LTSM – Laboratoire tri ionique par les systèmes moléculaires auto-assemblés

Lipophilic Derivatives of AminoPolyCarboxylic Acids as New Extractants for the Fuel Cycle and the Recycling of Non-Radioactive Rare Earth Elements: Context and Examples.

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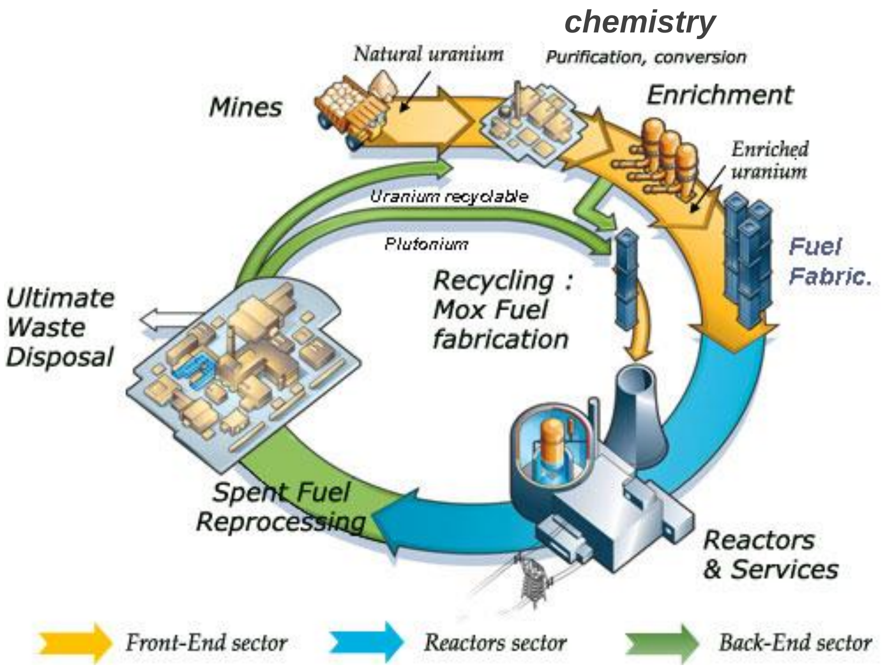
F. Giusti & S. Pellet-Rostaing.

ICSM, Univ Montpellier, CEA, CNRS, ENSCM, Marcoule, France

CONTEXT:
Liquid-Liquid Extraction (LLE) & Hydrometallurgy of Actinides & Lanthanides

Mining & Recycling of Lanthanides & Actinides

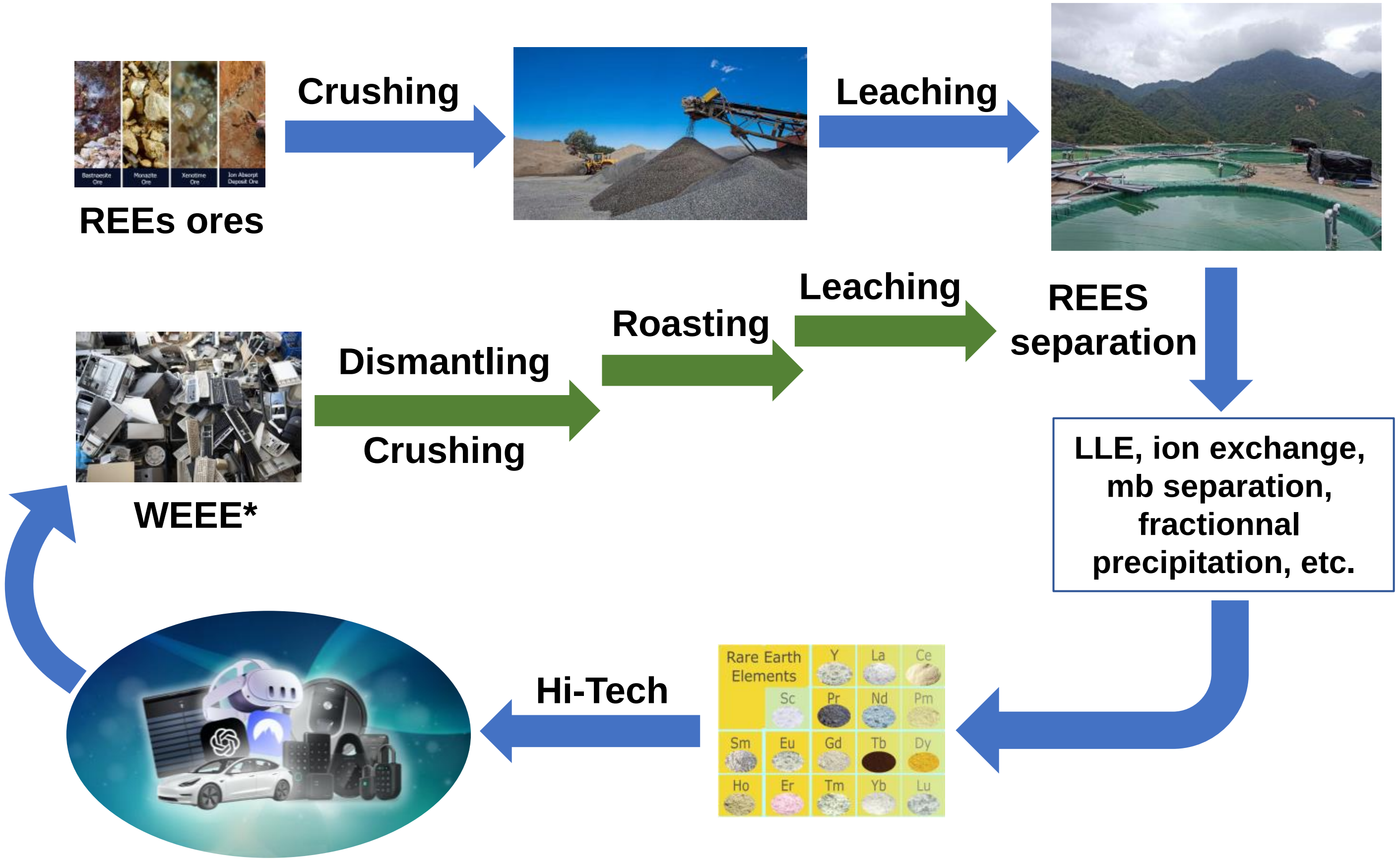
❑ Uranium: the fuel cycle



https://laradioactivite-prod-en.apps.wok3.in2p3.fr/articles/nuclearenergy/fuel_cycle

- LLE processes involved
  - ➢ Front-end
    - ✓ AMEX in sulfuric media
    - ✓ URPHOS in phosphoric media
  - ➢ Back-end
    - ✓ PUREX in nitric media

❑ REEs: extraction and recycling



REEs ores

Crushing

Leaching

REES separation

LLE, ion exchange, mb separation, fractionnal precipitation, etc.

Hi-Tech

WEEE*

Dismantling

Crushing

Roasting

Leaching

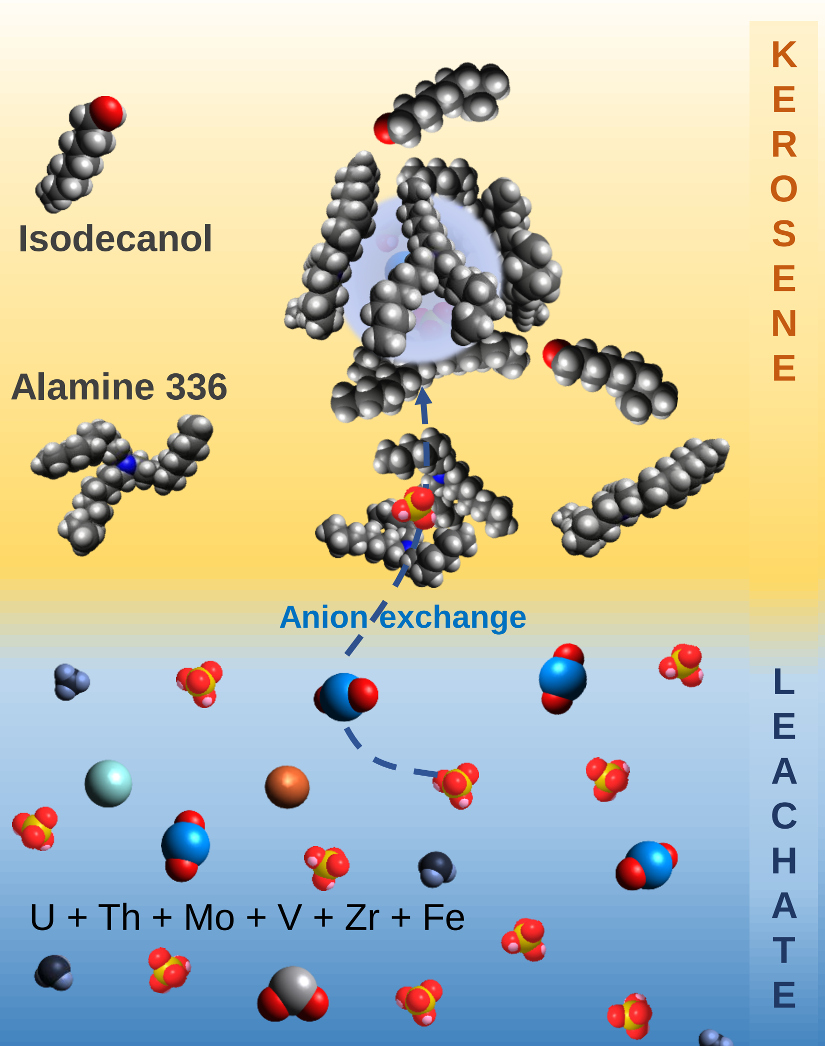
- LLE processes involved
  - ➢ Similar processes are applied in both cases
  - ➢ From nitric, hydrochloric or sulfuric media

*WEEE = Waste from Electrical and Electronic Equipment

LEE for selective separation of actinides and lanthanides

❑ AMEX process

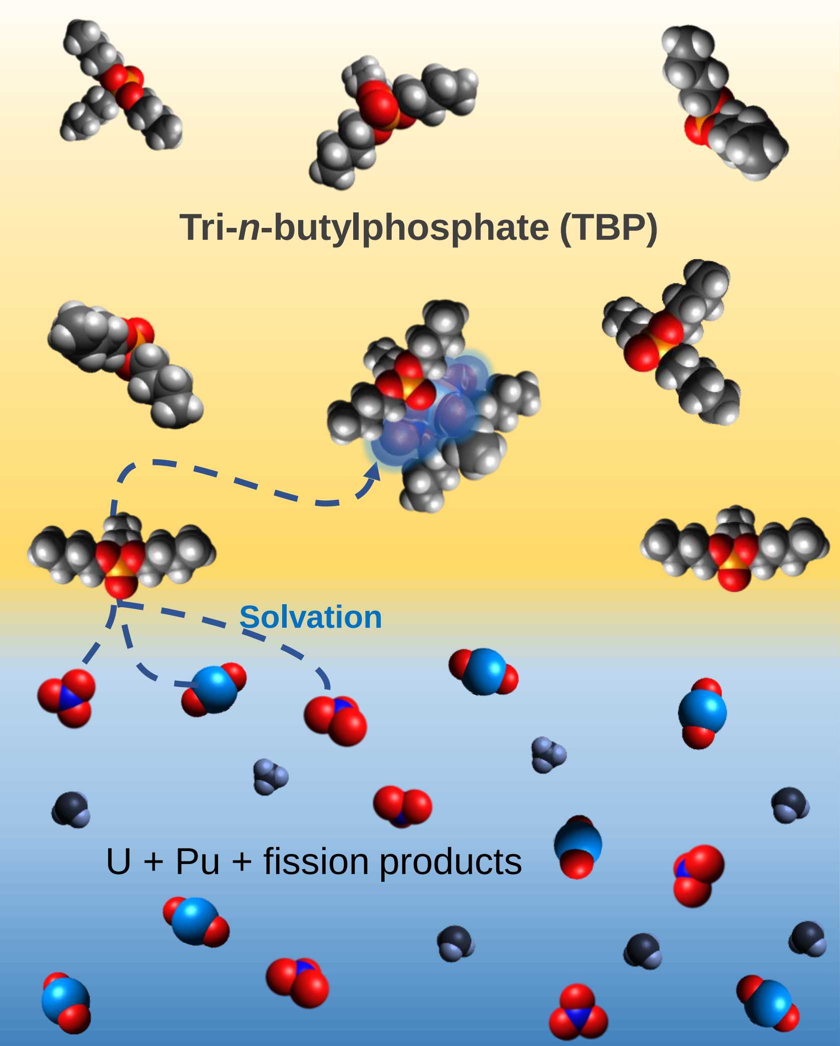
$\overline{2\,(R_3NH)_2SO_4} + UO_2SO_4 \rightleftharpoons \overline{(R_3NH)_4UO_2(SO_4)_3}$ (1)



