Interest of NMR in the field of radioactive environments

Examples and limits.

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overview

• NMR facilities to handle radioactive samples

• Liquid state analysis example
  – Radiolysis study
  – Characterization of metallic complexes
  – Conformational study (paramagnetic probe)
  – Diffusion and localized spectroscopy

• Solid state analysis
  – U Aluminate, Pu-doped glasses, ashes… same problem.

• Conclusion
Scientific device

Mass spectrometry

Tr Laser Fluorescence

Calorimeter

Raman

FTIR

X-Ray Diffraction

NMR

HPLC

06/ two level glove box

05/ Conditioning glove box liquid sample

16/ Conditioning glove box for MAS probe

TR Laser Fluorescence

NMR

FTIR

X-Ray Diffraction
Radioactive samples and NMR

The two level glove box is linked to a normal glove box for the teflon tube conditioning.

Magnet room of the 400MHz spectrometer
Safe and reliable management of radioactive liquid samples in use in Atalante lab.

Liquid state sample management

Teflon and glass tubes are commercial items
Checking of the NMR tube exterior before it leaves the glove box and... 

...is inserted into the magnet.
The two level glove box:

Solid state sample management

Commercial insert manage through a screw (drilled at the bottom)

Tool designed to handle rotor and... to plug the cap safely.
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α radiolysis studies

- TBP (Tributyl Phosphate) degradation mechanism:

TBP radiolysis in organic phase (30% in TPH).

**Purpose:** Find a model to quantify degradation products depending on:

- $\alpha$ radiation $^{238}\text{Pu} / ^{239}\text{Pu}$, hydrolysis: $[\text{Pu}^{4+}]$, $[\text{HNO}_3]$ and temperature effects.

Degradation products have specific $^{31}\text{P}$ NMR signal.

$I_{^{31}\text{P}} = 1/2$; 100% natural abundant sensitive signal.

⚠️ paramagnetic element must be removed before analysis.
After Pu(IV) extraction: phase separation and organic phase left.

Preparation stage: the organic phase is washed:
• to remove Pu(IV),
• to separate organic compounds.
Wide experimental conditions:

- \(0.5M<[\text{HNO}_3]_{aq}<6M\)
- Pu isotope: 0.65\% \(<^{238}\text{Pu}\)< 20\%
- Pu concentrations: 0.4mM\([\text{Pu}]_{org}\)< 0.1M (25g.L\(^{-1}\))
- Experiments lasted up to 7000 hours

No problem of concentration from a radiological point of view (mainly \(\alpha\) emitters)

(TBP experiences \(< 2.7W.L^{-1}\))
Example of HDBP formation

Results:

Linear variation of the concentrations with plutonium contact time:

zero-order apparent reaction.

Kinetic constants $k_i$ depend on some parameters which can be expressed in this empirical equation:

$$k_i = k_{i0} + k_{iH^+}[H^+] + k_{iPu^{4+}} \frac{[Pu^{4+}]}{239} + k_{iD} \dot{D}$$

can be neglected other 500mW.L$^{-1}$.

hydrolysis effect

nitric acid

plutonium

$\alpha$ radiolysis effect
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Characterization of metallic diglycolamide complexes in aqueous phase.

With longer alkyl chains diglycolamide are promising extractants for coextraction of An(III) and Ln(III).

Aim of the study:
– Characterization of metallic complexes formed.
– Determination of the constant formation.

\[ \text{Nd(III)} + n\text{TEDGA} \overset{\beta_{1n}}{\longrightarrow} \text{Nd(TEDGA)}_n \]

\[ n=? \quad \beta_{1n}=? \]

Nd(III) and Am(III)

Monitoring chemical shift of TEDGA solutions according to different ratios:

\[ 0,1 < \frac{[\text{TEDGA}]}{[\text{Nd(III)}]} < 10 \]
$^{13}$C chemical shift vs [Nd(III)] [TEDGA]=0.1M at 25°C Ionic Strength: NaNO₃=1; pH=2

Do these species really exist?

