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FOREWORD

Welcome to **Alumina 2018**, the 11th AQW International Conference, 9-13 September 2018 in Gladstone Queensland. Alumina 2018 is organised by the non-profit organization AQW Inc. The conference host for 2018 is Rio Tinto and we are delighted to be holding the conference in Gladstone, a modern city that has grown around an industrial backbone featuring two alumina refineries with a combined annual production of 7 Mt of alumina.

The Alumina Quality Workshop began in 1988 as a forum to bring the world's alumina producers and their customers together to exchange ideas and information around a common goal of improved product quality. The symposia have been held in at an interval of three years. Over time, the workshop has evolved into a major international conference, incorporating all aspects of the production of alumina. In recognition of this evolution we have rebranded the conference name Alumina 2018.

We thank everyone who has participated in the Alumina 2018 conference to make it a success. Thank you to all of our generous sponsors and exhibitors who demonstrate their strength within our industry through their support, making this important event possible. We gratefully acknowledge all of the authors for writing and presenting their papers and posters, which form the heart of the conference. Thank you to the technical review panel for reviewing the large number of submitted abstracts and papers. Particular thanks need to be given to Dr. Meagan Ladhams-Zieba, Technical Chair, who coordinated the massive effort for this technical review.

The conference theme Efficiency for the Future reflects the current industry focus on cost reduction, optimisation of raw materials & energy use and the adoption of new technology. This continual drive for improved efficiency will ultimately result in a sustained and thriving alumina industry for the future. A feature of Alumina 2018 is the ATR 4.0 workshop on the final day, which will develop a roadmap to help guide research and development in the alumina industry to 2050 and beyond.

In addition to these proceedings, we trust that Alumina 2018 delegates find ample opportunity for lasting value from the conference through several days of networking, personal interactions and discussions with old friends and new colleagues.

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SMALL M$_w$ HYDROXY- AND OXOCARBOXYLATE TYPE ORGANICS RELEVANT TO THE BAYER PROCESS - ACID-BASE PROPERTIES AND CALCIUM-COMPLEXATION IN MODERATELY TO HIGHLY ALKALINE MEDIUM

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ABSTRACT

In the current study, the solution chemistry of organic ligands relevant to the Bayer process was studied in neutral and highly alkaline aqueous solutions in presence of calcium. Their deprotonation in pH > 12 region was also examined by pH-potentiometry, NMR spectroscopy and UV-Vis spectrophotometry. It was shown that these ligands underwent deprotonation in these hyperalkaline solutions; the deprotonation occurred on an OH group (hydroxycarboxylates) or on a CH$_2$ group (oxocarboxylates). In certain cases, two deprotonation steps were detected. The deprotonation constants of these ligands were found to be rather different, between pK_a = 13–15.5, which is explained in terms of the difference in their structure and/or that in the functional groups they contain. The complexation interactions with calcium were studied in neutral as well as in highly alkaline medium by Ca-ISE (ion selective electrode) and pH-potentiometry (H$_2$/Pt electrode), respectively. In neutral solutions, complexes with 1:1 (ML) and in certain cases 1:2 (ML$_2$) compositions were identified. In caustic solutions mono- and/or multinuclear calcium complexes were detected, and in these complexes the ligand contained deprotonated alcoholic hydroxide moiety. Multinuclear complex formation was found in systems containing certain sugar carboxylates as well as α- and β-ketoglutarate. The unexpectedly high stability of some high pH calcium complexes found highlights the importance of these organics in the Bayer process, where the prevailing physico-chemical conditions (high pH and temperature) may facilitate their formation.