1. Sato, *J. Inorg. Nucl. Chem.*, **25**, 441-446, **1963**

❑ PUREX process

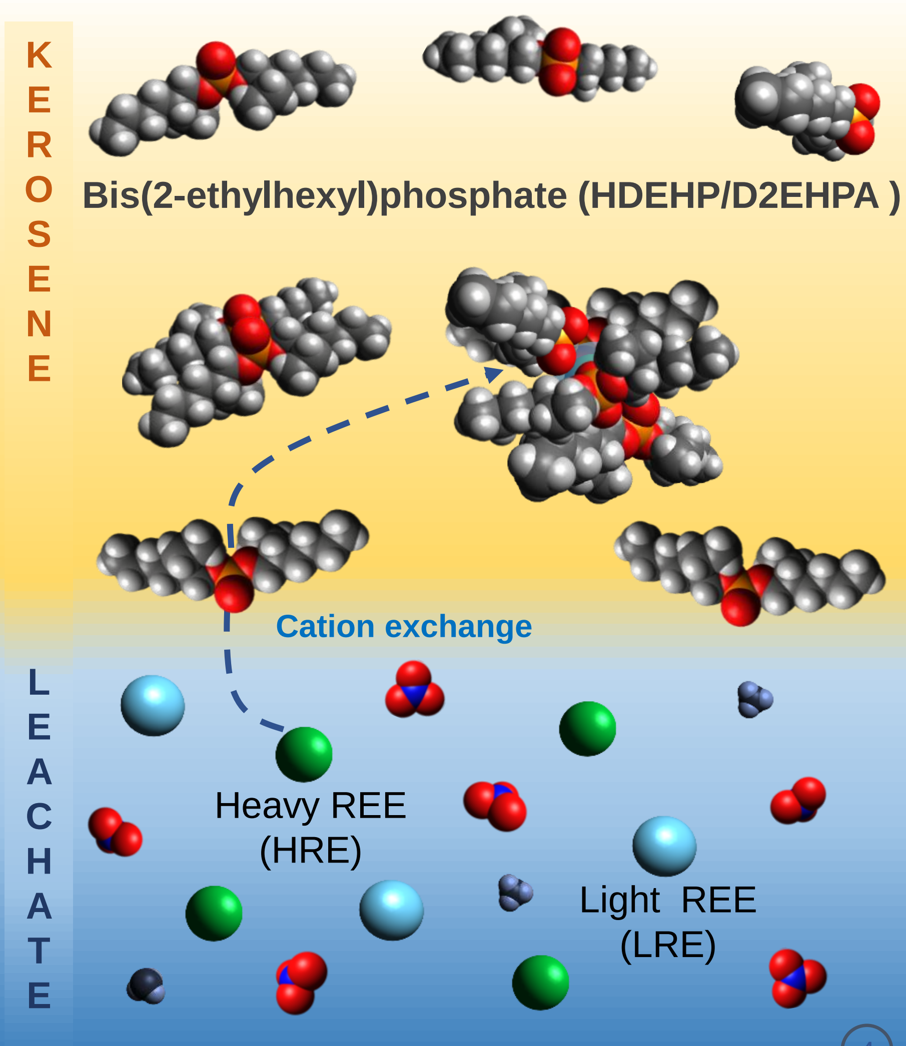
$\overline{2\,TBP} + UO_2(NO_3)_2 \rightleftharpoons \overline{(TBP)_2UO_2(NO_3)_2}$ (2)



2. Le traitement-recyclage du combustible usé, CEA DEN, **2008**

❑ REEs extraction

$\overline{3\,(HDEHP)_2} + RE^{3+} \rightleftharpoons \overline{RE(H(DEHP)_2)_3} + 3\,H^+$ (3)



3. Cheisson & Schelter, *Science*, **363**, 489-493, **2019**

Limitations of LLE Processes Applied at Large Scale

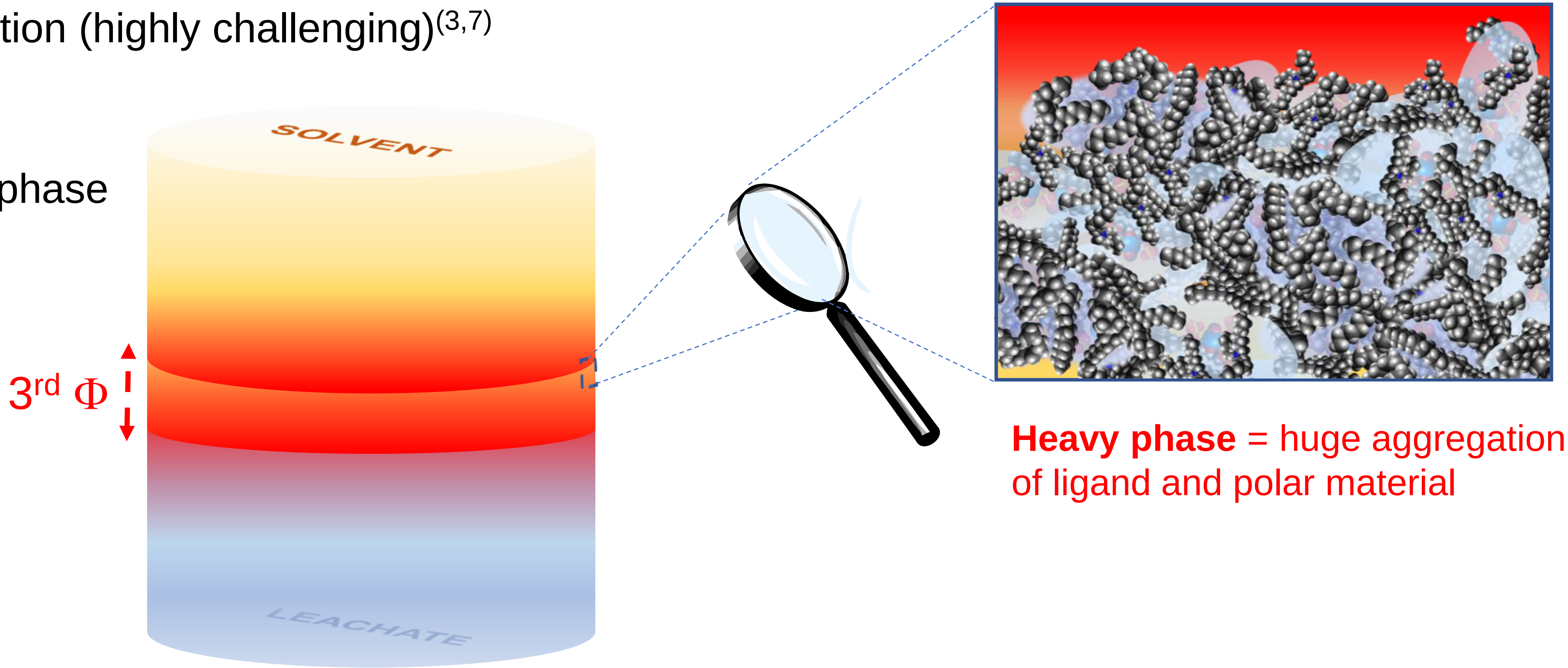
❑ Selectivity of transfer can be improved

- U vs Fe, V, Mo, Zr (AMEX)(4)
- U vs Fe (URPHOS)(5)
- Ln(III) vs. An(III) (back-end fuel cycle)(6)
- HRE vs LRE(3)
- Intra-lanthanide separation (highly challenging)(3,7)

❑ Third phase formation

- Splitting of the organic phase
- AMEX(8)
- REE extraction(9)

= Cumbersome phenomenon that jeopardizes the ELL process



Heavy phase = huge aggregation of ligand and polar material

➡ **Must be adressed**

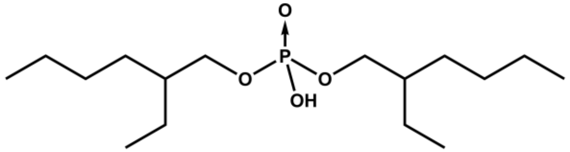
3. Cheisson & Schelter, *Science*, **363**, 489-493, **2019; 4.** McDonald *et al*., *J. South Afr. Instit.Min.Metall*., **81**, 303-308 **1981**; **5.** Leydier *et al*., Hydrometallurgy, **171**, 262-266, **2017**; **6.** Leoncini et al., Chem. Soc. Rev., **46**, 7229-7273, **2017**; **7.** Stamberga *et al*., *Inorg. Chem*., **59**, 17620-17630, **2020**; **8.** Guérinoni *et al., J. Mol. Liq.,* **403**, 124820, **2024**; **9.** Ellis *et al*., *J. Phys. Chem*. B, **119**, 11910-11927, **2015**.

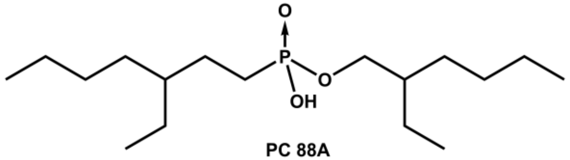
Limitations of LLE Processes Applied at Large Scale

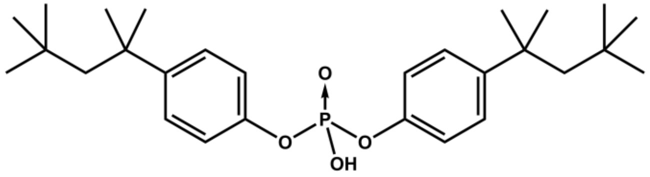
- **Selectivity of transfer can be improved**

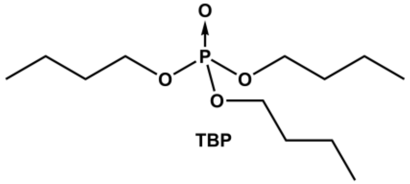
- **Third phase formation**

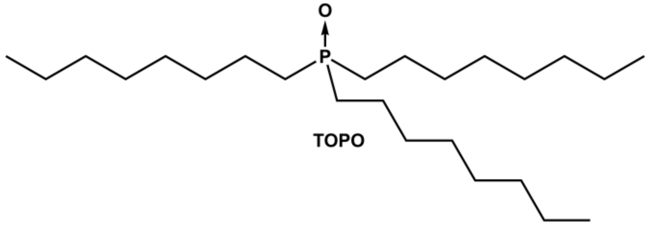
- **Organophosphorous extractants**
  - "Former" concern
    - Incineration of solvents leads to phosphates accumulation


HDEHP


PC 88A


D4TOPHP


TBP


TOPO

To be replaced by extractants consisting of C, H, O, N

CHON system

Understand and Optimize Processes at the Lab. Scale

❑ Role of constituents? Mechanism?

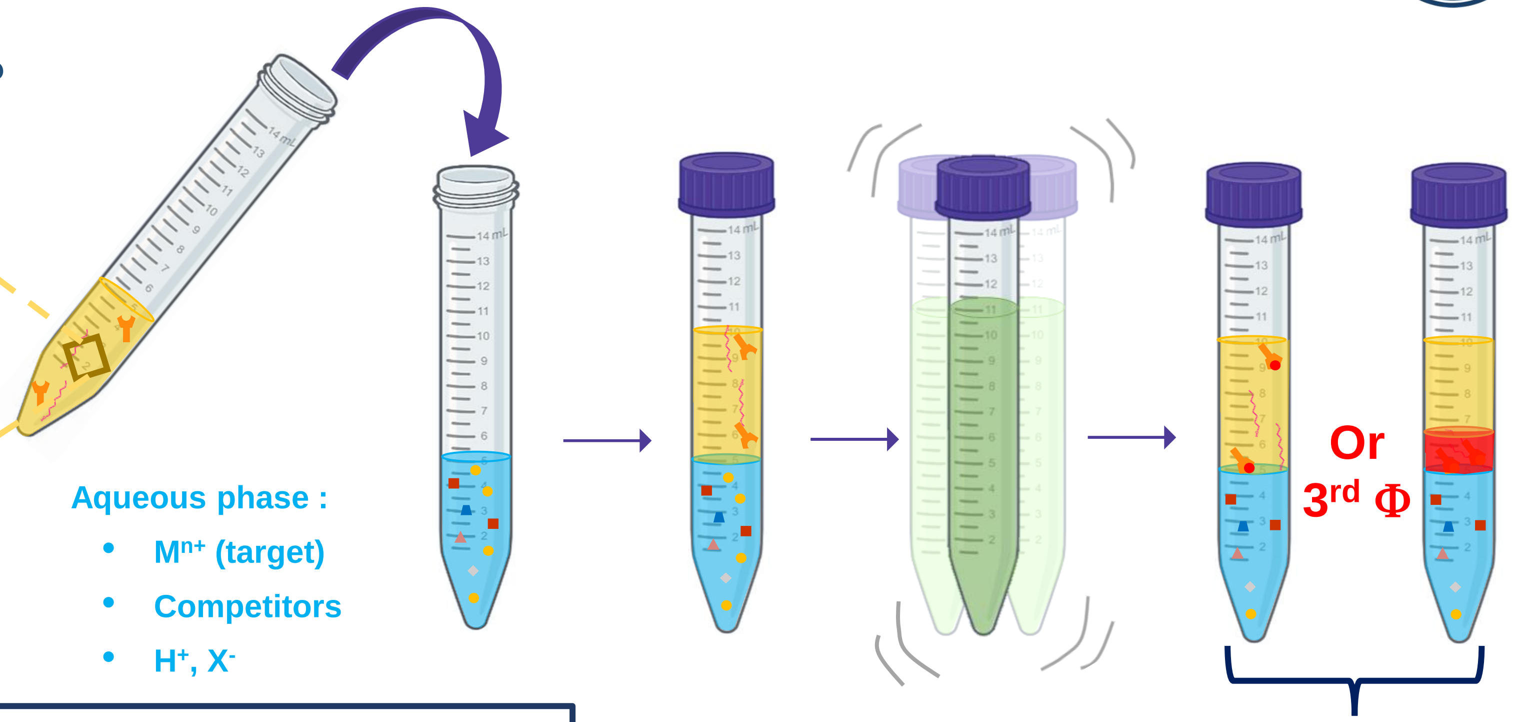
Solvent:

