, unfortunately, only a very subtle decrease in the slope was observed once all the available ligand was complexed. To a first approximation, the point of inflection in the plots occurs close to the point at which the ratio of metal to ligand is two to one and the result supports the $M_2(L)(OH)_4$ stoichiometry proposed for each of the complexes formed at high pH.

2.1.3 *Spectrophotometric studies*

Further confirmation of the stoichiometry of the complexes formed at neutral pH was achieved by studying the UV-visible spectra of solutions of the complexes and using Job's method[38] of continuous variations. Initial studies of the UV-absorption spectra for the various complexes formed at both neutral and high pH identified a main absorption band at 393 nm.

2.1.3.1 *Job's method[38,39]*

In Job's method of continuous variation the concentration of ligand was increased from 0 M to 0.05 M whilst the concentration of nickel in solution was reduced from 0.05 to 0 M and the experiments were maintained at constant ionic strength. When the experiment was performed at neutral pH the absorption at 393 nm increased as the mole fraction of nickel in the system increased (Fig. 5); the absorption increase matching the increased formation of the complex. An inflection point was observed in

each of the traces at the point where the ratio of ligand to nickel was one to one confirming the one to one stoichiometry of the complex formed at pH <7.5
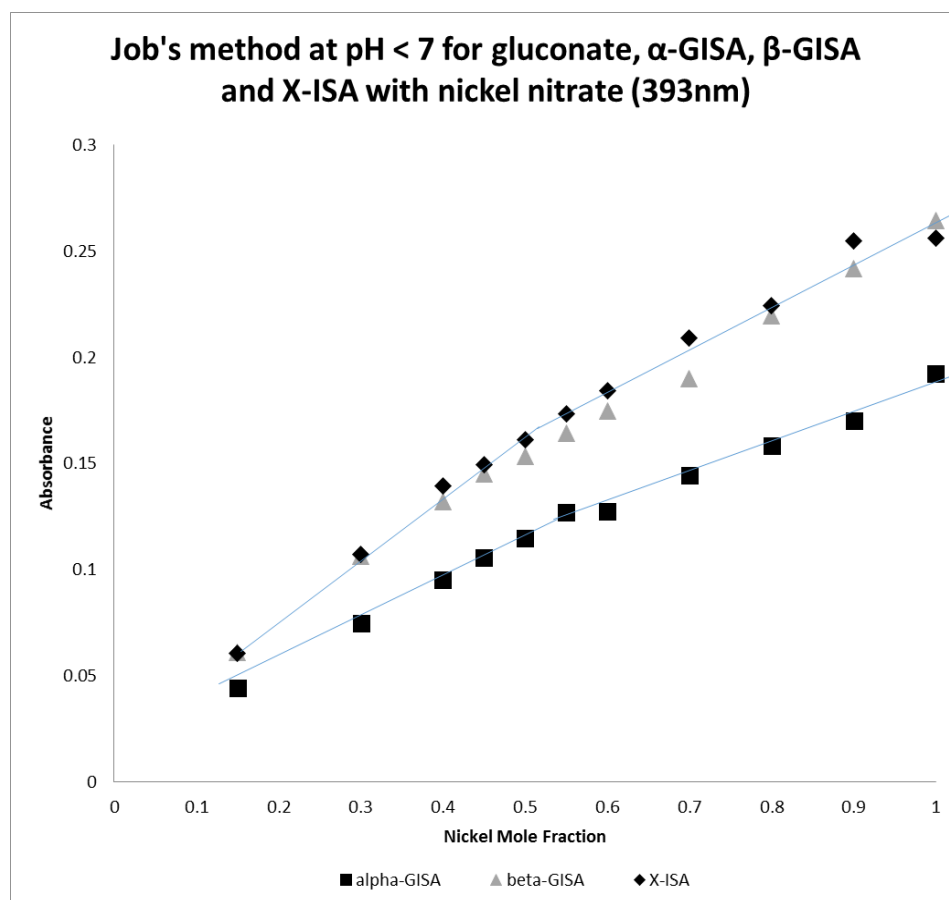

Figure 5. Job's plots; plot of the absorbance at 393 nm of solutions of constant ionic strength and at pH 7 containing different mole fractions of nickel and ligand (diamonds: sodium xyloisosaccharinate; triangles: sodium beta-glucoisosaccharinate and squares: sodium alpha-glucoisosaccharinate).