1. INTRODUCTION

Small molecular weight organics containing hydroxy, oxo and carboxylate functionalities (for example, lactate, tartrate, α- and β-ketoglutarate, various sugar-carboxylates) are known to be relevant to the Bayer process (The et al., 1985). In neutral medium these ligands form relatively weak metal complexes (Kutus et al., 2017; Pallagi et al., 2011)). However, in hyperalkaline solutions the hydroxyl moiety is able to deprotonate resulting in an alcoholate group which acts as a strong complexing agent binding metal ions (such as Ca^{2+}, Al^{3+} or radioactive nuclides) effectively (Pallagi et al., 2014). Due to this effect, these ligands may increase the solubility of Ca(OH)$_2$ in strongly caustic aqueous solutions. Another important aspect of the metal ion binding capability of these organic ligands is their behaviour in low and intermediate level nuclear waste repositories. D-gluconate (Gluc$^-$) and α-D-isosaccharinate (Isa$^-$) are present in relatively high concentrations in cementitious radioactive wastes (Richards and Sephton, 1957; Glaus and Van Loon, 2008). Due to their complexing ability towards radioactive nuclides (for example La(III), Eu(III), Th(IV), Pu(IV), Np(IV)), it may enhance the mobility of these actinides and thus lead to the contamination of the environment near the repositories (Baston, et al., 1994; Vercammen, et al., 2001; Tits et al., 2005; Gaona et al., 2008). In the current study, the solution chemistry of organic ligands relevant to the Bayer process, especially D-gluconate (Gluc$^-$), D-heptagluconate (Hpgl$^-$), L-gulonate (Gul$^-$), α-D-isosaccharinate (Isa$^-$), lactate (Lac$^-$), L-tartrate (Tar^{2-}), α-ketoglutarate (α-Ket^{2-}) and β-ketoglutarate (β-Ket^{2-}) was studied in neutral and highly alkaline aqueous solutions in presence of calcium.

2. EXPERIMENTAL

2.1 Reagents and solutions

NaGluc (Sigma-Aldrich, ≥ 99% purity), NaHpgl (Sigma-Aldrich, ≥ 99% purity) and Na$_2$Tar (VWR, ≥ 99% purity) were used without further

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purification. NaGul, Na₂(α-Ket) and Na₂(β-Ket) solutions were prepared by neutralizing L-gulonic acid-γ-lactone (Sigma-Aldrich, ≥ 95% purity), H₂(α-Ket) (Sigma-Aldrich, ≥ 99% purity) and H₂(β-Ket) (Acros Organics, ≥ 97% purity) with NaOH (Analar Normapur, a.r. grade). NaIsa stock solution was prepared by using the method of Whistler and BeMiller (Whistler and BeMiller, 1963) from lactose monohydrate (Sigma-Aldrich, ≥ 99% purity). The structure of the ligands are shown on Figure 1.
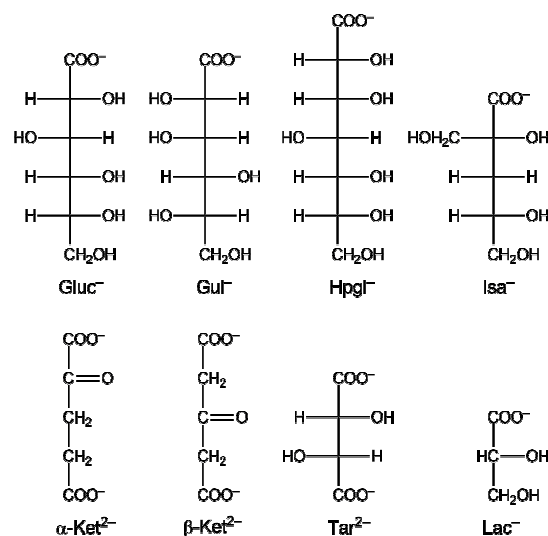

Figure 1. Structure of the ligands investigated in this work

2.2 Potentiometric titrations

Ca-ISE potentiometric titrations were conducted on a Metrohm Titrando 974 instrument using a combined calcium ion-selective electrode (Metrohm).

H₂/Pt-potentiometric titrations were performed on a Metrohm Titrando 888 instrument using a standard H₂/Pt electrode combined with a thermodynamic Ag/AgCl reference electrode.

2.3 NMR measurements

¹H and ¹³C NMR spectra were recorded on a Bruker Avance DRX 500 MHz spectrometer equipped with a 5 mm inverse broadband probe head furnished with z-oriented magnetic field gradient capability. The magnetic field was stabilized by locking it to the ²D signal of the solvent prior to the measurements.