- Extractant: reference or new one
- Diluent: *n*-dodecane

- Phase modifier (PM): 1-octanol

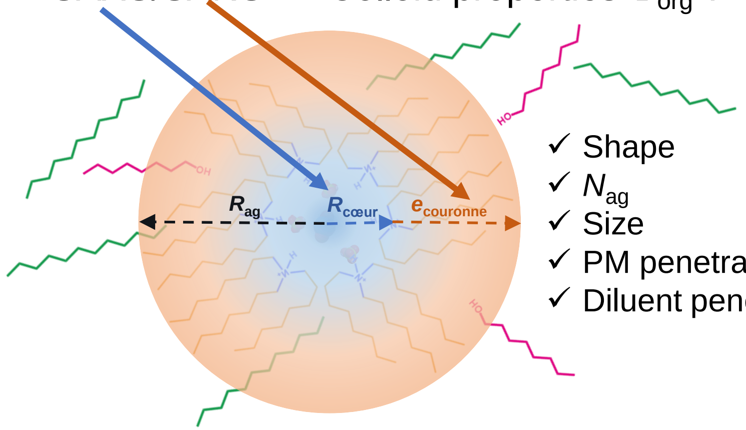
Aqueous phase :

- **M^{n+} (target)**
- **Competitors**
- **H^+, X^-**



Analysis at equilibrium

- SAXS/SANS => Colloid properties Φ_{org} ?



✓ Shape
✓ N_{ag}
✓ Size
✓ PM penetration
✓ Diluent penetration

- pH-metry/KF => Composition H^+/H_2O Φ_{Org}?
- log *D* = *f*(log [ligand]) => Stœchiometry M:L?
- ln K_{ex} = *f*(1/T) => $\Delta H°$, $\Delta G°$, $\Delta S°$
- Tensiometry => Surface properties + CAC

- ICP => Distribution of M Φ_{Org}/Φ_{aq} ?

$$\boxed{D_M = \frac{[M]_{org}}{[M]_{aq}} \cdot \frac{V_{org}}{V_{aq}}}$$ ⇨ Efficiency

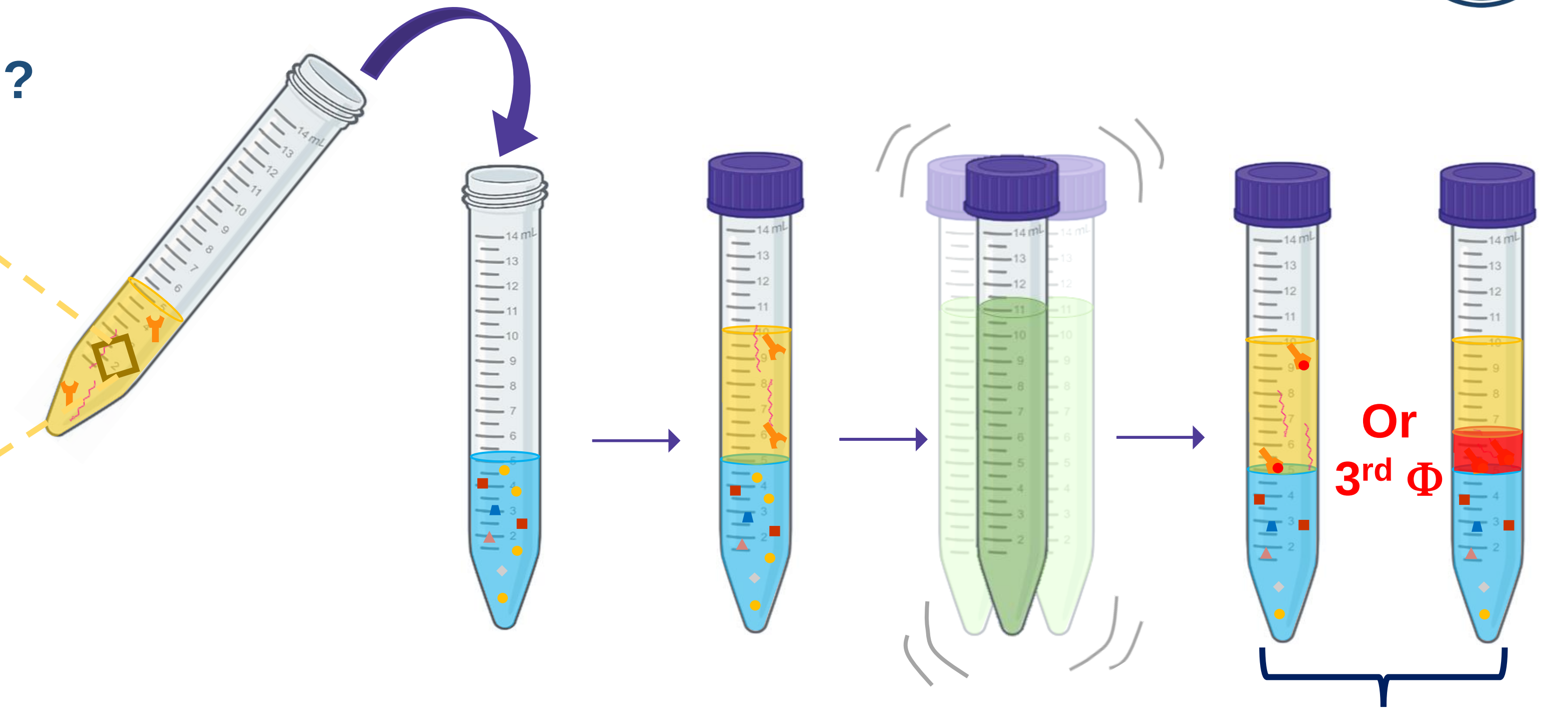
$$\boxed{SF_{M_1/M_2} = \frac{D_{M_1}}{D_{M_2}}}$$ ⇨ Selectivity

Understand and Optimize Processes at the Lab. Scale

❑ Role of constituents? Mechanism?

Solvent:

- Extractant: tailoring the structure
  or
- Diluent: tuning the chains length
  or
- PM: tuning the structure



Analysis at equilibrium

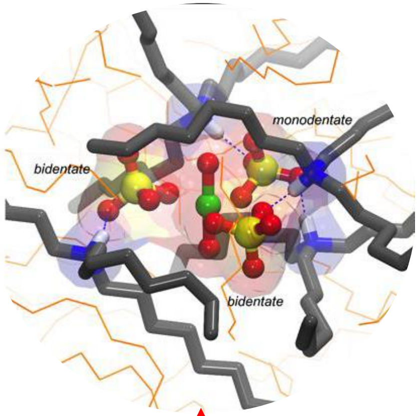
Data collection and processing

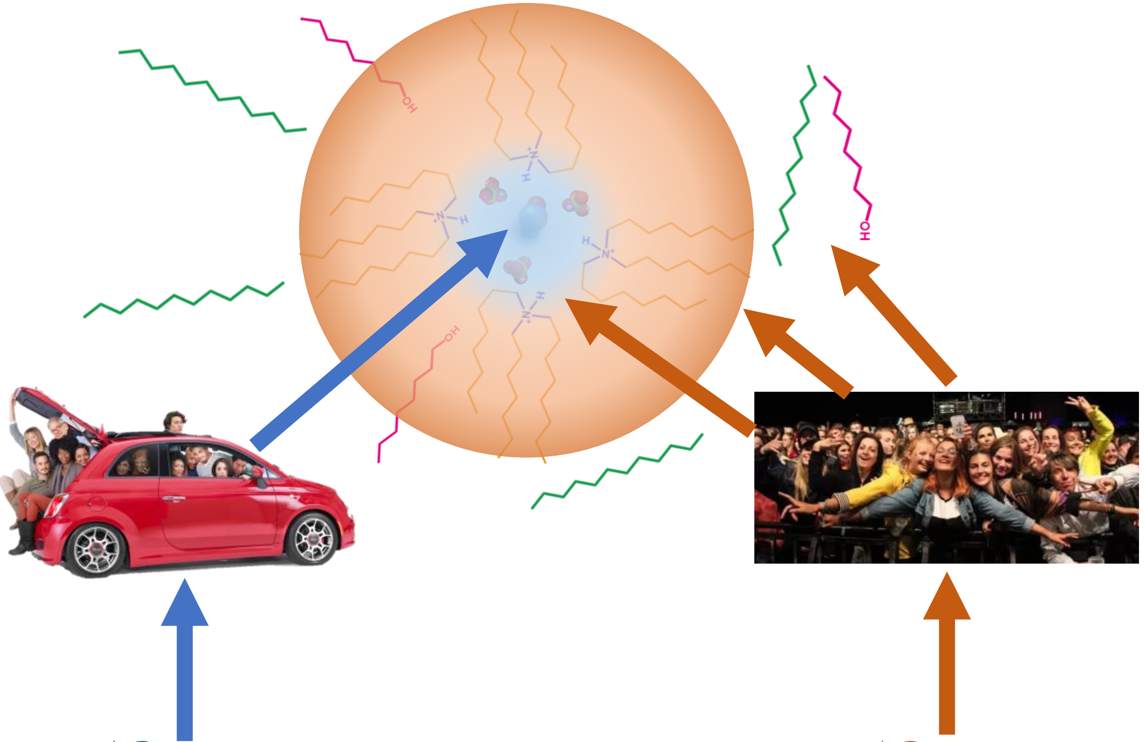
RATIONALIZATION:
equations + subtle analysis of
the thermodynamic of the system
⇨ Ienaic: extraction = *f*(colloid properties of solvent)

Ienaic Approach: Thermodynamic & Theory(10,11)

$\Delta G_{\text{transfer}}$ = **$-k_BT\ln(D_U)$**

(From Sukhbaatar *et al.*(12))





$\Delta G_{\text{Complexation}}$

Complexation of the cation by ligands

$+\ \Delta G_{\text{Drop}}$

$$\Delta G_{droplet}\left(UO_2^{2+}\right) = \boldsymbol{i}\ln\left(\frac{m^{org}_{SO_4^{2-}}\gamma^{org}_{SO_4^{2-}}}{m^{aq}_{SO_4^{2-}}\gamma^{aq}_{SO_4^{2-}}}\right) + \ln\left(\frac{m^{org}_{UO_2^{2+}}\gamma^{org}_{UO_2^{2+}}}{m^{aq,0}_{UO_2^{2+}}\gamma^{aq}_{UO_2^{2+}}}\right) + \boldsymbol{i}\ln m^{org}_{(R_3NH^+)_2}\gamma^{org}_{(R_3NH^+)_2} + (2\boldsymbol{i}+1)(\Phi^{org}-\Phi^{aq})$$

Containment of polar species in 1 nanogoutte (saturated solution)

$+\ \Delta G_{\text{Chains}}$

$\Delta G_{\text{Micellisation}}$ **+** **$\Delta G_{\text{Curvature}}$**

$-N_{ag}\ln(\text{CAC})$

Extractants assembled in a reverse micelle

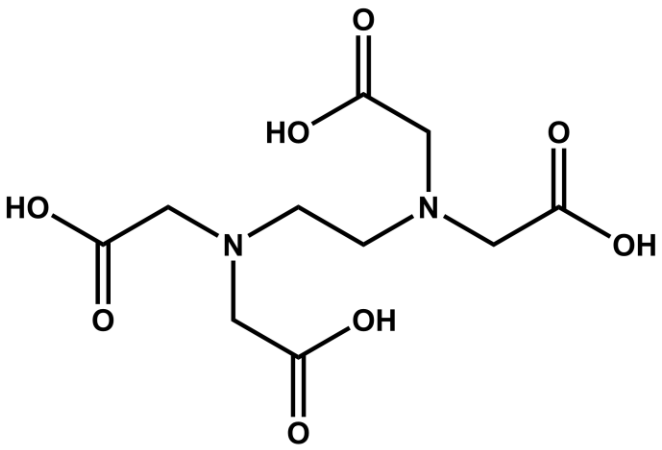
$$\frac{K^*}{2}N_{Ag}(P_S-P_e)^2$$

Core/Corona Interface biding energy => Film stiffness

10. Dufrêche & Zemb, *Chem. Phys. Lett.*, **622,** 45–49, **2015**; **11**. Rey *et al.*, *Langmuir*, **33**, 13168-13179, **2017**; **12**. Sukhbaatar *et al.*, *Chem. Commun. RSC*, **55**, 7583-7586, **2019**.

