DE LA RECHERCHE À L'INDUSTRIE



Département de Physico-chimie / Service d'études Analytiques et de la Réactivité des Surfaces



Laboratoire PECSA, UMR 7195

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Etude des interactions entre Eu(III) et des particules d'alumine en présence d'acides phénoliques

> SOUTENANCE DE THÈSE PAULINE MOREAU 21/11/2012

Composition du Jury:

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Study of the interactions between Eu(III) and alumina particles in the presence of phenolic acids

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 Human activities lead to dissemination of radionuclide in the environment which can be mobile in natural water and possibly harmful for water resources.

What is the fate of radionuclides in soils ?

- Interactions with soil components modify the bioavailability and mobility of cations in natural water:
 - Sorption onto mineral surfaces may favour immobilization
 - Complexation with organic molecules possibly makes them more mobile.
 - Natural organic matter (NOM) has been widely studied but the impact of smaller molecule such as lignin degradation products is less described

For safety assessment, it is necessary to know the speciation of radionuclides in complex samples.



Europium(III)

- Chemical analogue to actinides at the +3 oxidation state: americium(III), curium(III)
- Non radioactive
- Luminescence properties

Phenolic acids

- Same chemical functions as in organic matter (carboxylate and phenolate)
- Antifungi and parabens precursors
- Naturally present in soils as they are degradation products of lignin (forestian soils, pH 4-6)

Alumina

- Surface sites have similar properties as ferrous oxides and as aluminol sites in non-stratified clays
- Sorption of cations onto aluminum oxides and ferrous oxides are similar
- Compatible with spectroscopic analyses

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A picture of the systems



- Properties of the single components:
- 2 oxide surface sites
 - pK_a of phenolic acids
 - \rightarrow Not detailed in this presentation
 - Binary systems
 - ✓ Eu(III)/Al₂O₃ (surface), partially described in literature
 - Not detailed in this presentation
 - ✓ Eu(III)/Phenolic acid
 - **2** \checkmark Phenolic acid/ Al₂O₃ (surface)

✓ Ternary systems

HOW TO DESCRIBE THE INTERACTIONS OCCURING IN TERNARY SYSTEMS?

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Analytical techniques



STUDY OF BINARY SYSTEMS EUROPIUM / PHENOLIC ACIDS





Study of Eu(III) / phenolic acid binary systems 1 –Studied acids

Parahydroxybenzoic acid
 4- hydroxybenzoic acid
 H₂Phb

p*K*a₁ = 4.58



p*K*a₂ = 9.46

Protocatechuic acid
 3,4- dihydroxybenzoic acid
 H₂Proto

 $pKa_1 = 4.49$

О ОН ОН ОН Р*К*а₂ = 8.75

 $pKa_3 = 13$

✓ Gallic acid
 3,4- dihydroxybenzoic acid
 H₂Gal

 $pKa_1 = 4.44$



p*K*a₃ = 11.38 p*K*a₄ n. m.

From Strobel, 2001

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Study of Eu(III) / phenolic acid binary systems 2 – Jablonski diagram, Eu(III) spectroscopy

Information about chemical environment of Eu(III)



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Study of Eu(III) / phenolic acid binary systems 2 –TRLS of Eu(III)





Study of Eu(III) / phenolic acid binary systems 3 – TRLS raw data

TRLS spectra of Eu(III) are modified upon addition of acid





Intensities of ${}^{5}D_{0} \rightarrow {}^{7}F_{1} ({}^{7}F_{1})$ and ${}^{5}D_{0} \rightarrow {}^{7}F_{2} ({}^{7}F_{2})$ transitions are used to determine the complexation constant (β_{n}) and the stoichiometry of the complex



Study of Eu(III) / phenolic acid binary systems 4 – TRLS data treatment

Measured in the binary systems



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From Vercouter,

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Study of Eu(III) / phenolic acid binary systems 5 –Results



$$lg \frac{[EuHA^{2+}]}{[Eu^{3+}]_{nc}} = lg \beta_{app} + n lg [HA^{-}]$$

Intercept Slope

Complexation constants extrapolated to 0 ionic strength using Davies equation:

Acid name	formula	lgβ° ₁	
H ₂ Phb	Н С С С	2.6 (± 0.2)	
H ₂ Proto	о он он	2.75 (± 0.2)	
H ₂ Gal	но он	> 5 (scattered data)	
\rightarrow Degradation of H ₂ Gal?			