2.2 Measurement of stability constants

The stability constants for the metal ligand complexes formed at neutral pH were determined using polarography. Half-wave potentials were measured for solutions of nickel nitrate in the presence of varying concentrations of the ligands, with the ionic strength of the solutions being maintained at a constant value. Plots of the corrected half-wave potential versus the logarithm of the ligand concentration (Fig. 6a-c) where used to determine the stability constants using the Lingane equation[40]:

$$\Delta E_{1/2} = \frac{RT}{nF} \ln K_d - p\frac{RT}{nF} \ln L$$

Where, R is the ideal gas constant (8.314 JK^{-1}mol^{-1}); F is Faraday's constant (96,485 J); T is the absolute temperature (298 K); p is the coordination number of ligand per metal ion in the complex; n is the number of electrons transferred in the metal's oxidation; $\Delta E_{1/2}$ is the shift in half-wave potential; L is the ligand concentration (mol dm^{-3}) and K_d is the dissociation constant of the ligand complex. The natural log of the dissociation constant, K$_d$, is determined as the y-intercept of a plot of ln[L] vs. $\Delta E_{1/2}$.
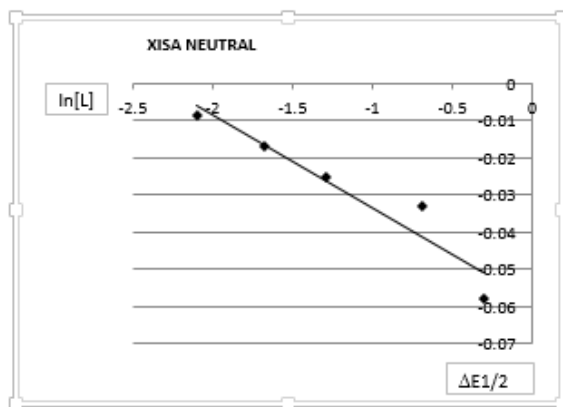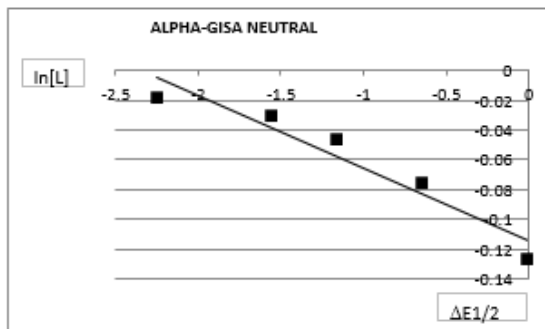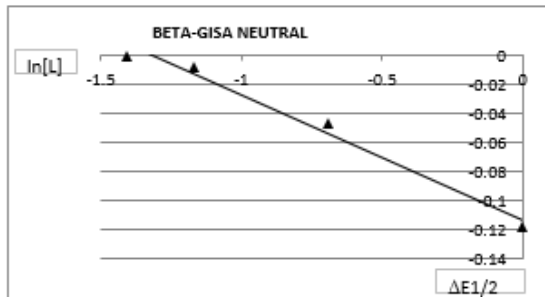
Figure 6. Determination of the stability constants at neutral pH using polarography studies: plot of the change in the half-wave reduction potential of solutions containing nickel and varying concentrations of the individual ligands. Top: beta-GISA; middle: alpha-GISA; bottom XISA.

The calculated K_d values and the corresponding stability constants are presented in the table.

$Log_{10}\beta$	Nickel Xylo-ISA	Nickel α-ISA	Nickel β-ISA
pH <7.5, Polarography	0.83 ± 0.04	2.07 ± 0.13	1.94± 0.15
pH 13; Schubert Method	Not Determined	29.0 ±0.5	30.6 ±0.5

Table: Stability Constants for the nickel complexes of α-GISA, β-GISA and XISA

Warwick *et al*[32] have previously reported the use of polarography for the measurement of the stability constants for complexes formed by nickel and α-GISA. In the experiments reported here a number of difficulties were encountered in determining an accurate value for the change in the half-wave reduction potential when working with small concentrations of nickel and low ratios of nickel to ligand. In order to improve the accuracy of the data it was necessary to employ relatively high concentrations of nickel and also high ratios of metal to ligand, to maintain a constant ionic strength the measurements had to be performed at high ionic strengths (1M) and above those used in previous experiments (0-0.3 M). As one of the main objectives of the current work was to determine the relative stability of the complexes formed, the use of a high ionic strength was considered appropriate.