Fast chemical exchange at room temperature → HypNMR software

$Nd(III) + TEDGA \underset{\beta_{11}}{\longrightarrow} Nd(TEDGA)$  $\log \beta_{11} = 1.9 \pm 0.1$

$Nd(III) + 2TEDGA \underset{\beta_{12}}{\longrightarrow} Nd(TEDGA)_2$  $\log \beta_{12} = 4.4 \pm 0.1$

$^{13}$C chemical shift ppm

$[Nd(III)] \text{ mol/L}$
Characterization of complexes by slowing down chemical exchange (Temperature)

\[
\frac{[TEDGA]}{[Nd(III)]} = 2
\]

\[
\frac{[TEDGA]}{[Nd(III)]} = 0.5
\]

\(^1\)H spectra: TEDGA/Nd(III) 1% in acetoneD6 T=-50°C ([TEDGA]=1mM)

\(^{13}\)C spectra: more difficult to get at such TEDGA concentration
What about the same study with Am(III)?

1,5 \times 10^{-2} \text{ mol/L of Am(III) in nitric solution}  

\[ 400 \mu\text{Gy/h contact} \quad \text{100} \mu\text{Gy/h body} \]

Safety radioprotection involves experimental concentrations and monitoring:

- [Am(III)] used lower than those of Nd[III]
- [TEDGA]=10^{-2} \text{ mol/L}

\[ \text{1H} \text{ spectra} \]

\[ \text{1H chemical shift vs [Am(III)]} \]

[TEDGA]=10^{-2}M at 25°C

Ionic Strength: NaNO\textsubscript{3} = 0,6

HypNMR software calculation:

\[ \text{Am(III)} + TEDGA \xrightleftharpoons{\beta_{11}} Am(TEDGA) \]
\[ \text{Log} \beta_{11} = 3,9 \pm 1 \]

\[ \text{Am(III)} + 2TEDGA \xrightleftharpoons{\beta_{12}} Am(TEDGA)_{2} \]
\[ \text{Log} \beta_{12} = 7,8 \pm 1 \]
Characterization of Am(III) complexes by slowing down chemical exchange

1% dilution: [TEDGA]=0.1 mmol/L too low to be detected with a standard reverse probe. 10% too much water. Slow exchange not reached before freezing.

\[ \frac{[TEDGA]}{[Am(III)]} = 3.5 \]

\[ HOD \]

\[ acetoneD6 \]

\[ T=-50^\circ C \]

\[ T=-70^\circ C \]

\[ 1^H \text{ spectra: TEDGA/Am(III) 10\% in acetoneD6 ([TEDGA]=1mM)} \]

Cryogenic probe useful for \(^{13}C\) chemical shift monitoring and \(^1H\) spectra at low temperature.
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Conformational studies

Room temperature ionic liquid (RTIL) are potential solvent to develop new processes for recovery and purification of actinides.

[Image of molecular structure]

X-Ray data for $[\text{BuMeIm}]_2\text{UCl}_6$

hydrogen bonding between the chlorine and the proton of the imidazolium moity.

**Purpose:** What about the structure in solution (dichloro methane)?
U(IV) paramagnetic behavior: lines are broadened and shifted:
Chemical shift changes on NMR spectra are well described through equations:

\[
\Delta \delta_i = \Delta \delta_{\text{cont}} + \Delta \delta_{\text{dip}}
\]

Contact term: electron-nucleus coupling

\[
\Delta \delta_i = \langle S_Z \rangle F + \frac{g^2 \beta^2 S(S + 1)}{3kT} \left( \frac{3 \cos^2 \theta_i - 1}{r_i^3} \right)
\]

Dipolar term: geometric factors $\theta$, $r$. 

\[
C^D G
\]
From XRD structural data it has been possible to calculate the geometric (or dipolar) contribution in the U(IV) induced shift.

The contact term of the H2 chemical shift proves the hydrogen bonding in solution.
Simple structural study thanks to available XRay data, but ….

- **Relaxation time measurements:**  
  \[
  \frac{1}{T_{1p}} = \frac{2}{15(\gamma_I \gamma_J \hbar)} \left( J(J+1) \right) \frac{r_{IJ}^6}{1 + \left( \omega_I \tau_{c1} \right)^2 + \left( \omega_J \tau_{c2} \right)^2} \\left[ \frac{3\tau_{c1}}{1 + \left( \omega_I \tau_{c1} \right)^2} + \frac{7\tau_{c2}}{1 + \left( \omega_J \tau_{c2} \right)^2} \right] + \frac{2}{3} J(J+1) \left( \frac{A}{\hbar} \right)^2 \frac{\tau_{e2}}{1 + \left( \omega_J \tau_{e2} \right)^2}
  \]

  Dipolar term  
  Contact term

- **Chemical shifts:**  
  \[
  \Delta \delta_{IS} = D_1 \frac{3 \cos^2 \theta - 1}{r^3} + D_2 \frac{\sin^2 \theta \cos \theta - 1}{r^3} + \frac{\langle S_z \rangle}{3kT \gamma_I} \frac{\beta A}{\hbar}
  \]

  \[
  \Delta \delta_{IS} = C^D G + \langle S_z \rangle F
  \]

  \(C^D\) and \(\langle S_z \rangle\) are characteristic of the cation, independent of the ligand.