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Study of Eu(III) / phenolic acid binary systems 6 – Comparison to published data

Linear Free Energy Relationship (LFER) between $\lg \beta^{\circ_1}$ and pKa was proposed by Vitorge et al. (2007) for various Ln³⁺ and An³⁺ with small ligands with O donor atoms



H₂Phb and H₂Proto fall into the LFER

³Hasegawa et al., 1990 ⁴ Wang *et al.*, 1999



Study of Eu(III) / phenolic acid binary systems 7 – Computational studies (1)

What could be an explanation for the increase of complexation from H₂Phb (or H₂Proto) to H₂Gal ?

Mesomeric effects ?



Inductive effects ?

 \Rightarrow They are limited to maximum 3 or 4 bonds

The meta OH groups of H₂Proto and H₂Gal are not congugated with the carboxylate group

DFT/B3LYP calculations were performed (with Stuttgart basis set and ECP):

- Calculation was done with La because it has the simplest electronic configuration among the analogue f-block element at the +3 oxidation state
- Calculations are performed in the gas phase (qualitative interpretation of the bonding)
- ✓ The carboxylate group of the acid is ionized (formation of LaHA²⁺ complexes)
- ✓ The OH substituents are forced to remain linear and in the plane of the molecule



What differences were evidenced between the complexes LaHPhb²⁺ and LaHGal²⁺?



- Atom charge: not significantly different
- The La-O_{carb} bond is partially covalent (charge transfer from O_{carb} to La)

➡ Study of donations between O_{carb}, C_{carb} and La(III), to evidence electron transfer



Study of Eu(III) / phenolic acid binary systems 7 –Computational studies (3)

 One particular donation specifically exists in LaHGal²⁺ that was not present in LaHPhb²⁺, involving 2_{px} orbital of C_{carb} and 5d_{xz} of La



➡ Both orbitals include non-negligible contributions of the p_x functions of distal OH substituents.



Study of Eu(III) / phenolic acid binary systems 7 – Interim conclusion

- ✓ $Ig\beta^{\circ}_{1}(EuHPhb^{2+}) = 2.6 \pm 0.2$
- ✓ $Ig\beta^{\circ}_{1}(EuHProto^{2+}) = 2.75 \pm 0.2$
- ✓ These values are in fair agreement with published data for similar ligands
- The complexation constant seems to be higher for EuHGal²⁺ but the data are more scattered
- In the gas phase, the La-Carboxylate bond is partly covalent, involving d orbitals of La
- Evidence of some electron transfer from the acid to La(III) only in LaHGal²⁺

CHARACTERIZATION OF ALUMINA SURFACE SITES





- Hydrodynamic diameter ≈ 250 nm (controlled by dynamic light scattering)
- Specific area :110 m²/g (supplier data)
- Acid-base properties of surface sites:
 - Potentometric titrations of the oxide at 3 ionic strengths (10, 100, 250 mM NaCl) Intersection point is called **PZSE** = Point of Zero Salt Effect
 - Electrophoretic mobility (μ_{ep}) measurements at 2 ionic strengths (10 and 50 mM (NaCl) pH for which μ_{ep} is nil is called IEP = Isoelectric Point



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Description of the oxide-solution interface (CCM)

Amphoteric surface sites: $\equiv MOH_{2}^{+} \rightleftharpoons \equiv MOH + H^{+} \qquad K_{1} = \frac{\left[\equiv MOH\right] \left[H^{+}\right]}{\left[\equiv MOH_{2}^{+}\right]} = \operatorname{int} K_{1} \exp\left(\frac{F \psi_{0}}{2RT}\right)$ $\equiv MOH \rightleftharpoons \equiv MO^{-} + H^{+} \qquad K_{2} = \frac{\left[\equiv MO^{-}\right] \left[H^{+}\right]}{\left[\equiv MOH\right]} = \operatorname{int} K_{2} \exp\left(\frac{F \psi_{0}}{2RT}\right)$ Constant capacitance model (CCM) Particle $\checkmark \quad \text{Developed since the 1970's by Schindler \& Kamber^{1}, \text{ Hohl \& Stumm^{2}, Sposito^{3} and Schindler \& Stumm^{4}.}$

- Simple description of the interface
- Linear surface charge/surface potential relationship

$$\sigma = C \psi_0$$

Model used to fit potentiometric titration data



Description of the oxide-solution interface (DLM)



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Description of the oxide-solution interface (summary)

	ССМ	DLM
Ig ^{int} K ₁	-7.5	-8.9
Ig ^{int} K ₂	-9.6	-10.1
IEP/PZSE	8.5	9.5

Will be used to fit the sorption experimental data with FITEQL 4.0 software

STUDY OF BINARY SYSTEMS PHENOLIC ACID / ALUMINA



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Study of phenolic acid / Al_2O_3 binary systems 1 - Sorption of H_2Phb and H_2Proto onto 1 sorption site