The measured $log_{10}\beta$ values of 2.07 for Ni(α-GISA) and 1.94 for Ni(β-GISA) are very similar and higher than the value of 0.83 measured for Ni(XISA). As indicated previously, the stability constants will vary as the ionic strength of the solution changes, however, the value reported here for α-GISA ($log_{10}\beta$=2.07) measured at an

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ionic strength of 1M is close to the values of 2.20 & 2.58 measured by Warwick *et al* for Ni(α–GISA) at an ionic strength of 0.1M.

The structures of the complexes formed between divalent transition metal cations and polyhydroxylated carboxylic acids has been discussed by van Duin *et al*[41]: at neutral pH's (<8) ligands are expected to co-ordinate to the metal through a bidentate complexation involving the carboxylate group and the C2-α-hydroxyl. Whilst the epimeric α-GISA and β-GISA are diastereotopic, coordination to nickel will involve the functional groups at C1 and C2 which are away from the second stereocentre (C4) and, as such, the two might be expected to generate complexes with similar stability constants.

At the higher pH (13) stability constants were measured using the Schubert method[42]. The Schubert method requires measurement of the distribution of nickel between the complex in solution and nickel bound to a cation exchange resin. In the experiments reported here, ICP-MS was used to measure the solution phase nickel concentrations. It has previously been shown[32] that for a metal to ligand stoichiometry of 2:1, the form of the general algebraic expression relating the stability constant to the distribution constant is:

$$\beta = \frac{A^2 D_O}{[M_{sol}][L][OH]^4 D} \left(\frac{D_O}{D} - 1 \right)$$

where β is the stability constant, A is related to the sum of the concentration of the metal present as metal hydroxides ($A = 1 + \beta_{1HO}[OH^-] + \beta_{2HO}[OH^-]^2 + ...])$[43]. The value of A will be a constant at a fixed pH and ionic strength and the data have previously

been collated by Glaus *et al*[44] and the values (measured at an ionic strengths between 0 and 0.3 M) were extrapolated to an ionic strength of 1.0 M ($\log\beta_{1HO} = 10.16$ and $\log\beta_{2HO} = 19.35$). D_o is the distribution coefficient of the metal between the solution phase and the resin in the absence of the ligand which is also a constant and is measured in the experiment, [L] is the concentration of the ligand and M_{sol} is the concentration of the nickel in solution. Ideally, the stability constants should be determined using more than one starting nickel concentration as the stability constants may vary with the metal ion concentration however, measurements of the stability constants for a similar ligands by other workers[32] have demonstrated that the absolute values do not vary with change in M_{sol}. Due to the limited availability of the β-GISA, stability constants were only measured at a single metal concentration. The main focus of the work reported here was to establish the relative metal binding capacity of the three CDP ligands and, as such, an attempt was made to determine the stability constants (β) at the same metal ion concentration for each of the ligands: α-GISA, β-GISA and XISA.

For α-GISA and β-GISA, the stability constants were determined from plots of $\log_{10}(D')$, where $D' = \left(\dfrac{D_0^2 - DD_o}{D^2}\right)$, vs log[L] which were linear (Fig. 7). The values for

$\log_{10}\beta'$ were determined from the y-intercept of the plots and are presented in the table. Unfortunately, at high pH, it wasn't possible to determine the stability constant for XISA with nickel as it wasn't possible to determine the distribution coefficient (D) for the metal bound ligand with the same degree of accuracy as that for the other two ligands.