2.4 ESI-MS measurements

Electrospray Ionization Mass Spectrometric measurements were made using a Micromass Q-TOF Premier (Waters MS Technologies, Manchester, UK) mass spectrometer equipped with electrospray ion source. Samples were introduced into the MS by applying direct injection method: the built-in syringe pump of the instrument with a 25-mL Hamilton syringe was used. The electrospray needle was adjusted to 3 kV and N₂ was used as nebulizer gas.

2.5 UV-Vis measurements

UV-Vis spectra of solutions containing α-Ket²⁻ or β-Ket²⁻ were recorded on a Shimadzu UV-1650 PC instrument in the 200-400 nm wavelength range.

3. RESULTS AND DISCUSSION

3.1 Calcium complexation in neutral medium

The complex formation between Ca²⁺ and a series of organic ligands has been investigated by Ca-ISE potentiometry. Figure 2 shows the titration curves of the Isa⁻-containing solutions. The systematic displacement of the cell potential with increasing $[Isa^-]_T$ indicates complex formation. The titration curves were fitted simultaneously with the aid of the PSEQUAD program (Zékány et al). Assumption of only one complex, CaIsa⁺ was sufficient to fit the experimentally observed cell potentials (Figure 2, solid lines). The formation constant of the CaIsa⁺ complex was determined to be $\log\beta_{1,1,0} = 1.12(2)$ (Dudás et al., 2017). In general, $\beta_{p,q,r}$ can be defined as

$$\beta_{p,q,r} = \frac{[Ca_pL_qOH_r^{(2p-q-r)+}]}{[Ca^{2+}]^p[L^-]^q[OH^-]^r\,M^{1-p-q-r}} \quad (1)$$

where L⁻ is a ligand with a single negative charge and $M = 1$ mol·dm⁻³.

These show that Isa⁻ forms weak complex with Ca²⁺ in neutral solutions. Similar results were obtained for α-Ket²⁻ and β-Ket²⁻ (the obtained formation constants are listed in Table 1).

However, certain ligands were found to form another aqueous species in the presence of calcium with 1:2 composition beside the 1:1 complex. The formation of the Ca(Gluc)₂, Ca(Gul)₂, Ca(Hpgl)₂, Ca(Lac)₂ and Ca(Tar)₂ complexes was detected by potentiometric measurements, with the corresponding formation constants listed in Table 1.

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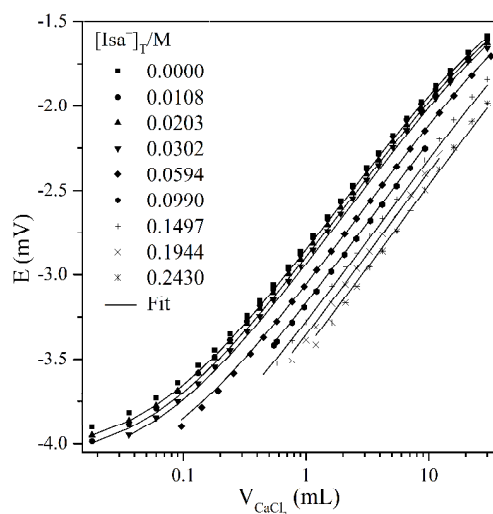COMPLEXATION IN MODERATELY TO HIGHLY ALKALINE MEDIUM

Figure 2. Ca-ISE potentiometric titration curves of solutions containing Isa⁻ and Ca²⁺, in neutral medium, in terms of added titrant volume. $V_0 = 45$ cm³, $[Ca^{2+}]_{T,0} = 10^{-4}$ M, titrant: $[CaCl_2]_T = 0.2$ M, initial $[Isa^-]_T$ values are shown in the figure, I = 1 M (NaCl), T = 25,0 ± 0,1 °C. The symbols and solid lines correspond to the measured and fitted data, respectively (Dudás et al., 2017)

Table 1. Formation constants for complex formation reactions of several organic ligands with calcium in neutral medium, T = 25 °C, ± 3 SE given in parentheses