Acid	Oxide	Ig ^{int} K _{sorb,H2} A	Γ _{max} (µmol.m ⁻²)	pН	I (mmol.L ⁻¹)	Model	Ref
H ₂ Phb	Al ₂ O ₃	0.4	1.8	5	0.5-NaCl	Langmuir	Das, 2010
H ₂ Phb	Fe ₂ O ₃	2.9	1.2	5.5	50-NaClO ₄	Langmuir	Kung, 1989
H ₂ Phb	Al ₂ O ₃	3.4 ± 0.1	1.8 ± 0.1	5	10-NaCl	ССМ	This work
H ₂ Proto	Al ₂ O ₃	1.8	1.1	5	0.5-NaCl	Langmuir	Borah, 2011
H ₂ Proto	Al ₂ O ₂	5.4 ± 0.1	2.0 ± 0.1	5	10-NaCl	ССМ	This work

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Sorption of phenolic acids onto alumina 2 - Sorption of H₂Gal and H₂Proto onto 2 sorption sites



- Both sorption sites have the same protolytic properties
- Total site number is the one determined in this work

 $\equiv \! \mathrm{XOH} + \mathrm{H}_2 \mathrm{A} \rightleftharpoons \equiv \! \mathrm{XHA} + \mathrm{H}_2 \mathrm{O}$

 $\equiv \mathrm{YOH} + \mathrm{H}_2\mathrm{A} + \mathrm{H}^+ \rightleftarrows \equiv \mathrm{YOH}_2\mathrm{H}_2\mathrm{A}^+$

Acid	$Ig^{int}K_{sorb,X,H_2A}$	$Ig^{int}K_{sorb,Y,H_2A}$
H ₂ Gal	4.7 ± 0.1	13.9 ± 0.7
H ₂ Proto	4.3 ± 0.1	14.0 ± 0.7

➡ For H₂Proto, the presence of 2 sorption sites is less clear

IgK_{sorb,X,HA} are comprised between IgK_{sorb,H2Phb} (3.4 ± 0.1) IgK_{sorb,H2Proto} (5.4 ± 0.1)

Sorption of phenolic acids onto alumina 3 - Sorption of H₂Phb as a function of pH



	Oxide	l (mmol.L ⁻¹)	Ref
	AI_2O_3	10-KNO ₃	Hidber, 1997
Δ	AI_2O_3	0.05-NaCl	Das, 2010
\diamond	α -Fe ₂ O ₃	10-NaCl	Gu, 1995
	AI_2O_3	10-NaCl	This work

Sorption decreases as pH increases

$Ig^{int}K_{sorb,H_2A,1}$	3.4
$Ig^{int}K_{sorb,H_2A,2}$	10.8 ± 0.8
$Ig^{int}K_{sorb,H_2A,3}$	-0.1 ± 0.05

¹Hidber, 1997, J. Eur. Cer. Soc., 17 ²Das, 2010, JCIS, 344 ³Gu, 1995, Geochim. Cosmochim. Acta, 59

 Sorption cannot be described using only one sorbed species as previously at pH 5

 $\equiv MOH + H_2A \rightleftharpoons \equiv MHA + H_2O$

✓ Two other surface species were taken into account:

 $\equiv MOH + H_2A + H^+ \rightleftharpoons \equiv MOH_2H_2A^+$ $\equiv MOH + H_2A \rightleftharpoons \equiv MA^- + H_2O + H^+$

Sorption of phenolic acids onto alumina 4 -Sorption of H_2 Proto as a function of pH



		Ligand	Oxide	l (mmol.L ⁻¹)	Ref
		H ₂ Proto	Al ₂ O ₃	10-KNO ₃	Hidber, 1997
		H ₂ Proto	Al ₂ O ₃	0.05-NaCl	Borah, 2011
		H ₂ Proto	Goethite	10-NaCl	Evanko, 1998
		H ₂ Proto	Goethite	100-NaNO ₃	Davis, 1978
(0	Catechol	Al ₂ O ₃	100-NaClO ₄	Kummert, 1980
		Catechol	Al ₂ O ₃	0.05-NaCI	Borah, 2011
4	Δ	Catechol	α-Fe ₂ O ₃	10-NaCl	Gu, 1995
	\diamond	Catechol	Goethite	10-NaCl	Evanko, 1998
		H ₂ Proto	Al ₂ O ₃	10-NaCl	This work

Sorption of H₂Proto is approx.
 constant as a function of pH

- Sorption of catechol increases with pH
- As for sorption of H_2 Phb, 3 surface species were taken into account to fit the data

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\equivMOH + H<sub>2</sub>A \rightleftharpoons \equivMHA + H<sub>2</sub>O
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 $\equiv MOH + H_2A + H^+ \rightleftharpoons \equiv MOH_2H_2A^+$

 $\equiv MOH + H_2A \rightleftharpoons \equiv MA^- + H_2O + H^+$ Moreau P.