The measured binding constants for β-GISA (30.6) is an order of magnitude larger than the value determined for α-GISA (29.0); these results suggest that the Ni$_2$(β-

GISA)(OH_4) complex is more stable than $Ni_2(\alpha\text{-GISA})(OH_4)$. At alkaline pH, both GISA ligands form substantially more stable nickel complexes than XISA.
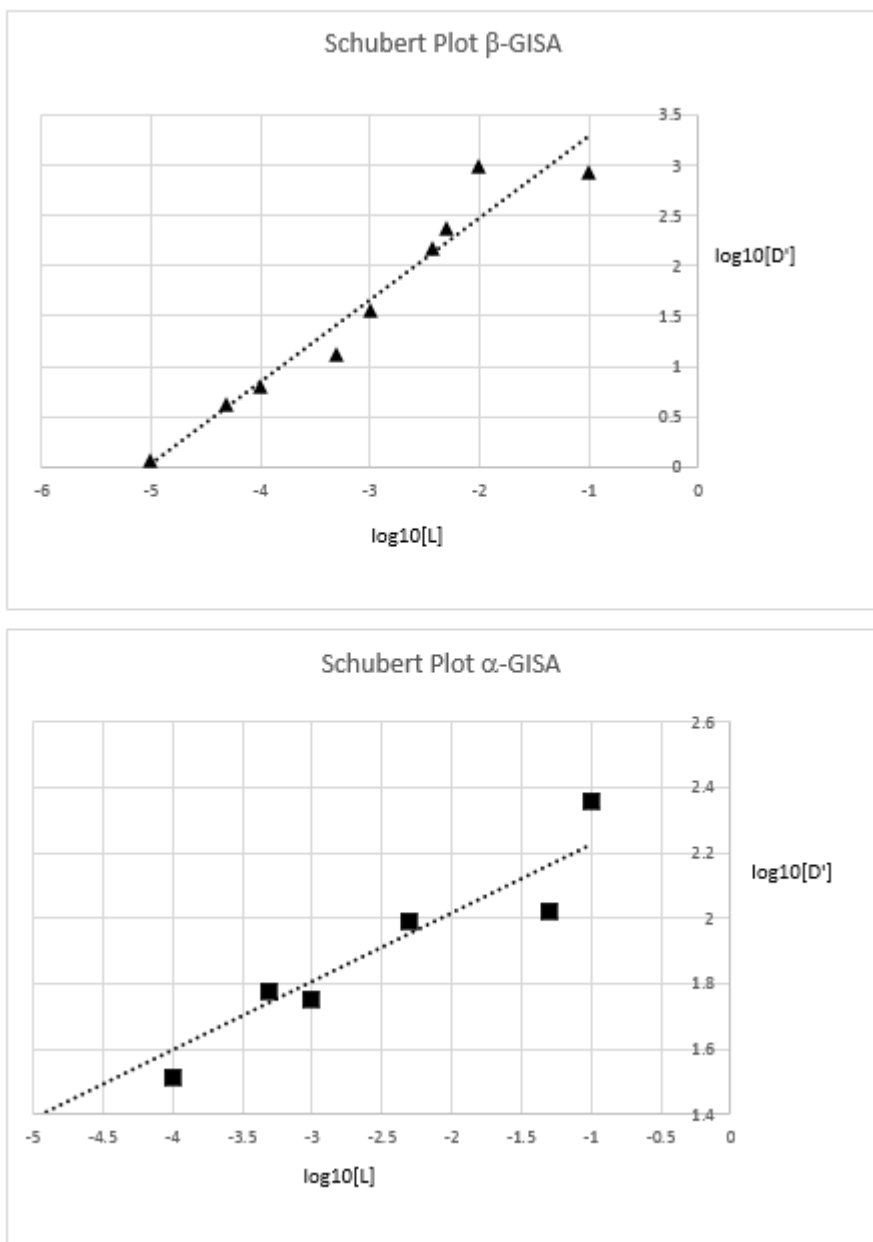

Figure 7: Determination of the stability constants at high pH using the Schubert methods: plot of log of the distribution of nickel between a cation exchange resin and solution (D'-see results section for an explanation of D' for metal-ligand stoichiometries of 2:1) versus the log of the ligand concentration. Top: beta-GISA; bottom: alpha-GISA.

The stability constant reported here for α-GISA is in close agreement with the value measured by Warwick *et al* (29.85)[32].