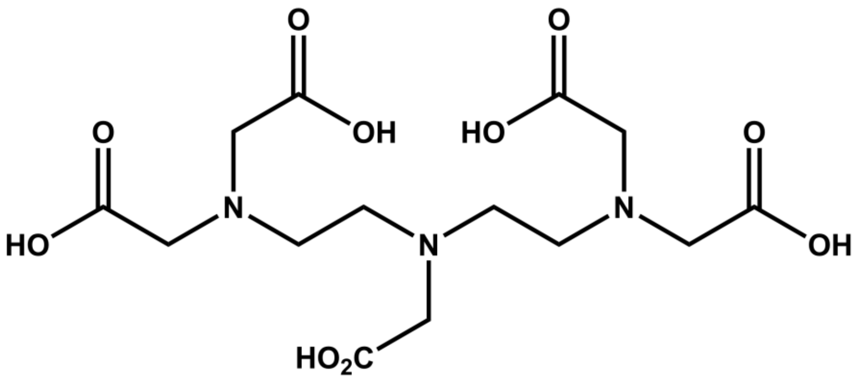
EXAMPLE: Development of Lipophilic AminoPolyCarboxylic Acid Derivatives

What Are AminoPolyCarboxylic Acids (APCAs)?



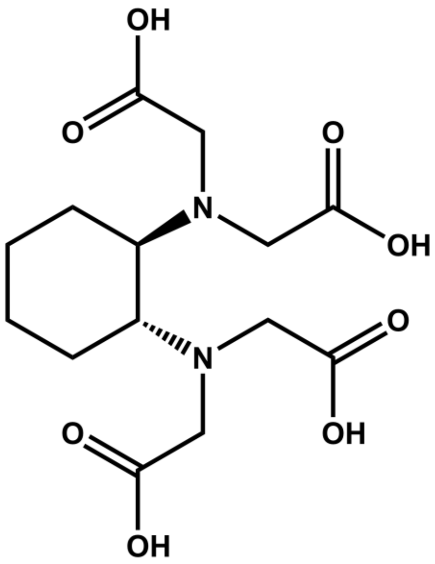
2,2',2",2"'-(ethane-1,2-diylbis(azanetriyl))tetraacetic acid

EthyleneDiamineTetracetic Acid (EDTA)



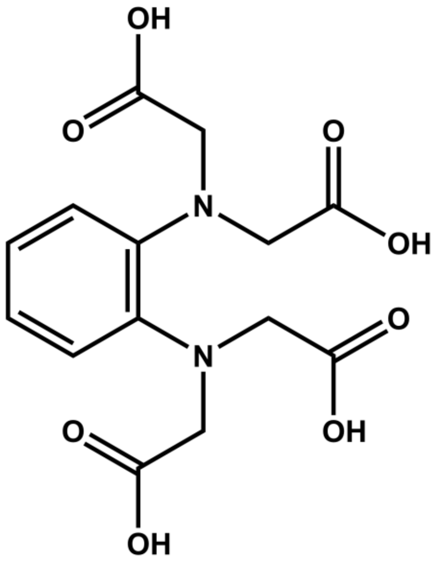
2,2',2",2"'-((((carboxymethyl)azanediyl)bis(ethane-2,1-diyl))bis(azanetriyl))tetraacetic acid

DiethyleneTriaminePentaacetic Acid (DTPA)



2,2',2",2"'-(((1*R*,2*R*)-cyclohexane-1,2-diyl)bis(azanetriyl))tetraacetic acid

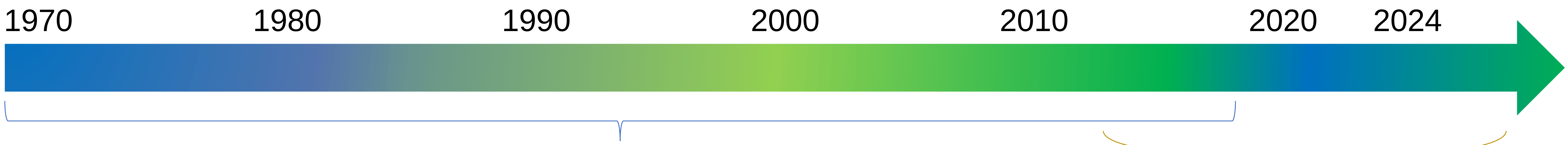
trans-1,2-CyclohexaneDiamineTetraacetic Acid (CyDTA)



2,2',2",2"'-(1,2-phenylenebis(azanetriyl))tetraacetic acid

1,2-PhenylDiamineTetraacetic Acid (PDTA)

When/Why/How Developing Lipophilic EDTA Derivatives?

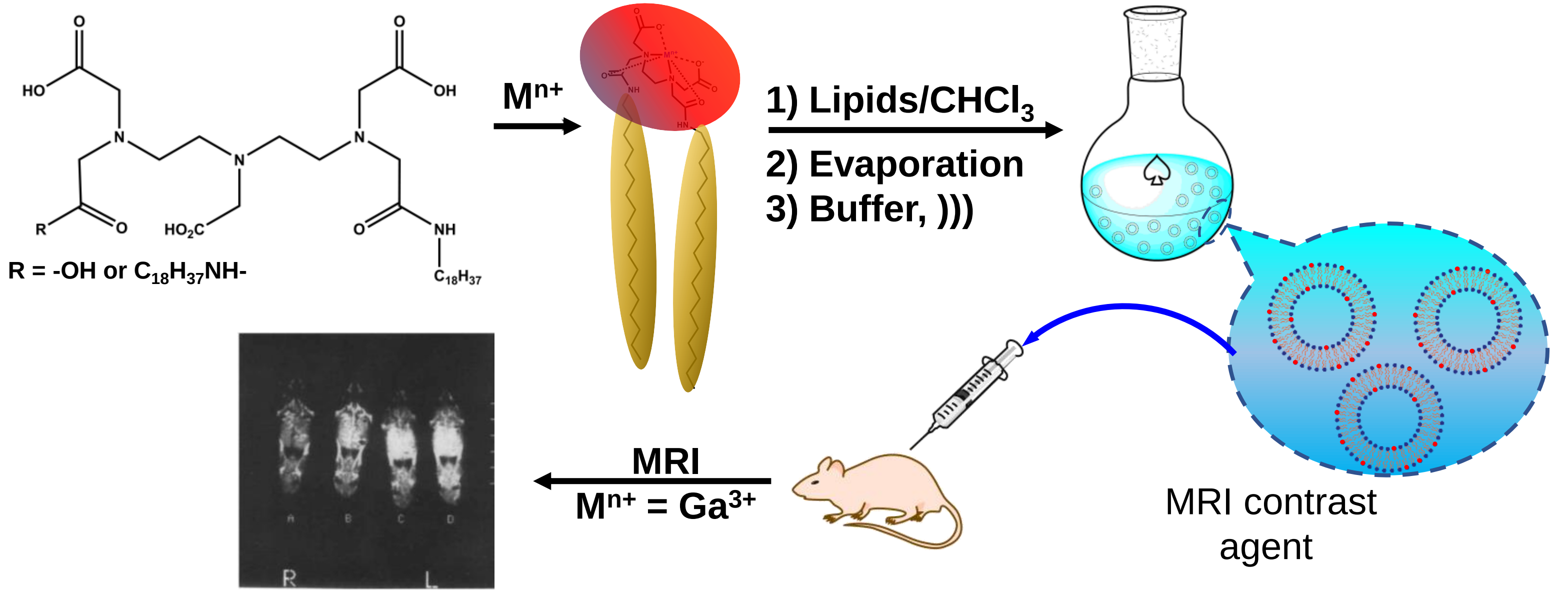


Development of **hydrophobic** EDTA/DTPA derivatives as surfactants or MRI contrast agents(13)

Development of **lipophilic** EDTA/DTPA derivatives for LLE of metal cations

🟦 Development of hydrophobic EDTA/DTPA diamide derivatives

🟩 Development of hydrophobic *C*-alkylated EDTA/DTPA derivatives



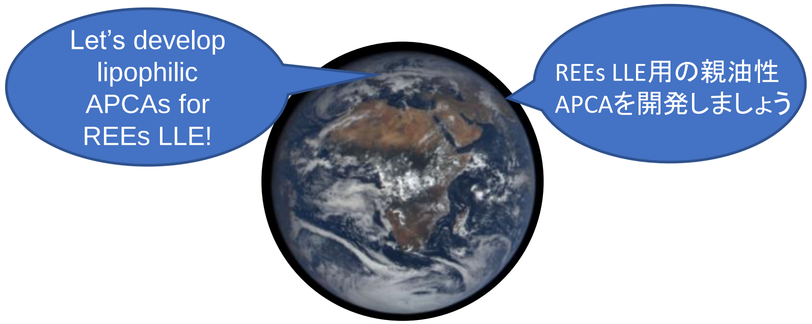
R = -OH or $C_{18}H_{37}NH$-

M^{n+}

1) Lipids/$CHCl_3$
2) Evaporation
3) Buffer,)))

MRI contrast agent

MRI
$M^{n+} = Ga^{3+}$



- Technical note ICSM in 2014(14)
- Claimed but not achieved in a Japanese patent in 2015(15)
- Patented in France (ICSM)(16)
- Published by LTSM & co(17)
- ANR (NEODREAM)
- E. Fauvel's Ph. D. (2024-2027)

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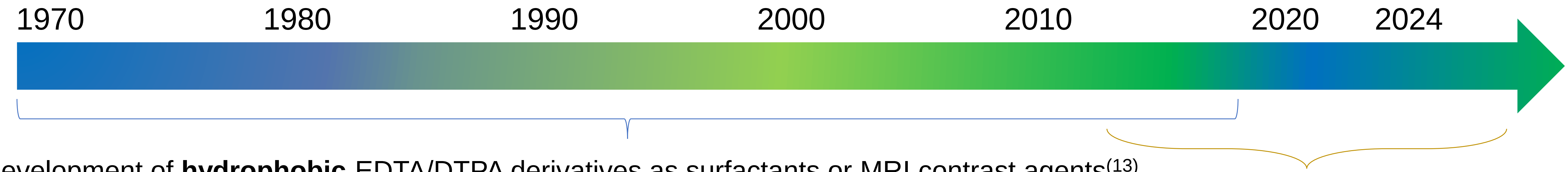
13. Kabalka *et al.*, *Magn. Res. Med*, **19**, 406-415,**1991**; **14.** Mary & Arrachart, Technical note, **2014; 15.** JP2016028021A, **2015**; **16**. FR2210237, **2022**; **17.** Sukhbaatar *et al.*, *Hydrometallurgy*, **231**, 106415, **2025**.

When/Why/How Developing Lipophilic EDTA Derivatives?



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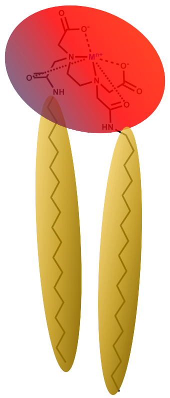
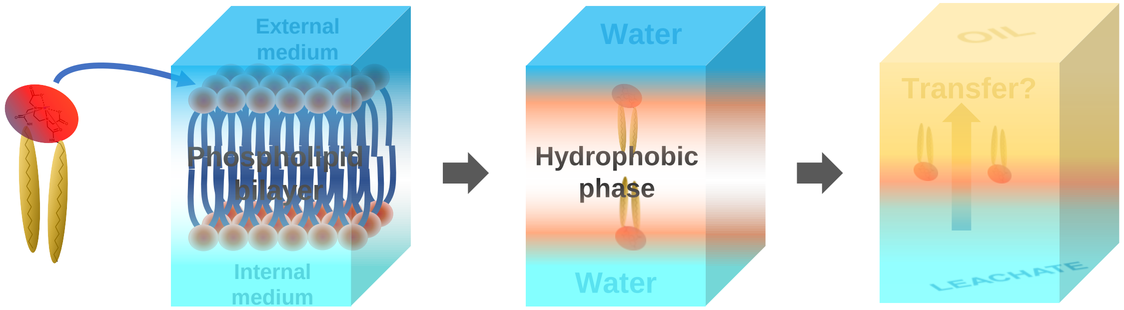
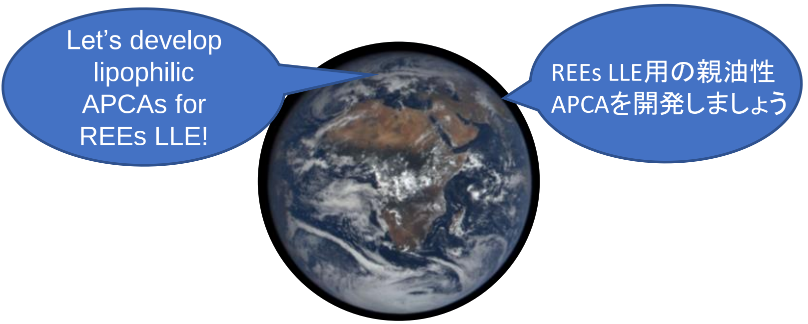
🟩 Development of hydrophobic *C*-alkylated EDTA/DTPA derivatives