Ligand	$\log\beta_{1,1,0}$	$\log\beta_{1,2,0}$	Ref.
Gluc⁻ᵃ	1.08(1)	1.65(3)	Kutus et al., 2017
Gul⁻ᵃ	0.88(2)	1.51(3)	Kutus et al., 2016
Hpgl⁻ᵃ	1.00(1)	1.61(2)	Kutus et al., 2017
Isa⁻ᵃ	1.12(2)	–	Dudás et al., 2017
Lac⁻ᵇ	0.89(2)	1.34(2)	this work
Tar²⁻ᵇ	1.09(1)	2.01(2)	Gácsi et al., 2016
α-Ket²⁻ᵇ	1.15(2)	–	this work
β-Ket²⁻ᵇ	0.78(2)	–	this work

ᵃDetermined at I = 1 M ionic strength.
ᵇDetermined at I = 4 M ionic strength.

3.2 Alkaline deprotonation of hydroxy and oxocarboxylates

The alkaline deprotonation of the hydroxy carboxylates were examined by ¹H and ¹³C NMR spectroscopies or H₂/Pt potentiometry.

Upon addition of NaOH to a solution containing Gul⁻, the carbon peaks shift downfield pointing to the OH deprotonation process (Figure 3). The deprotonation constant of the ligand can be obtained by fitting the δ values of each carbon atom as a function of $[OH^-]_T$. The thus obtained deprotonation constant for the reaction Gul⁻ = GulH₋₁²⁻ + H⁺ was found to be $\log\beta_{0,1,-1} = -13.75(2)$. H₂/Pt potentiometric measurements provided similar values for the deprotonation of Gluc⁻ and Hpgl⁻ (see Table 2). Isa⁻, however, was found to be a weaker acid than Gluc⁻ or Hpgl⁻, its deprotonation constant being $\log\beta_{0,1,-1} = -14.5(1)$. These values clearly indicate that under the conditions of the Bayer liquor these ligands are present (partially) in deprotonated form.

The two oxocarboxylates, α-Ket²⁻ and β-Ket²⁻ were found to undergo CH-deprotonation in alkaline medium resulting in an enolate form after tautomerism. From UV-Vis measurements the deprotonation constant of α-Ket²⁻ and β-Ket²⁻ was determined to be $\log\beta_{0,1,-1} = -15.16(1)$ and $-14.41(1)$, respectively.

Because of the formation of such alcoholate or enolate functionalities, these organic ligands become very effective complexing agents in highly caustic medium, the alcoholate and enolate groups having very strong metal ion sequestering capability compared to the hydroxyl or oxo groups.
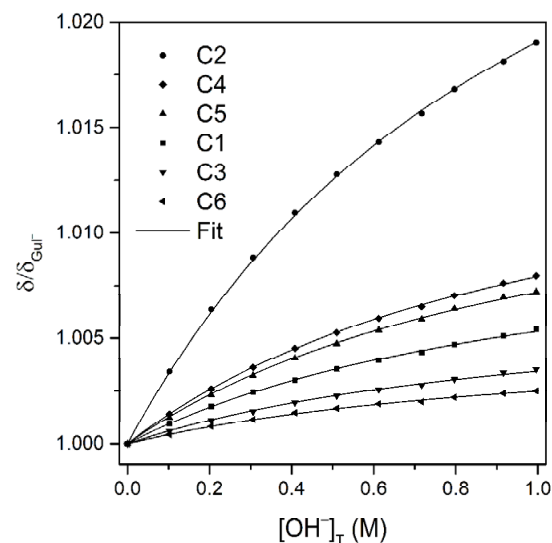

Figure 3. ¹³C NMR chemical shifts of each carbon atom of Gul⁻ (normalized to those of the 'neat' ligand) as a function of $[OH^-]_T$. Experimental conditions: $[Gul^-]_T = 0.200$ M, T = 25 °C, I = 1 M. The symbols and solid

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lines correspond to the measured and fitted data, respectively (Kutus et al., 2018)

Table 2. Deprotonation constants of several organic ligands in highly alkaline medium, T = 25 °C, ± 3 SE given in parentheses