In the general coordination–ionisation scheme for polyhydroxylated-carboxylic acids proposed by van Duin *et al*[41] with nickel as a cation and at pHs greater than eight, coordination should involve the carboxylate group and an ionised α-hydroxyl-group (C2-OH). For the GISA epimers, coordination of the carboxylate group and the ionised C2-hydroxyl would generate the dianion **4** as the active ligand. However, at higher pHs and with more electron deficient and highly polarisable metal cations, polyhydroxylated carboxylic acids frequently coordinate as doubly ionised geminal diols; for the GISA ligands this would involve the trianion species **5**. Whilst the current experiments do not allow us to identify precise details about the type of binding present at pH 13, the presence of two geminal diol in the GISAs and only one in XISA would account for the different stability of the ligand complexes. The results of experiments studying the influence of XISA and GISA on their ability to increase solubility of radionuclides suggests that GISA is also better at forming complexes with europium and thorium compared to XISA[45].

4   **5**
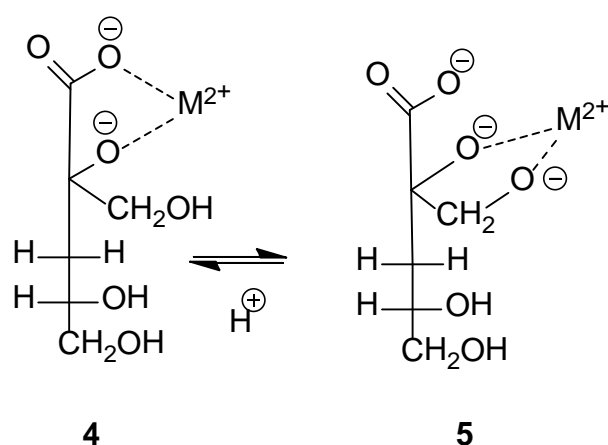
3. Conclusion

In conclusion, at neutral pHs all three ligands form one to one complexes with nickel, the stability constants for the Ni.(α-GISA) ($\log_{10}\beta$=2.07 ± 0.13) and for the Ni(β-GISA)

(log$_{10}\beta$=1.94 ± 0.15) are very similar whereas the value for Ni(XISA) (log$_{10}\beta$= 0.83± 0.04) is an order of magnitude smaller.

At high pH (13) all three ligands form Ni$_2$(Ligand)(OH)$_4$ complexes but with significantly different stability constants. The most stable complex is the Ni$_2$(β-GISA)(OH)$_4$ (log$_{10}\beta$=30.6) which is approximately an order of magnitude more stable than the Ni$_2$(α-GISA)(OH)$_4$ complex (log$_{10}\beta$=29.0 measured under identical conditions and 29.85 measured by Warwick *et al*). Our failure to be able to measure the stability constant for the Ni$_2$(XISA)(OH)$_4$ complex suggests that the ability of XISA to bind nickel is much lower than that of the glucoisosaccharinic acids.

It is clear that at neutral pH all three ligands behave in a similar manner and form relatively weak Ni.L complexes. At high pH, β-GISA forms the most stable Ni$_2$L(OH)$_4$ complex. If similar behaviour is observed in β-GISA complexation with actinides, then it is important that future safety assessments for radioactive waste disposal facilities[46] explicitly consider the impact that β-GISA will have on the mobility of radionuclides, rather than assuming that the two epimers have the same properties. This is especially pertinent if one considers the much greater solubility of the salts of the alkaline earth metals of β-GISA in aqueous solution compared to those of α-GISA which will result in precipitation of the calcium salts of α-GISA in the cement dominated radioactive waste disposal facilities.

Table here:

4. Experimental

4.1 Materials and methods

Potassium nitrate (≥99 %); sodium gluconate (≥99 %); nickel nitrate (≥98.5 %) and nickel chloride (98 %) were purchased from Sigma-Aldrich (Poole, UK). Analytical grade sodium hydroxide was purchased from Fisher Scientific (98.87 %). Sodium α-GISA and sodium β-GISA were synthesised using the procedures detailed by Whistler et al[27] and by Shaw et al[47] respectively. A racemic mixture of XISA was prepared according to the method initially described by Greenfield et al[48] and adapted by Shaw[49]. Ultra-pure water produced by a Thermo Scientific Barnstead nanopure (D23750; 0.20 µm) fibre filter was used in the preparation of all solutions. The resin used in the determination of stability constants was purchased from BioRad (Hemel Hempstead UK) and was 50W-X2 cation exchange resin.