Development of **lipophilic** EDTA/DTPA derivatives for LLE of metal cations



- ❑ **Isolated ligand-REE complex easily incorporated in lipids membrane(13)**
  - Ligand-REE complex is typically more lipophilic than the free ligand
  - Transfer of REE in solvent should be favored





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13. Kabalka *et al*., *Magn. Res. Med*, **19**, 406-415,**1991**; **14.** Mary & Arrachart, Technical note, **2014; 15.** JP2016028021A, **2015**; **16.** FR2210237, **2022**; **17.** Sukhbaatar *et al*., *Hydrometallurgy*, **231**, 106415, **2025.**

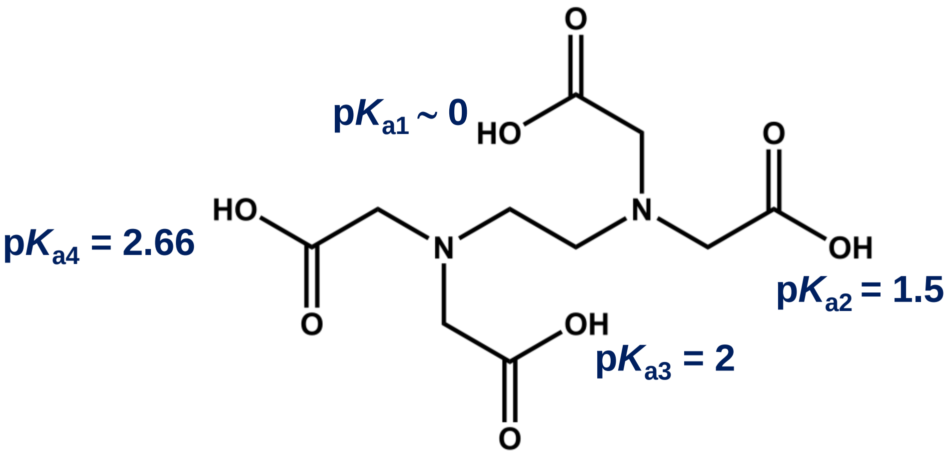
When/Why/How Developing Lipophilic APCAs Derivatives?

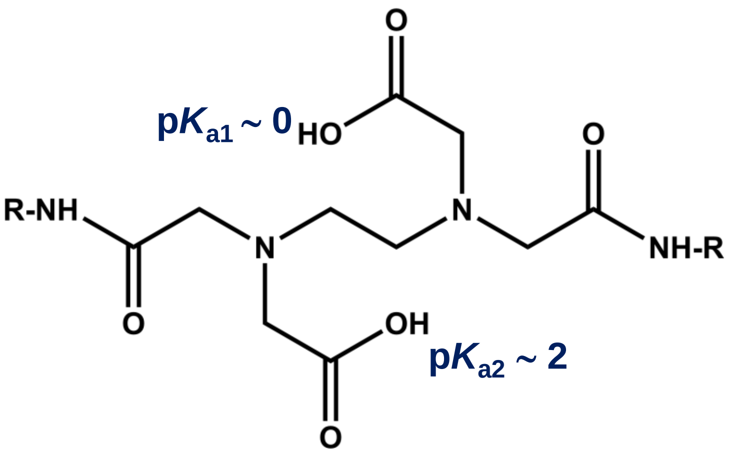
☐ High affinity(15-17) of parent molecules towards lanthanides and actinides

- $\boldsymbol{LH_4 + M^{n+} \overset{K}{\rightleftharpoons} [LH_{4-n}M] + nH^+}$ with $K \sim 10^{15}$-10^{30}
- But poor intra-Ln selectivity(3)
  - ➢ Tuning affinity/selectivity by chemical modification
    - ✓ Modification of carboxylic acid function => affinity lowered by 1000(18)
    - ✓ Modification of the hydrocarbon backbone increases affinity by 10-100(19)

☐ Potential CHON cation exchanger

- Strong first acidity maintained after modification(20)
  - ➢ Advantageous replacement of organophosphorus extractants





With R = *i*Pr or *t*Bu

15. Martell & Smith, *Critical Stability Constants,* **6**, **1989**; **16.** Cernochova *et al*., *Radiochim. Acta*, **93**, 733-739, **2005**; **17.** Thakur *et al*., *Radiochim. Acta*, **101**, 221-232, **2013; 18.** Keana *et al*., *J. Org. Chem*., **55**, 2868-2871, **1990**; **19**. Smith & Martell, Critical Stability Constants, Vol. 4-6, **1974-1983**; **20.** Wang *et al*., *Polyhedron*, **18**, 109-117, **1999**.

When/Why/How Developing Lipophilic APCAs Derivatives?

❑ Potential applications in the fuel cycle

- Front-end process: extraction of U from sulfuric or phosphoric leachates (E. Fauvel's Ph. D.)
- Back-end process: reversal of the SANEX
  - ➢ Hydroxylated EDTA analogous (HEDTA) used in the SANEX process of the fuel cycle
  - ➢ Amphiphilic derivatives as bypass for actinides recovering in organic medium

❑ Recycling of REEs from WEEEs via LLE (CEFIPRA project 2017-2021)

NML

TATA

TATA CONSULTANCY SERVICES

CEFIPRA

TND

La recherche des métaux rares

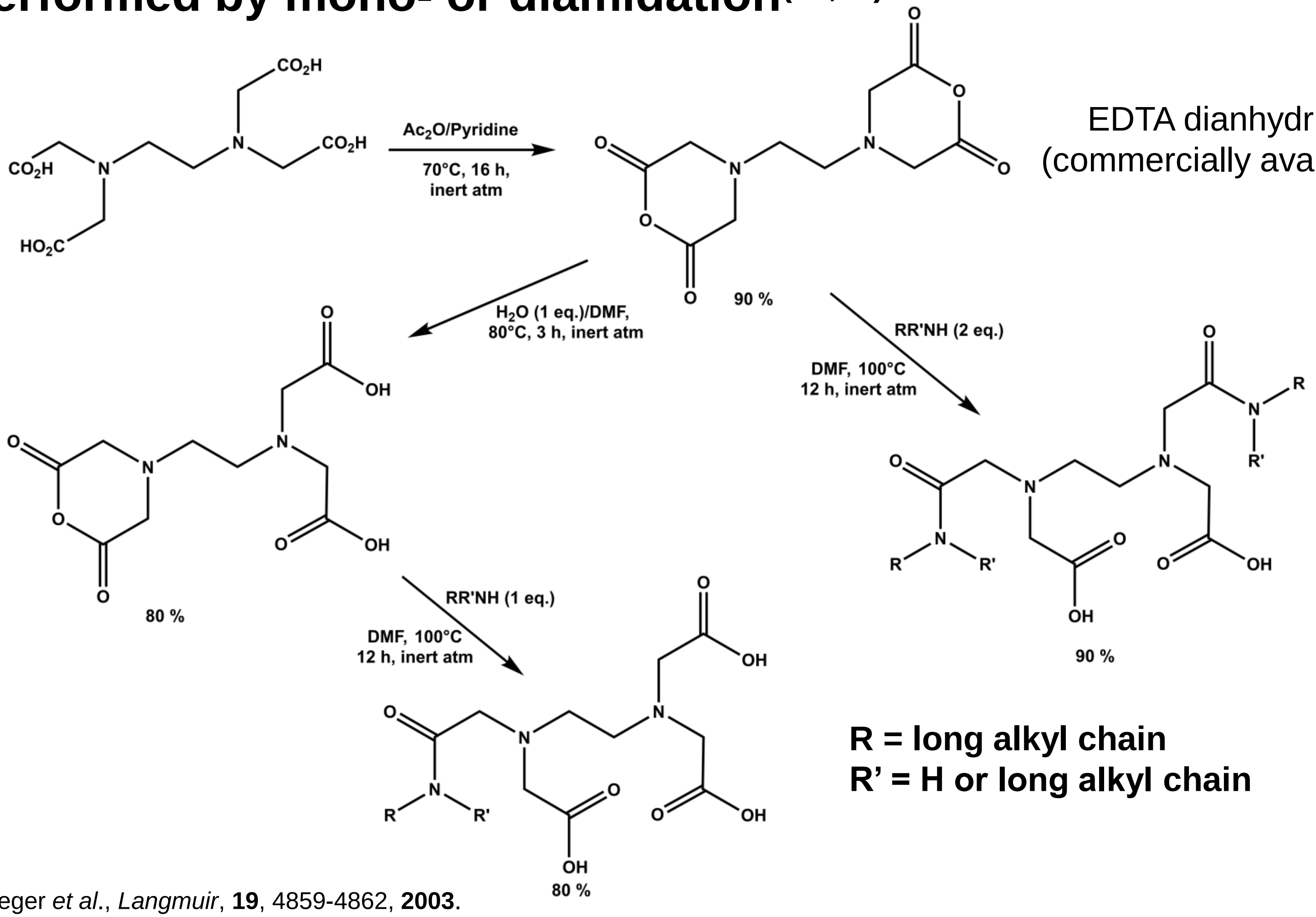
Marcoule Institute of Separation Chemistry

Terra Nova Development

When/Why/How Developing Lipophilic APCAs Derivatives?

- ❑ **Hydrophobic modification of APCAs must yield lipophilic derivatives**
  - Solubility ≥ 0.2 M in *n*-dodecane

- ❑ **Modification may be performed by mono- or diamidation**(13,21)



EDTA dianhydride
(commercially available)

R = long alkyl chain
R' = H or long alkyl chain

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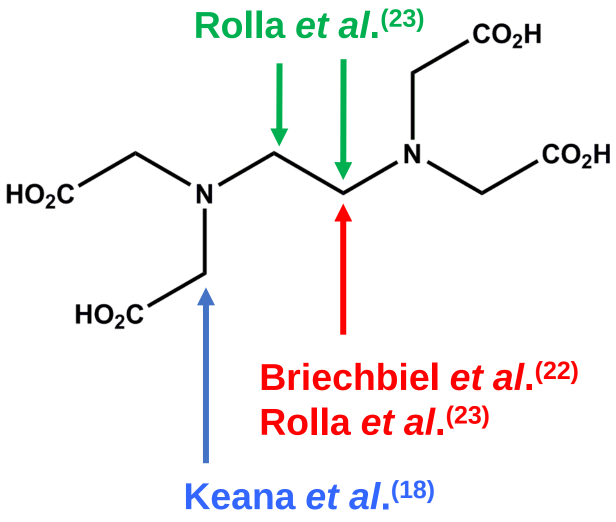
13. Kabalka *et al*., *Magn. Res. Med*, **19**, 406-415,**1991**; **21.** Jaeger *et al*., *Langmuir*, **19**, 4859-4862, **2003**.

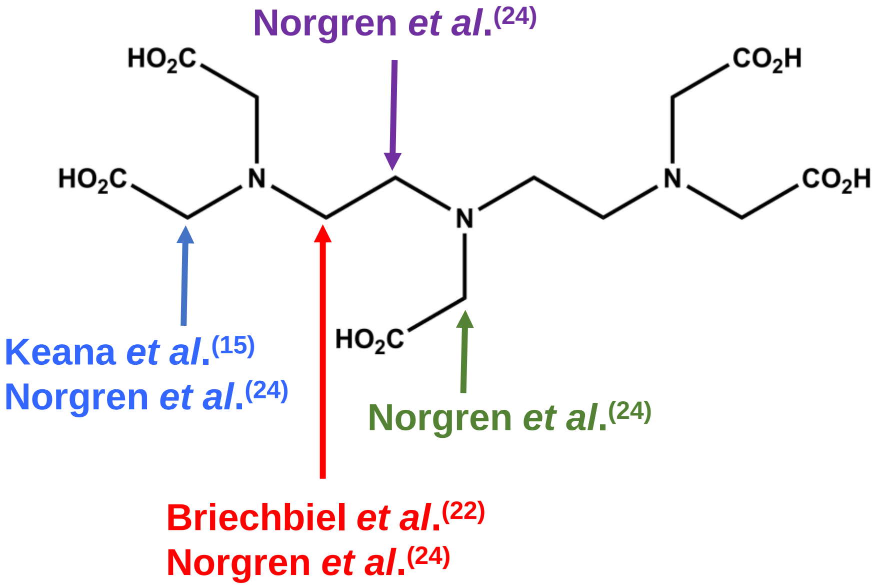
When/Why/How Developing Lipophilic APCAs Derivatives?