Ligand	$\log\beta_{0,1,-1}$	Ref.
Gluc[−a]	-13.68 ± 0.01[c]	Pallagi et al., 2014
Gul[−a]	-13.75 ± 0.02[d]	Kutus et al., 2018
Hpgl[−a]	-13.41 ± 0.01[c]	Pallagi et al., 2013
Isa[−a]	-14.5 ± 0.1[d]	Dudás et al., 2017
Lac[−b]	-15.6 ± 0.2[d]	this work
Tar[2−b]	-15.4 ± 0.2[d]	Gácsi et al., 2016
α-Ket[2−b]	-15.16 ± 0.01[e]	this work
β-Ket[2−b]	-14.41 ± 0.01[e]	this work

[a]Determined at I = 1 M ionic strength.
[b]Determined at I = 4 M ionic strength.
[c]Determined from H_2/Pt potentiometry.
[d]Determined from ^1H and ^{13}C NMR spectroscopy.
[e]Determined from UV-Vis spectrophotometry.

3.3 Calcium complexation in highly alkaline medium

The complex formation between hydroxy and oxocarboxylates and calcium was investigated by several methods. H_2/Pt potentiometry was suitable to examine the calcium complexation of ligands able to deprotonate significantly below pH = 14. Figure 4 shows the titration curves of solutions containing Ca^{2+} and Gluc[−]. The unique curvature indicates the simultaneous formation and coexistence of several aqueous species.

The titration curves were evaluated with the aid of the PSEQUAD program. Beside the formation of the mononuclear $CaGlucH_{-1}^0$ complex, two charge neutral multinuclear species, $Ca_2GlucH_{-3}^0$, and $Ca_3Gluc_2H_{-4}^0$ were detected with unexpectedly high stability (see Table 3). The existence of these multinuclear complexes was also proven by ESI-MS measurements. These details clearly indicate that Gluc[−] significantly increases the solubility of portlandite ($Ca(OH)_2$) in highly alkaline medium.

Similar multinuclear complex formation was detected in solutions containing Hpgl[−] and Gul[−]

The complex formation between Ca^{2+} and α/β-Ket[2−] was examined by UV-Vis spectro-photometry. Upon addition of Ca^{2+} to a solution containing OH^{−} and α-Ket[2−], a new peak appears corresponding to the enolate form. (Figure 5.) During calculations, the

absorbance values were fitted as a function of $[Ca^{2+}]_T$. For α-Ket[2−], the formation of Ca(α-Ket)H_{-1}^+ and Ca_2(α-Ket)H_{-3}^- was detected.

β-Ket[2−] was found to form similar complexes with Ca(β-Ket)H_{-1}^- and Ca_2(β-Ket)H_{-1}^- composition.

The composition of the calcium complexes of the ligands investigated and their formation constants are summarized in Table 3.

The formation of these complexes has profound practical relevance, given that their formation is possible only in highly alkaline medium. Also, these complexes may act as precursors for the formation of ternary, heteropolynuclear complexes with e.g. Al(III) or radioactive nuclides, thus increasing their solubility and mobility.
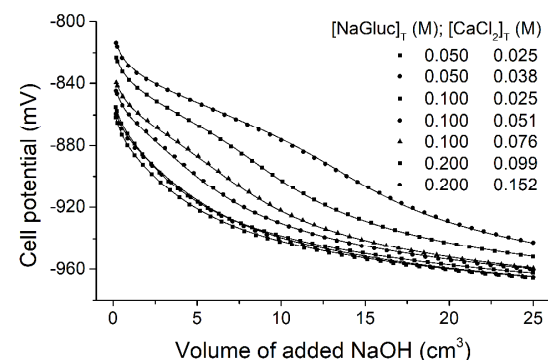