4.1.1 Ultraviolet-Visible spectroscopy

The UV-Vis spectroscopy data collected in these studies was obtained using an Agilent Technologies Cary 60 spectrometer (Cheadle, UK) with samples being prepared in Fisherbrand macro-cuvettes (FB55143-optical path-length of 1 cm). Spectrophotometric scans were taken over the range 300 nm to 1000 nm and specific absorbance readings were collected at 370.0 nm, 393.0 nm, 640.0 nm and 715.0 nm.

4.1.2 Conductometric and pH measurements

Conductometric titrations were performed using a Jenway 4510 (K = 0.89) conductivity meter. pH titrations were performed using a Jenway 3510 pH meter. The buffers used in the calibration of the pH probe were pH 4, 7 and 12. The pH 7 (7.00 ± 0.01 at 25 °C) and pH 4 (4.00 ± 0.01 at 25 °C) buffers were both purchased from Beckman Coulter with the pH 12 buffer was made up using 50 ml of potassium chloride (0.20 M) and 12 ml of a standardised potassium hydroxide solution (0.20 M).

4.1.3 Inductively Coupled Plasma-Mass Spectrometery

The inductively coupled plasma mass spectrometer used was an Agilent technologies 7700 Series ICP-MS with an ASX-500 Series Autosampler. This ICM-MS plasma was generated by a 27 MHz RF generator with a power range of 500 W to 1600 W. The mass analyser in this instrument was a 3 MHz quadrupole with a mass range of 2 - 260 amu; with a mass resolution of < 0.3 amu to > 1.0 amu.

4.2 Determination of the stoichiometry of nickel complexes at various pHs.

4.2.1 Bjerrum plots

A range of solutions containing sodium hydroxide (0.1 mol dm^{-3}) were added to a mixture of nickel chloride (0.01 mol dm^{-3}) and the sodium salt of the ligand, (0.01 mol dm^{-3} of either sodium gluconate, α-GISA, β-GISA or XISA) to produce solutions of varying nickel to hydroxide ratios (0 to 4). The ionic strength of the final solutions was adjusted to I= 0.1 mol dm^{-3} by the addition of potassium nitrate. At various time intervals (3, 7 & 14 days) the pH of the solutions was measured and plotted against the nickel to hydroxide ion ratio.

4.2.2 Conductometric titrations

Three different conductometric titrations were performed. In the first set (titration A) aliquots of nickel chloride (1cm^3, 0.1 M) were added to a solution of the sodium salt of the ligand (α-GISA, β-GISA and XISA; 20 mL, 0.1 M) and the conductance of the solution was measured after each addition. In the second set (titration B) excess of the sodium salt of the ligand (15 mL, 0.1 M) was added to sodium hydroxide (10 mL, 0.1 M) and the combined solution was titrated with nickel chloride (0.25 mL, 0.1 M) and the conductance of the solution was measure after each addition. In the final

conductance experiment (titration C) the sodium salt of the ligands (10 mL, 0.1 M) was titrated simultaneously with aliquots of nickel chloride (1 mL, 0.1 M) and aliquots of sodium hydroxide (1 mL, 0.2 M) and the conductance of the solution was measured after each addition.

4.2.3 Job's method of continuous variation

Job's method of continuous variation was performed at pH 7 for all three ligands. Eleven solutions were prepared containing nickel chloride (0-0.05 M) and the sodium salts of the relevant ligand (0.05 to 0 M) respectively. These were allowed to equilibrate for 3-days at which time the absorbance at 393 nm was measured and a graph was plotted of the absorbance against the mole fraction of nickel.

4.3 Measurement of stability constants

4.3.1 The Schubert Method (pH 13)

In polypropylene tubes, Analar sodium hydroxide 1000 ($\pm$ 10.0) mg was added with a solution of ligand (20.0 ml, 1×10^{-2} to 1×10^{-5} M). After allowing the samples to return to room temperature, four aliquots (5.0 ml each) of the ligand solution were taken and a solution of nickel nitrate (34.0 µl of 1.0 mM) was added to three of the aliquots with water (34.0 µl) being added to the fourth. Into these solutions, cation exchange resin (2 g) was added and the pH of the system was recorded.