- ❑ **Hydrophobic modification of APCAs must yield lipophilic derivatives**
  - Solubility > 0.2 M in *n*-dodecane

- ❑ **Modification may be performed by mono- or diamidation(13,21)**

- ❑ **Modification may be performed on hydrocarbon backbone(18,22-24)**

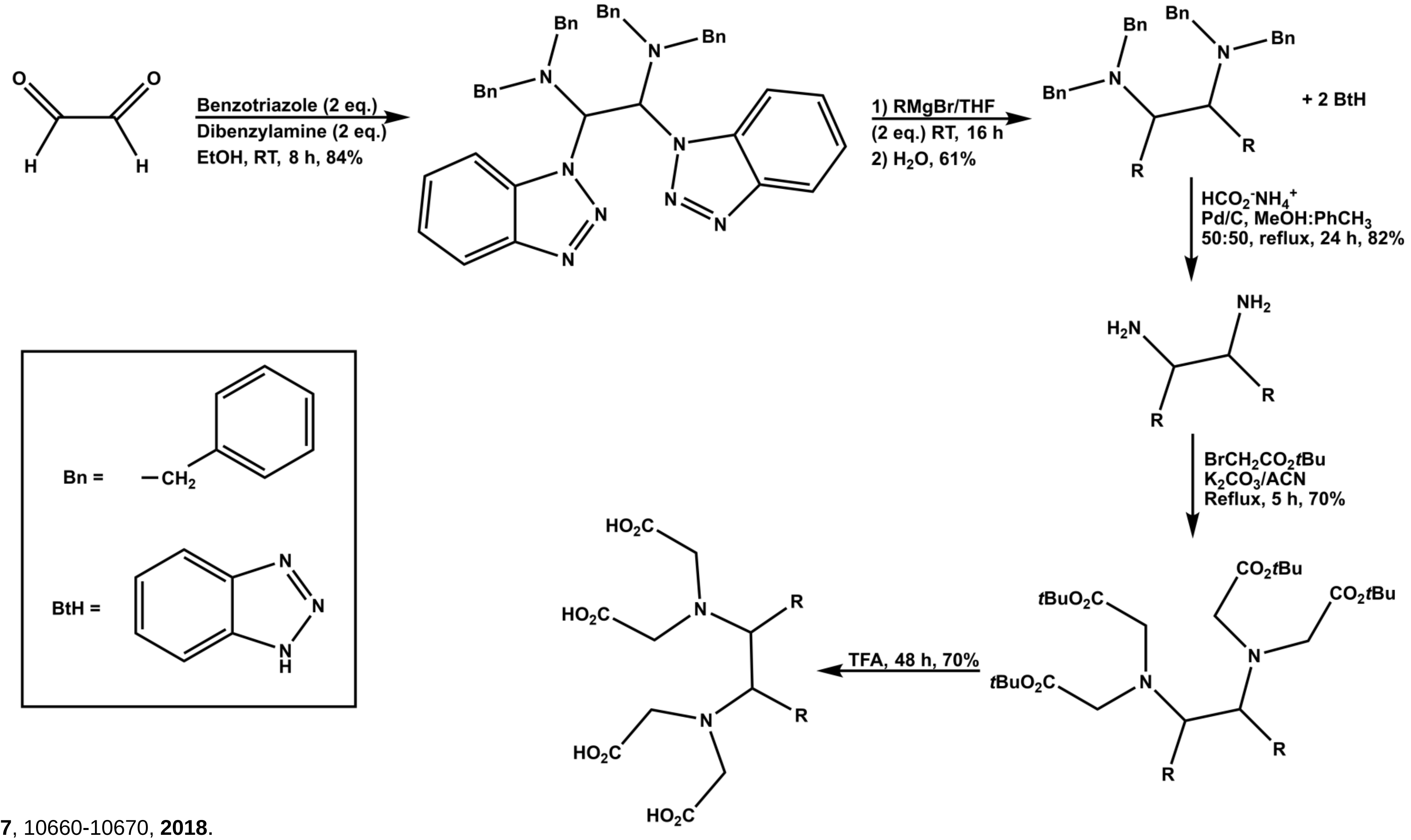




18. Keana *et al.*, *J. Org. Chem.*, **55**, 2868-2871, **1990**; **22.** Brechbiel *et al.*, *Inorg. Chem.*, **25**, 2112-2181, **1986**; **23.** Rolla *et al.*, Dalton Trans., **47**, 10660-10670, **2018**; **24.** Norgren *et al.*, *US Patent*, 8,658,814 B2, **2014**.

When/Why/How Developing Lipophilic APCAs Derivatives?

- ☐ **Modification may be performed on hydrocarbon backbone**(18,22-24)
  - Example: synthesis of symetrical di-*C*-alkylated EDTA derivatives(23)



23. Rolla *et al*., Dalton Trans., **47**, 10660-10670, **2018**.

Synthesis of Lipophilic APCAs Derivatives

❑ Synthesis of APCAs diamide derivatives

- Yield = 60-90%
- Only modification performed with dialkylamines led to derivatives soluble in conventionnal organic solvents
  - ➢ HNR_2 with R = C_8H_{17}-, 2-Ethylhexyl, $C_{10}H_{21}$-, $C_{12}H_{25}$-
- Only one EDTA derivative was found slightly soluble in n-dodecane:octanol mixture
  - ➢ EDTA derivative with R = decyl soluble at 0.015 M in 93:7 n-dodecane:octanol (DOm)
- All CyDTA and PDTA derivatives were found soluble at 0.2 M in pure dodecane
  - **But all compounds were too unstable**
    - ➢ Partial degradation within one week in diluent → **Modification cannot be performed on both carboxylic functions and hydrocarbon backbone**

❑ Synthesis of *C*-alkylated EDTA derivatives

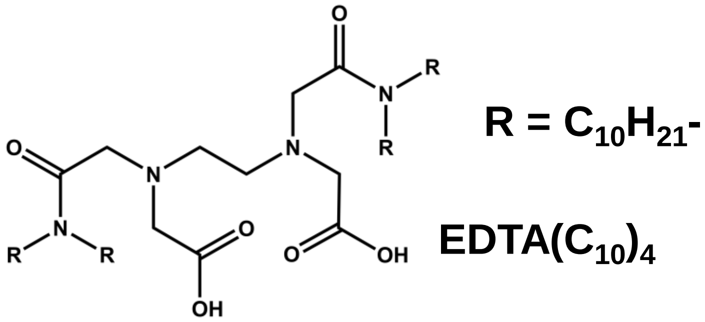
- R = $C_{10}H_{21}$- or $C_{12}H_{25}$-
- 30% overall yield
- Partially soluble in methanol

➡ Proof of concept adressed with CyDTA derivatives and EDTA diamide$(C_{10})_4$

Assessment of Extraction Properties: LLE of Ln(III)

❑ **Example: extraction of Nd(III) with ligand diluted in various diluents**(16,17)

- D_M vs pH => cation exchange properties
- From HCl or HNO_3 leachate ($[Nd^{3+}]$ = 0.01 M)
- $[EDTA(C_{10})_4]$ = 0.01 M in various diluents



- ➢ DOm = 93:7 n-dodecane:octanol mixture
- ➢ DiPB = 1,3-diisopropylbenzene
- ➢ Heptan-2-one
- ➢ MiBK = methylisobutyketone
- ➢ 11-Undecen-1-ol

}

Solubility~20 mM

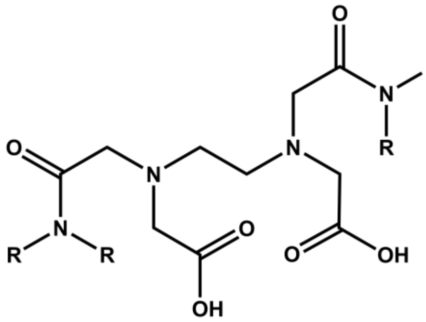
- ➢ Chloroform **=> Solubility~100 mM**

16. FR2210237, **2022**; **17.** Sukhbaatar *et al*., *Hydrometallurgy*, **231**, 106415, **2025**

Assessment of Extraction Properties: LLE of Ln(III)

❑ **Example: extraction of Nd(III) with ligand diluted in various diluents$^{(16,17)}$**

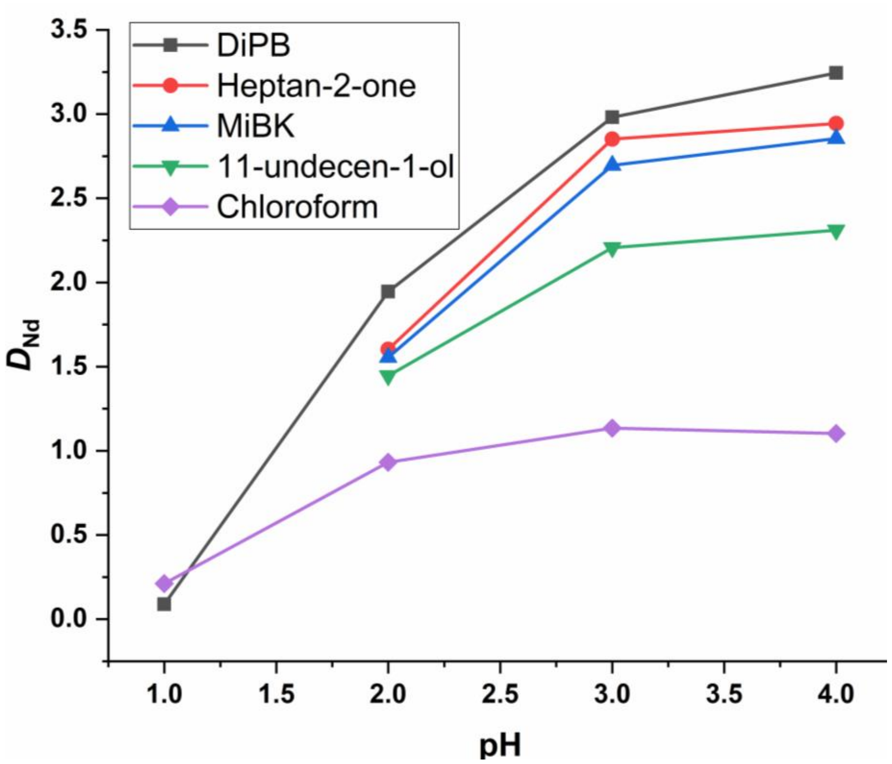
- D_M vs pH => cation exchange properties
- From HCl or HNO_3 leachate ($[Nd^{3+}]$ = 0.01 M)
- $[EDTA(C_{10})_4]$ = 0.01 M in various diluents



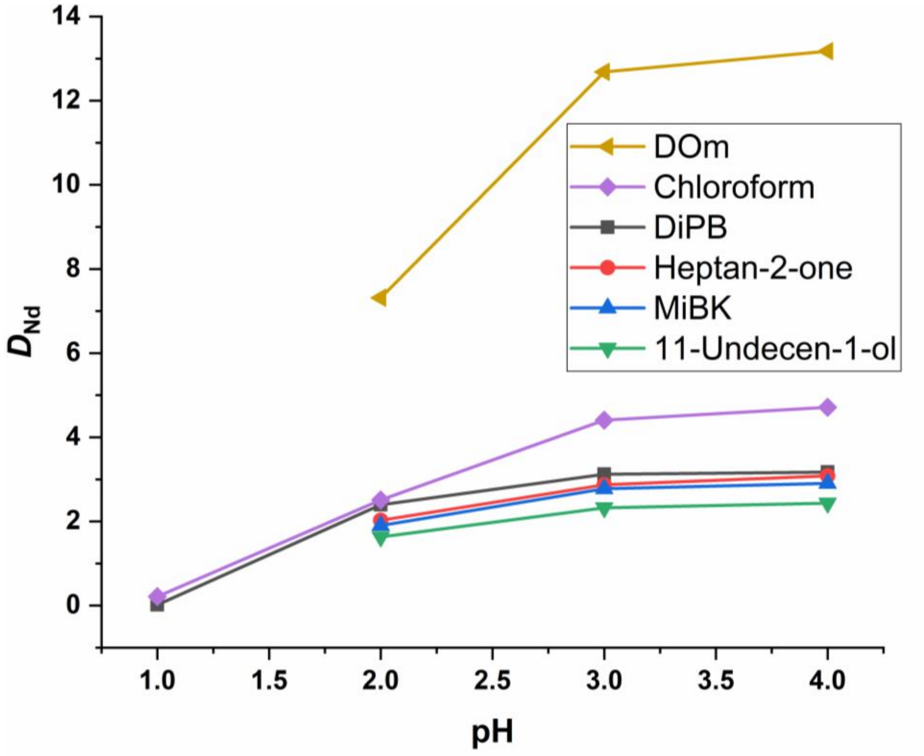
R = $C_{10}H_{21}$-

$EDTA(C_{10})_4$

HCl



HNO_3



16. FR2210237, **2022**; **17.** Sukhbaatar *et al*., *Hydrometallurgy*, **231**, 106415, **2025**

Assessment of Extraction Properties: LLE of Ln(III)

❑ Example: extraction of Nd(III) with ligand diluted in various diluents(16,17)