  Since the seventies, \(C^D, \langle S_z \rangle\) have been determined and calculated for Ln(III).
Very few studies have been published dealing with Actinides’ $C^D$ or $\langle S_z \rangle$.

Despite isoelectronic configuration between 4f and 5f ions paramagnetic behavior are different.

Example: $f^6$

Magnetic susceptibility measurements from $^1H$ NMR spectra according to Evans’ method for the $7F^0$ electronic configuration of Eu$^{3+}$ and Am$^{3+}$:

$$\mu_{\text{eff}} = f(\Delta \nu, m, MW)$$

Outlook: Ph D student (Steve JAN) to look at actinide paramagnetic behavior and correlation with electronic configuration.

Use of NMRD thanks to J. F. DESREUX.
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Diffusion and localized spectroscopy

NMR can help to understand what happens in a biphasic system:
- chemical reaction at the interface: thermodynamic and kinetic phenomena.
- transfer in the aqueous and organic phase: diffusion

Imagine you can get a spectrum from a slice perpendicularly to an NMR tube….
Concentration profile from the interface to the bulk
Diffusion coefficient (≠ self diffusion)
Look at new species formed next to the interface.
LOCSY pulse sequence developed with M. BARDET, S. HEDIGER (CEA-Grenoble team) and C. MANTEL (Post-doc). Implemented for standard probe with z-gradient.

$^1$H spectra of a biphasic system: malonamide (DMDBTDMMA) brings into contact with an aqueous phase. Slice thickness= 68µm
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**Solid state analysis**

Story started 5 years ago with $^{11}$B NMR to study borosilicate glass doped with Pu.

The main problem: get high resolution \[\text{High spinning speed of the samples (not only).}\]

**Safety problem:** crash and dissemination of radioactive material (powder).

$^{27}$Al spectrum 7mm probe 5kHz

And use of insert

Still difficult to distinguish between isotropic peaks and spinning sidebands

S. NIKITENKO aluminates

Without U

With 5% U
31 mm Varian probe + adaptation part

7mm CP/MAS Bruker probe

new design of the cover shim coil with locking parts

adaptation part looks like Bruker top probe.

5mm Varian probe + adaptation part

5mm Varian probe in a Varian narrow bore + adaptation for Bruker probes.
Alternative: no spinning speed limit  probe head nuclearization

1. To insure confinement of the stator.
2. Link to a glove box thanks to a MASII Bruker device
Case of $\frac{1}{2}$ spin: $^{31}$P
CP/MAS 7mm probe

TOPO solid state

$^{7}$kHz

$^{420}$Hz

$^{(TOPO)}_2PuO_2Cl_2$

Broadening paramagnetic effect

in $D_2CCl_2$

Solid state $^{420}$Hz

Prepared by S. CORNET (Post-Doc Atalante)
Before starting irreversible modifications of the probe ...

**Assumption:** spinning speed < 1KHz no hazard

Characterization / quantification of phosphorous species in TBP ash.

$^{31}$P MAS spectrum about inactive ash 5mm probe 10kHz
Double conditioning within 7mm rotor through insert (inactive powder).

$^{31}$P MAS NMR - TBP/MgO

$B_0 = 7.05 \, \text{T}$ - $\nu_{RM} = 5 \, \text{kHz}$ - $T_{\text{REP}} = 4\,s$

$^{31}$P MAS spectrum @ 5kHz

MAT pulse sequence @ 5kHz

T. CHARPENTIER

Outlook: to keep on decreasing spinning speed until 1kHz
Conclusion and outlooks

The applications of NMR in the field of nuclear material are:
  – Extremely wide
  – Fascinating: even standard experiments have something new
  – Challenging

To go further:
  – Cryogenic liquid probe ($^{13}$C, $^1$H)
  – Confined CP/MAS probe designed to radioactive solid state samples.