In addition, three solutions of nickel nitrate (34.0 µl of 1.0 mM) were added to UP water (5.0 ml) for use in measurement of the total metal concentration ($M_{res} + M_{sol}$) in the sample solutions before the resin was added. No resin was added to these solutions.

After 3 days of equilibration on a shaker (150 rpm; 25.0 $^{\circ}$C) the samples were filtered through 0.45 µm filters and the resulting solution (3.98 ml) was spiked with 20.0 µl of a 100 ppm rhodium solution for use as an internal standard. These were then analysed on a Perkin Elmer ICP-MS.

4.3.2 Polarographic studies (pH 7)

For the nickel-ligand complexation studies at near neutral pH, five solutions of varying ligand concentrations (10 ml, 0 to ~ 1.0 M) were prepared in UPW and equilibrated at 25.0 $^{\circ}$C for 48 h. The pH was recorded and the solutions were filtered through a 0.45 µm filter before analysis *via* differential pulse polarography. Nitrogen was bubbled through the samples for 10 mins to remove oxygen from the solution before scanning the applied voltage between -0.5 to 1.3 V. Each solution was analysed three times and values were tabulated to determine the $\Delta E_{1/2}$ values.

References:

(1) Isbell, H.S., *J. Res. Natl. Bur. Stand.*, **1944**, *32*, 45-59.
(2) Machell, G.; Richards, G. N., *J. Chem. Soc.*, **1960**, 1924-1931.
(3) Nef, J. U., *Justus Liebigs Ann. Chem.,* **1907**, *357*, 214-312.
(4) Knill, C. J.; Kennedy, J. F., *Carbohydr. Polym.*, **2003**, *51*, 281-300.
(5) Machell, G.; Richards, G. N., *J. Chem. Soc.,* **1957**, 4500-4506.
(6) Richards, G. N.; Sephton, H. H., *J. Chem. Soc.,* **1957**, 4492-4499.
(7) Sowden, J.C., *Adv. Carbohydr. Chem.*, **1957**, *12*, 35-79.
(8) Gakhokidze, R.A., *Russ. Chem.Revi.,* **1980**, *49*, 222-236.
(9) Pavasars, I., PhD Thesis, *Linköping University*, **1999**.
(10) Niemelä, K., *Carbohydr. Res.,* **1990**, *204*, 37-49.
(11) Sjostrom, E., *Tappi,* **1977**, *60(9)*, 151-154.
(12) Pavasars, I.; Hagberg, J.; Boren, H.; Allard, B., *J. Polym. Environ.* **2003**, *11*, 39-47.
(13) Niemela, K.; Alén, R.; Sjöström, E., *Holzforschung*, **1985**, *39*, 167
(14) Niemela, K.; Sjostrom, E., *Biomass*, **1986**, *11*, 215-221.
(15) Glaus, M.; Laube, A.; Stallone, S., *Radiochim. Acta*, **1999**, *86*, 183-189.
(16) Glaus, M. A.; Laube, A.; Stallone, S.; Van Loon, L. R., *Mater. Res. Soc. Symp. Proc.*, **1998**, *506*, 977-978.
(17) Glaus, M. A.; Van Loon, L. R., *Environ. Sci. Technol*, **2008**, *42*, 2906-2911.
(18) Greenfield, B. F.; Hurdus, M. H.; Spindler, M. W.; Thomason, H. P., Nirex Report, NSS/R376, Didcot, UK: Nirex, 1**997**.
(19) Greenfield, B. F.; Moreton, A. D.; Spindler, M. W.; Williams, S. J.; Woodwark, D. R. *Mater. Res. Soc. Symp. Proc,,* **1992**, *257*, 299-306.
(20) Van Loon, L. R.; Glaus, M. A. In *Experimental and theoretical studies on alkaline degradation of cellulose and its impact on the sorption of radionuclides*, Paul-Scherrer-Institut, 5232 Villigen PSI, 1998, PSI-Bericht 98-07.
(21) Gaona, X.; Montoya, V.; Colàs, E.; Grivé, M.; Duro, L., *J. Contam. Hydrol.,***2008**, *102*, 217-227.
(22) Keith-Roach, M. J., *Sci. Total Environ.,***2008**, *396*, 1-11.
(23) Bourbon, X.; Toulhoat, P., *Radiochim. Acta*, **1996**, *74*, 315-319.
(24) Evans, N.; Warwick, P.; Felipe-Sotelo, M.; Vines, S., *J. Radioanal. Nucl. Chem.*, **2012**, *293*, 725-730.
(25) Evans, N. D. M.; Antón Gascón, S.; Vines, S.; Felipe-Sotelo, M., *Mineral. Mag.*, **2012**, *76*, 3425-3434.
(26) Von Schenck, H.; Källström, K., *Phys. Chem. Earth*, **2014**, 70-71, 114-126.
(27) Whistler, R. L.; BeMiller, J. N.; Melville, L. W. In *Advances in Carbohydrate Chemistry*; Academic Press: New York,, 1958; Vol. 13; pp 289-329.
(28) Vercammen, K.; Glaus, M. A.; Van Loon, L. R., *Radiochim. Acta*, **1999**, *84*, 221-224.
(29) Vercammen, K.; Glaus, M. A.; Van Loon, L. R., *Radiochim. Acta*, **2001**, *89,* 393-401.