- ΔG_{tr} = -RTlnD_M vs pH => cation exchange properties
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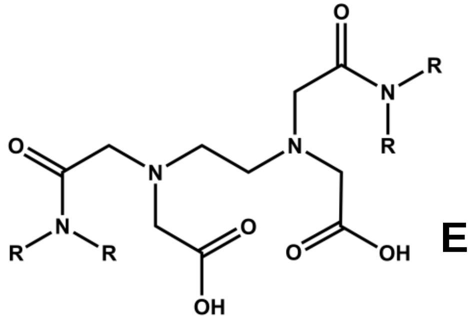

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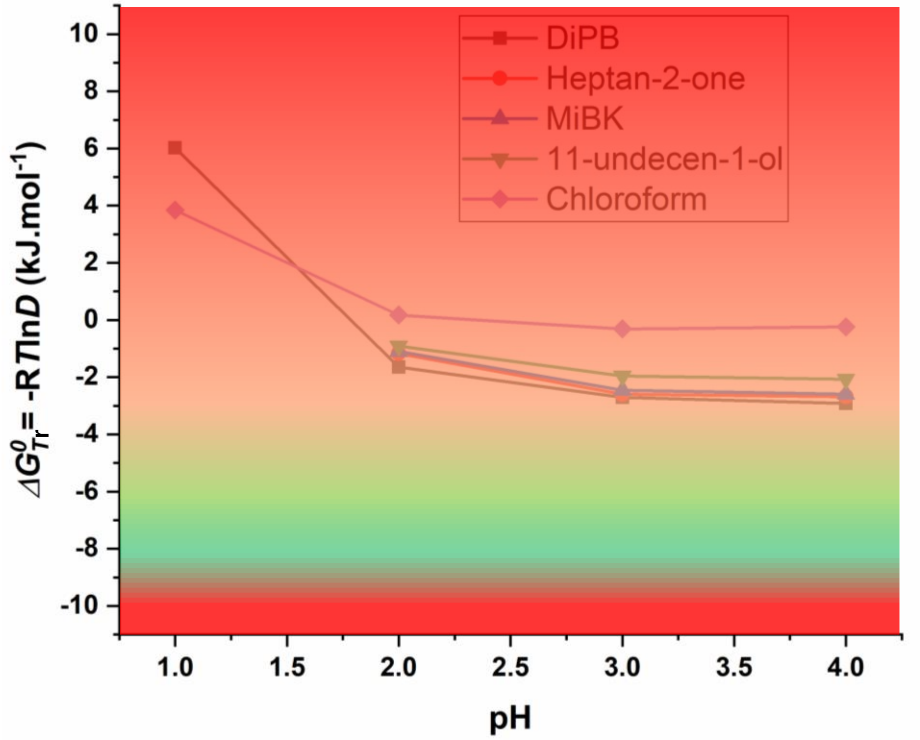
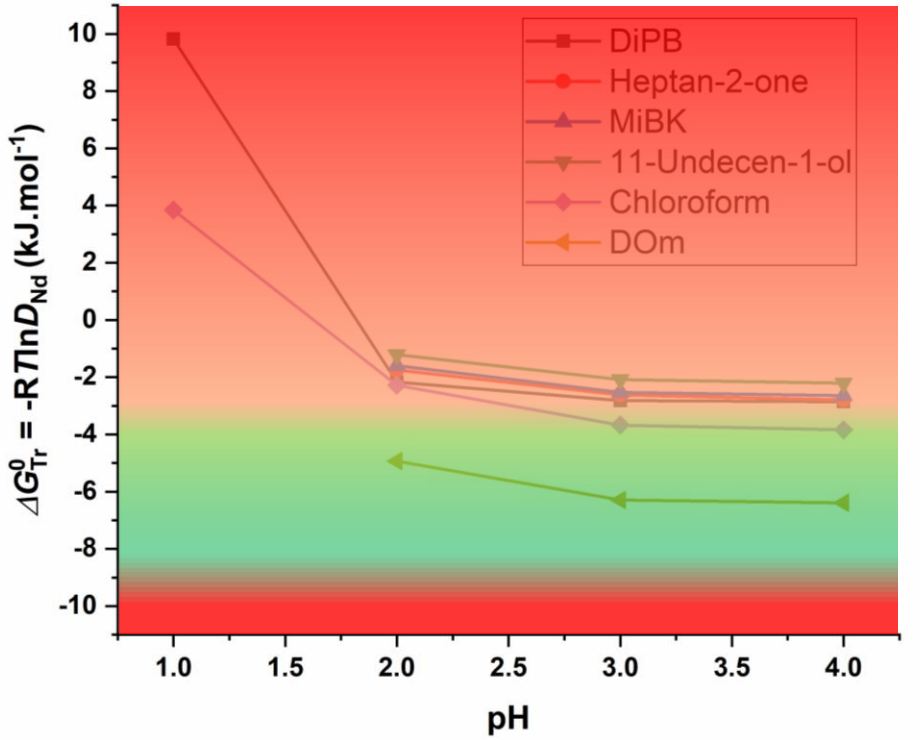
HCl



HNO_3



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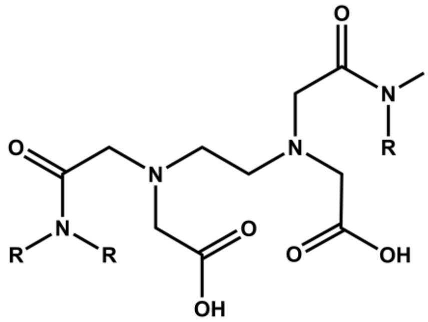

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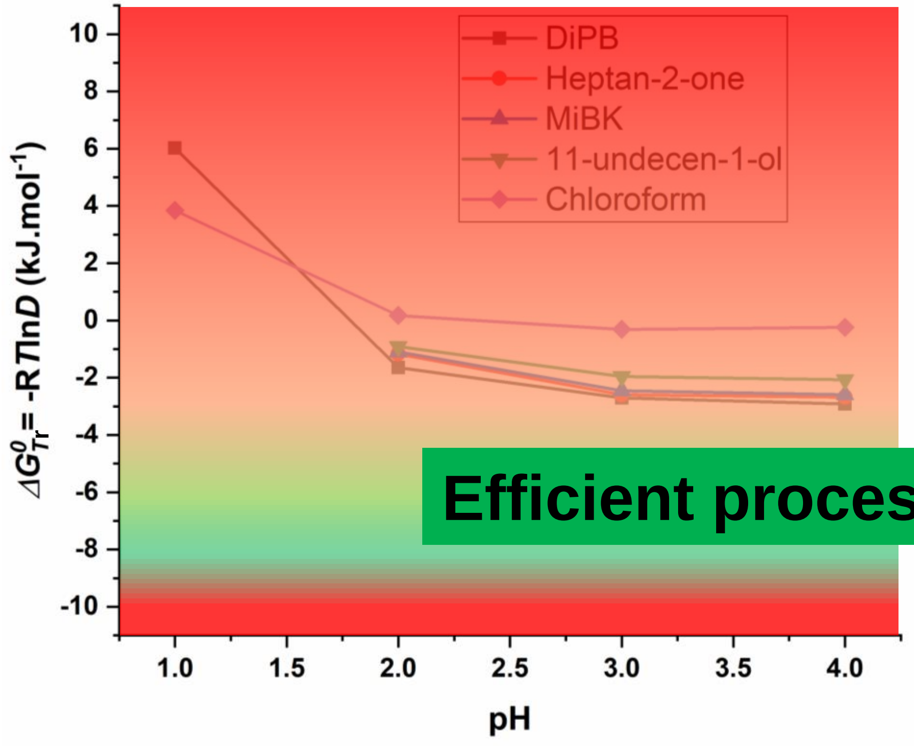
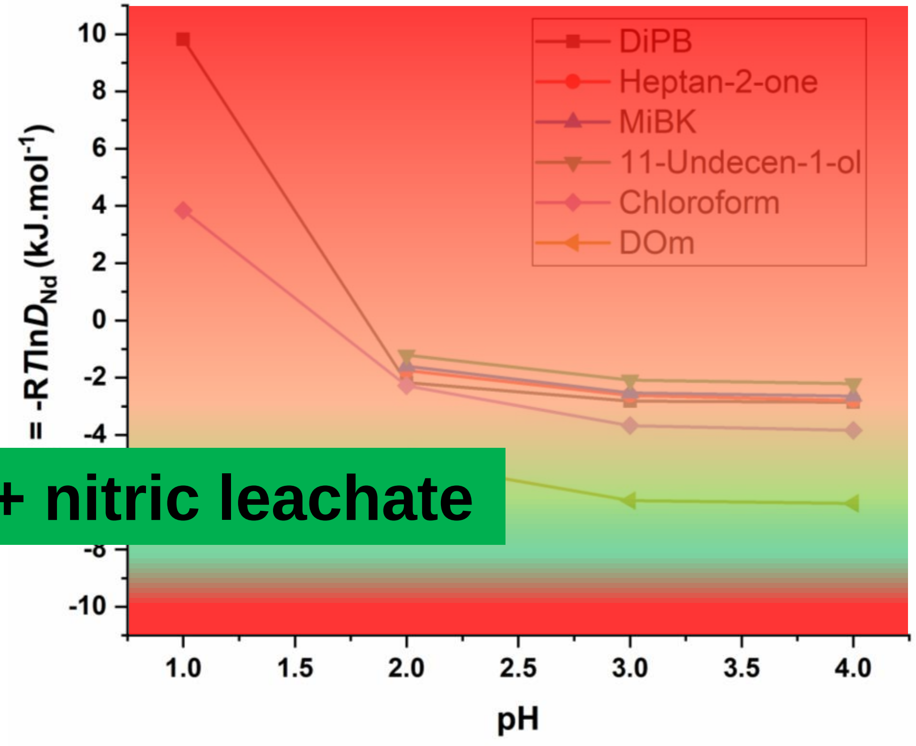
HCl



HNO_3



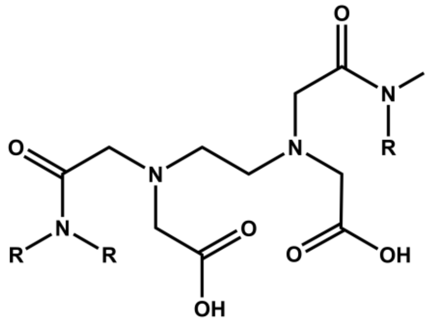
Efficient process = DOm + nitric leachate

16. FR2210237, **2022**; **17.** Sukhbaatar *et al.*, *Hydrometallurgy*, **231**, 106415, **2025**

Assessment of Extraction Properties: LLE of Ln(III)

❑ **Example: extraction of Nd(III) with ligand diluted in various diluents[16,17]**

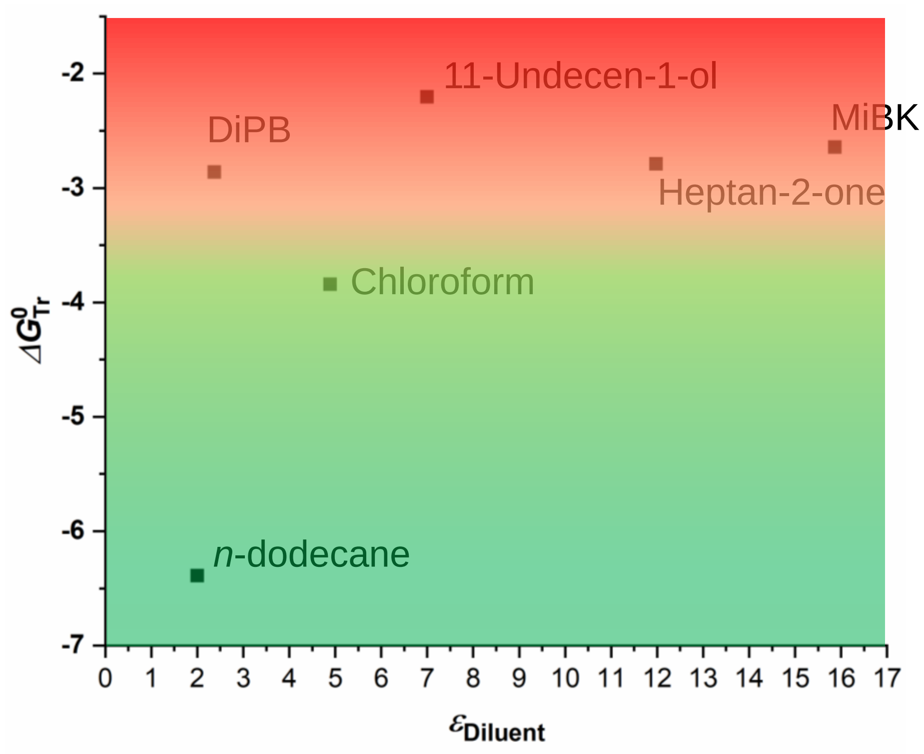
- ΔG_{Tr} vs polarity of the diluent
- From HNO_3 leachate ($[Nd^{3+}]$ = 0.01 M) at pH = 4
- $[EDTA(C_{10})_4]$ = 0.01 M in various diluents