$Ig^{int} \mathcal{K}_{sorb, H_2A, 1}$	5.4
$Ig^{int}K_{sorb, H_2A,2}$	9.2 ± 0.2
$Ig^{int}K_{sorb, H_2A,3}$	0.2 ± 0.1



Study of phenolic acid/Al₂O₃ binary system 5 – Interim conclusion

Sorption is increased upon \nearrow number of OH groups on the aromatic ring of phenolic acids

- Sorption was described in the framework of CCM and the sorption parameters obtained in the binary systems will be compared to those obtained in the ternary systems
- Sorption was also studied as a function of pH for the three acids:
 - Sorption of H_2 Phb with pH
 - ✓ Sorption of H_2 Proto ≈ constant as a function of pH
 - \checkmark Three surface species were needed to describe sorption H₂Phb and H₂Proto
 - Spontaneous degradation of H₂Gal occurred for pH > 6.5 it is not a good candidate for studying ternary systems

STUDY OF TERNARY SYSTEMS EUROPIUM / PHENOLIC ACID / ALUMINA



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1 - Ternary system Eu(III)/H₂Phb/Al₂O₃ at pH 5 1 - Macroscopic scale



1 - Ternary system Eu(III)/H₂Phb/Al₂O₃ at pH 5

2 - Microscopic scale



✓
$$T(EuHPhb^{2+}) \approx T(Eu(III)/Al_2O_3) \approx T(Eu^{3+})$$

т(ternary) > т(binaries)

➡ Speciation of Eu(III) is different in the ternary and in the binary systems for increasing [H₂Phb]



In order to evidence the new species, TRLS signal was acquired at a delay of 470 μ s = to « turn off » luminescence due to all binary species and Eu³⁺



Spectral fingerprint of a mixed H₂Phb/Eu(III) complex sorbed onto Al₂O₃

2 - Ternary system Eu(III)/H₂Proto/Al₂O₃ at pH 5

1 - Macroscopic scale



2 - Ternary system Eu(III)/H₂Proto/Al₂O₃ at pH 5 2 - Microscopic scale



- $\tau(EuHProto^{2+}) < \tau(Eu^{3+})$ reaching $\approx 20 \ \mu s$. \checkmark
- Quenching luminescence processes of Eu(III) \checkmark in the presence of H₂Proto
 - τ (ternary) $\leq \tau$ (all binaries)

It was not possible to examine TRLS spectra with higher delay time in the ternary system. because of the very fast decay time in the presence of H₂Proto

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0.08

0.07 0.06

0.05 0.04 0.03 0.02

0.01 - 0.05

[Eu(III)]_{sorbed} (µmol.m⁻²)

3 - Ternary systems at pH 5

Fitting experimental data in the framework of CCM

Ternary systems were first described as a sum of the three binary systems



[H₂Proto]_i (mmol.L⁻¹)

- Sorption of Eu³⁺ occurs via 2 sorption sites having the same protolytic properties
- Sorption of acid occurs on the two sites with the same sorption constant determine in this work
- EuHPhb²⁺ and EuHProto²⁺ are formed in solution
 - Sorption of Eu(III) is well fitted as a sum of binary systems
- The increase of Eu(III) sorption can be estimated by taking into account a ternary surface species but with a low formation constant

 $\equiv XOH + Eu^{3+} + H_2Proto \rightleftharpoons \equiv XOEuHProto^+ + 2 H^+$

With $Ig^{int}K_{sorb,ternary} = 0.01$

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0.50

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3 - Ternary systems at pH 5

Interim conclusion

Synergistic processes were evidenced in both binary systems with different tools Eu(III)/H₂Phb/Al₂O₃

- Macroscopic: unchanged, described as a sum of binaries
- Microscopic: evidence of a ternary species



- Macroscopic: evidence of a ternary species
- Microscopic: very similar to binaries, very fast decay time