Figure 4. H_2/Pt–electrode potentiometric titration curves of the systems containing Ca^{2+} and Gluc[−]. Total concentration data shown on the figure indicate initial compositions. The symbols and solid lines correspond to the measured and fitted data, respectively (Titrant: 1.01 M NaOH; T = 25 °C)
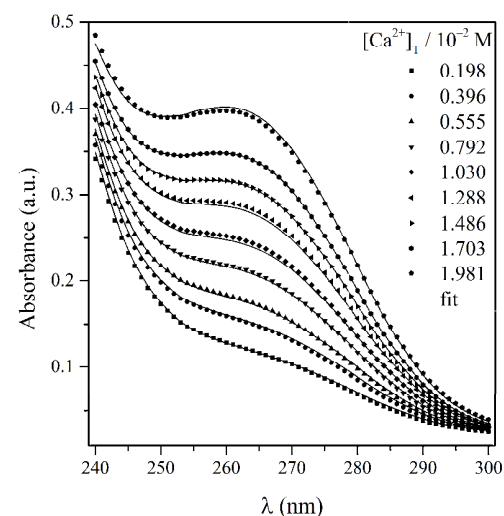

Figure 5. UV-Vis absorption spectra of solutions containing [α-Ket[2−]]$_T$ = 0.001 M

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and $[OH^-]_T = 0.07$ M and increasing amount of Ca^{2+}, T = 25 °C, The symbols and solid lines correspond to the measured and fitted data, respectively

Table 3. Formation constants for complex formation reactions of several organic ligands with calcium in highly alkaline medium, T = 25 °C, ± 3 SE given in parentheses

Species	$\log\beta^H$	$\log\beta^{OH}$	Ref.
$CaGlucH_{-1}^0$	-10.94(1)	2.82(1)	Pallagi et al., 2014[a,c]
$Ca_2GlucH_{-3}^0$	-33.24(2)	8.04(2)	
$Ca_3Gluc_2H_{-4}^0$	-42.60(4)	12.44(4)	
$Ca_3Gul_2H_{-3}^+$	-30.46(3)	10.82(3)	Kutus et al., 2018[a,c]
$Ca_3Gul_2H_{-4}^0$	-42.66(4)	12.38(4)	
$CaHpglH_{-1}^0$	-10.35(1)	3.41(1)	Pallagi et al., 2013[a,c]
$Ca_3Hpg_2lH_{-4}^0$	-41.28(1)	13.76(1)	
$CaIsaH_{-1}^0$	-11.36(2)	2.40(2)	Dudás et al., 2017[a,c]
$CaLacH_{-1}^0$	-12.3(2)	2.0(2)	this work[b,e]
$CaTarH_{-1}^-$	-11.2(1)	3.1(1)	Gácsi et al., 2016[b,c]
$CaTarH_{-2}^{2-}$	-25.3(1)	3.2(1)	
$Ca(\alpha\text{-Ket})H_{-1}^-$	-11.93(2)	2.33(2)	this work[b,d]
$Ca_2(\alpha\text{-Ket})H_{-3}^-$	-36.10(6)	6.68(6)	
$Ca(\beta\text{-Ket})H_{-1}^-$	-11.58(1)	2.68(1)	this work[b,d]
$Ca_2(\beta\text{-Ket})H_{-1}^+$	-10.80(3)	3.46(3)	

[a]Determined at I = 1 M ionic strength.
[b]Determined at I = 4 M ionic strength.
[c]Determined from H_2/Pt potentiometry.
[d]Determined from solubility measurements.
[e]Determined from UV-Vis spectrophotometry.

4. CONCLUSION

In the present study the behaviour of a series of hydroxy and oxocarboxylates (which may be present as impurities in Bayer liquor) was investigated in the presence of Ca^{2+} in neutral and highly alkaline medium. In neutral medium these ligands form weak complexes with calcium with 1:1 (ML) or in several cases 1:2 (ML₂) composition. In alkaline medium, however, they were shown to undergo deprotonation (OH deprotonation for hydroxycarboxylates and CH deprotonation for oxocarboxylates) resulting in the formation of alcoholate or enolate moieties. These deprotonated species have very strong calcium sequestering ability, therefore, they form rather strong mono- or multinuclear calcium complexes. The formation of such complexes increase the solubility of Ca^{2+} in highly caustic solutions and they may act as precursor for the formation of ternary, heteropolynuclear complexes involving for example, Al(III) or radioactive metal ions.

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