(30)   Warwick, P.; Evans, N.; Hall, T.; Vines, S., *Radiochim. Acta*, **2004**, *92*, 897-902.
(31)   Warwick, P.; Evans, N.; Vines, S., *Radiochim. Acta,* **2006**, *94*, 363-368.
(32)   Warwick, P.; Evans, N.; Hall, T.; Vines, S., *Radiochim. Acta,* **2003**, *91*, 233-240.
(33)   Rojo, H.; García-Gutiérrez, M.; Missana, T.; Galán, H., *Mater. Res. Soc. Symp. Proc.*, **2012**, *1475*; 361-366.
(34)   Rai, D.; Rao, L.; Moore, D. A., *Radiochim. Acta* **1998**, *83*, 9-13.
(35)   Rai, D.; Yui, M.; Moore, D. A.; Rao, L., *J. Solution Chem.*, **2009**, 38, 1573-1587.
(36)   Joyce, L. G.; Pickering, W. F., *Aust., J. Chem.*, **1965**, *18*, 783-94.
(37)   Bjerrum, J.; Schwarzenbach, G.; Sillen, L. G., In *Stability Constants. Part II: Inorganic Ligands,* Chem. Soc. Spec. Publ., Chem. Soc.: London, 1958; Vol. 7.
(38)   Job, P., *Ann Chim.,* **1928**, *9*, 113-203.
(39)   Rossotti, F. J. C.; Rossotti, H. In *The Determination of Stability Constants and Other Equilibrium Constants in Solution*, McGraw-Hill Book Company: New York, 1961; Vol. 66.
(40)   Lingane, J. J. Chemical Reviews 1941, 29, 1-35.
(41)   van Duin, M.; Peters, J. A.; Kieboom, A. P. G.; van Bekkum, H., *Recl. Trav. Chim. Pays-Bas*, **1989**, *108*, 57-60.
(42)   Schubert, J., *J. Phys. Colloid Chem.*, **1948**, *52*, 340-350.
(43)   Maes, A.; DeBrabandrere, J.; Cremers, A., *Radiochim. Acta*, **1992**, *44*, 45-51.
(44)   Glaus, M. A.; Hummel, W.; Van Loon, L. R., *Appl. Geochem.*, **2000**, *15*, 953-973.
(45)   Randall, M.; Rigby, B.; Thompson, O.; Trivedi, D. In Assessment of the effects of cellulose degradation products on the behaviour of europium and thorium, National Nuclear Laboratory, NDA-RWMD Didcot, 2013, Report NNL(12) 12239.
(46)   Nuclear Decommissioning Authority, *Geological Disposal: Radionuclide Status Report*, 2010. NDA-RWMD, Didcot NDA Report No. NDA/RWMD/034
(47)   Shaw, P. B.; Robinson, G. F.; Rice, C. R.; Humphreys, P. N.; Laws, A. P., *Carbohydr. Res.,* **2012**, *349*, 6-11.
(48)   Greenfield, B. J.; Harrison, W. N.; Robertson, G. P.; Somers, P. J.; Spindler, M. W. INSS/R272, AEA-D&R-0219 1993.
(49)   Shaw, P. B. Doctoral thesis, University of Huddersfield., 2013.