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CONCLUSIONS

- Study of complexation of Eu(III) by 3 phenolic acids by TRLS, determination of formation constant of EuHPhb²⁺ and EuHProto²⁺
- Complementary investigation using DFT calculation
- Characterization of the alumina surface sites, determination of IEP and PZSE independently
- \checkmark Characterization of sorption of the 3 phenolic acids and of Eu³⁺ onto Al₂O₃
- Modelling of sorption in the framework of CCM
- \checkmark Evidence of 2 sorption sites in the case of H₂Gal, and potentially in the case of H₂Proto
- Study of 2 ternary systems
- Evidence of synergistic sorption in both systems either using macroscopic or microscopic analysis
- Modeling sorption of Eu(III) in the ternary systems could be achieved by using a sum of binary systems



PERSPECTIVES

- Applying the same protocols to higher pH (controlling the carbonate concentration)
- Enlarging the panel of studied acids
 - catechol
 - studying the influence of other substituents on the aromatic ring (methoxy, alkyl chains...)
- Enlarging the panel of studied oxides: ferrous oxide, silica, clays...
- Using attenuated total reflectance Fourier transformed infrared spectroscopy (ATR-FTIR) to precise how sorption occur (denticity, what is/are the atom involved in sorption?)



DELS RECEIVER & L'HOURTES



Thank you for your attention

Acknowledgements



Ludivine Mironnet Tanphuc Bui-Van





Complexation of Eu(III) by phenolic acids Methodology

$$Eu^{3+} + n A^{-} \rightleftharpoons EuA_n^{(3-n)+}$$

$$\beta_n = \frac{[EuA^{(3-n)+}]}{[Eu^{3+}][A^-]^n}$$

Taking Eu(III) speciation into account...

$$[Eu]_{tot} = \alpha [Eu^{3+}] \qquad \qquad \beta_{app} = \frac{[EuA^{(3-n)+}]}{[Eu]_{tot} [A^-]}$$

$$\alpha = \left(1 + \sum_{n \ge 1} \frac{\beta_{\mathrm{H}^+,n}}{[\mathrm{H}^+]^n} + \beta_{\mathrm{Cl}^-,n} [\mathrm{Cl}^-]^n\right)$$

...and ionization of the acid

$$[A^{-}] = \frac{[A]_{tot}}{1 + 10^{pKa-pH}}$$

Al₂O₃ surface sites characterization DLM

Theoretical evolution of ψ and σ in the frawork of DLM

log K ₁	log K ₂	pzc
-8.8	-10.15	9.48



Calculated zeta potential

$$\sigma = \sqrt{8 RT} \varepsilon_{R} \varepsilon_{0} I 10^{3} \sinh\left(\frac{z F \psi_{0}}{2 R T}\right)$$

$$\sigma = \frac{F}{C_{s} s} \left(\left[=MOH_{2}^{+}\right] - \left[=MO^{-}\right]\right)$$

$$\sigma = \frac{F}{C_{s} s} \left[=MOH\right] \left(\frac{\left[H^{+}\right]}{intK_{1} \exp\left(\frac{F\psi_{0}}{RT}\right)} - \frac{intK_{2} \exp\left(\frac{F\psi_{0}}{RT}\right)}{\left[H^{+}\right]}\right)$$

$$\left(\frac{\left[H^{+}\right]}{intK_{al} \exp\left(\frac{F\psi_{0}}{RT}\right)} - \frac{intK_{a2} \exp\left(\frac{F\psi_{0}}{RT}\right)}{\left[H^{+}\right]}\right)}{\left[1 + \frac{\left[H^{+}\right]}{intK_{a1} \exp\left(\frac{F\psi_{0}}{RT}\right)} + \frac{intK_{a2} \exp\left(\frac{F\psi_{0}}{RT}\right)}{\left[H^{+}\right]}\right]}{\left[H^{+}\right]} = \frac{\sqrt{8 \varepsilon\varepsilon_{0} RT 1 10^{3}}}{\left[=MOH\right]} \times \frac{C_{s} s}{F} \times \sinh\left(\frac{F\psi_{0}}{2RT}\right)}{tanh\left(\frac{ze\zeta}{4 kT}\right)} = tanh\left(\frac{ze\psi_{0}}{4 kT}\right) \exp(-\kappa x)$$

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Al₂O₃ surface sites characterization calculating zeta potential from electrophoretic mobility

$$\mu_{ep} = \frac{2 \zeta \epsilon_R}{3 \eta} f(\kappa r)$$

$$\kappa^{-1} \approx \frac{0,304}{\sqrt{I}} \,(nm)$$

$$f(\kappa r) = 1 + \frac{1}{2 (1 + \delta / \kappa r)^3} = 1 + \frac{1}{2 \left(1 + \frac{\delta}{\kappa r}\right)^3}$$

$$\delta = \frac{2.5}{1 + 2 \exp\left(-\kappa r\right)}$$