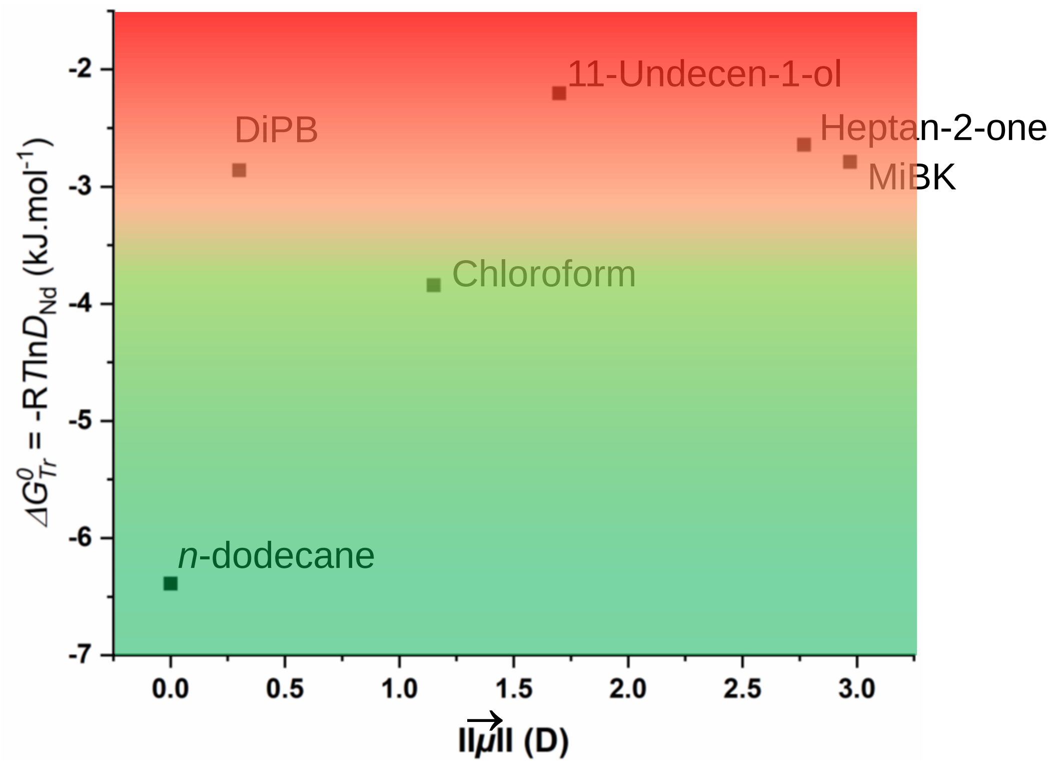


R = $C_{10}H_{21}$-

$EDTA(C_{10})_4$

=> Low polarity => Aggregation ↑ => extraction ↑ ↑





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Assessment of Extraction Properties: LLE of Ln(III)

☐ Example: extraction of Nd(III) with ligand diluted in various diluents(16,17)

- ΔG_{Tr} vs polarity of the diluent
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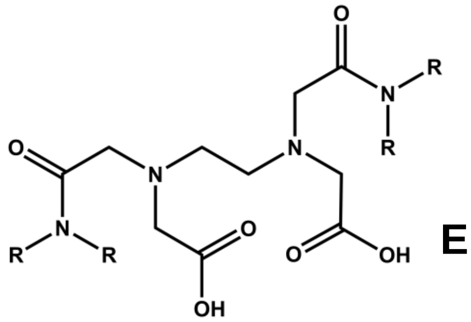

R = $C_{10}H_{21}$-

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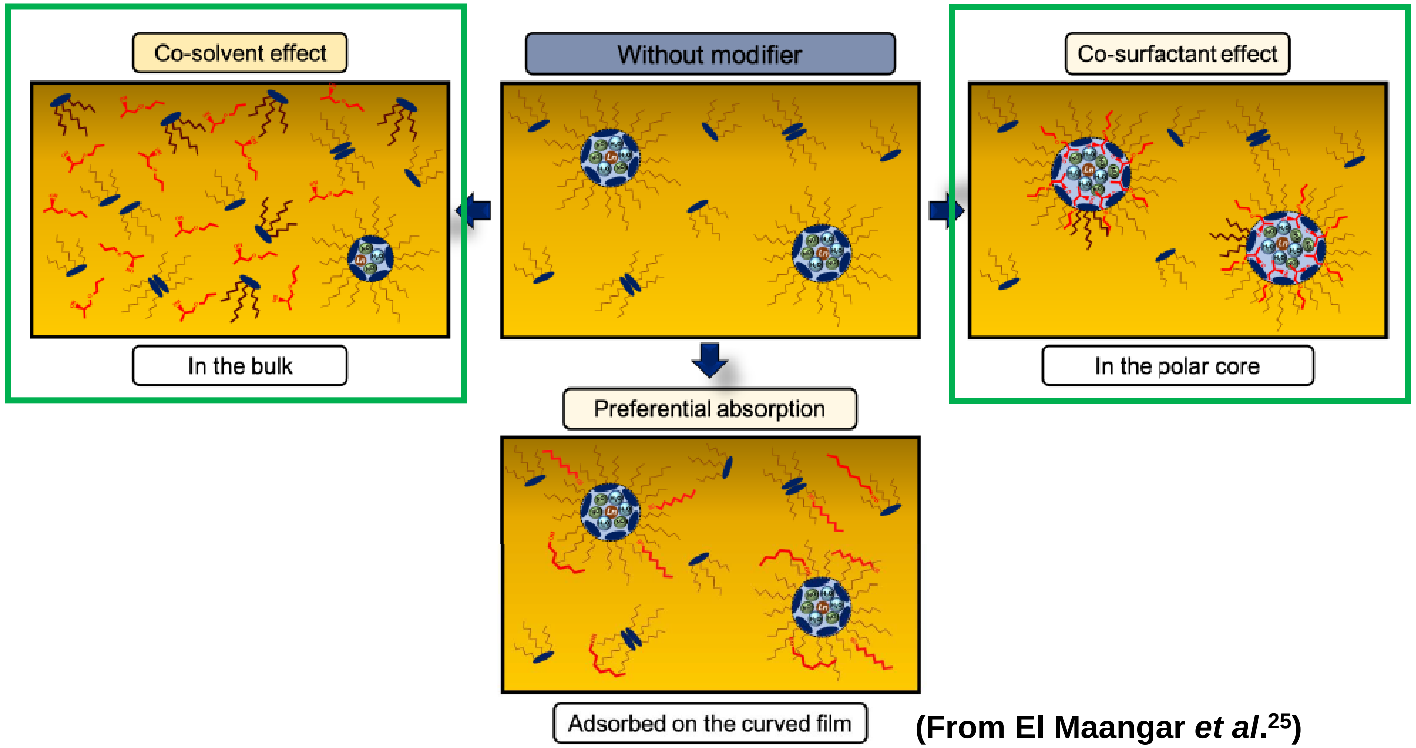
=> Role of the phase modifier (PM)

PM increases the solubility in *n*-dodecane



PM increases the stability of aggregates in *n*-dodecane

(From El Maangar *et al.*[25])

25. El Maangar *et al*., *CRAS*, **25**, 341-360, **2022**

Assessment of Extraction Properties: LLE of Ln(III)

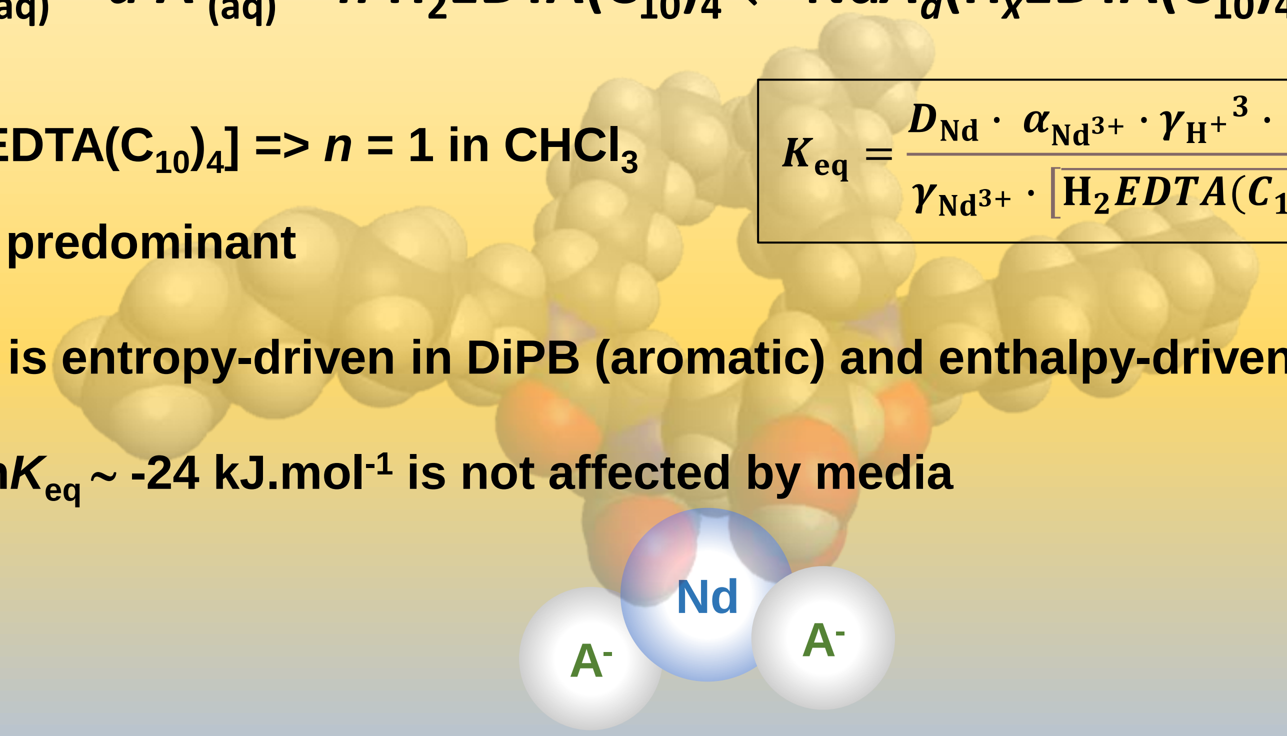
Diluent

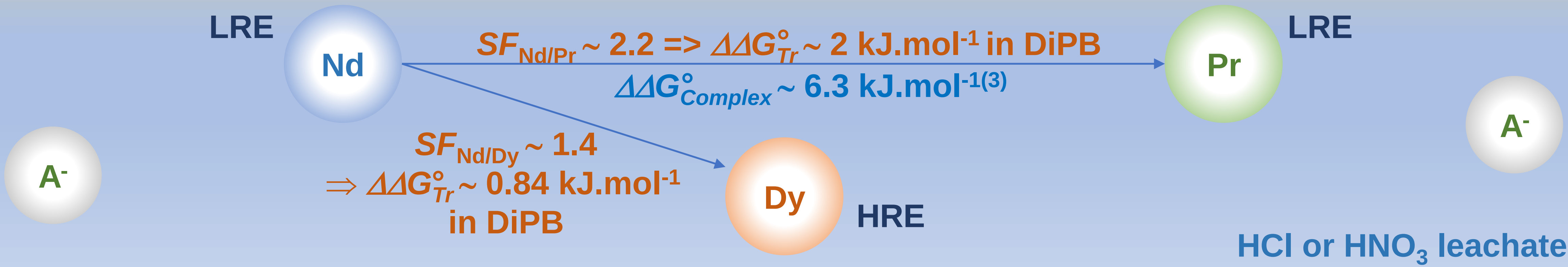
$$Nd^{3+}_{(aq)} + a\,A^{-}_{(aq)} + n\,H_2EDTA(C_{10})_4 \overset{K_{eq}}{\rightleftharpoons} \overline{NdA_a(H_xEDTA(C_{10})_4)_n} + (3-a)\,H^{+}_{(aq)}$$

- **LogD vs [EDTA(C_{10})$_4$] => n = 1 in CHCl$_3$**
- $\overline{\mathbf{HLNd}A_2}$ **is predominant**

$$\boxed{K_{eq} = \frac{D_{Nd} \cdot \alpha_{Nd^{3+}} \cdot {\gamma_{H^+}}^{3} \cdot [H^+]^{3}_{eq}}{\gamma_{Nd^{3+}} \cdot \left[\overline{H_2EDTA(C_{10})_4}\right]^{n}_{eq}} \cdot (\gamma_{H^+} \cdot \gamma_{A^-})^{-a} \cdot [H^+]^{-a}_{eq} \cdot [A^-]^{-a}_{eq}}$$

- **Extraction is entropy-driven in DiPB (aromatic) and enthalpy-driven in DOm (aliphatic)**
- **$\Delta G°= -RT\ln K_{eq} \sim -24$ kJ.mol^{-1} is not affected by media**





$SF_{Nd/Pr} \sim 2.2 \Rightarrow \Delta\Delta G^{\circ}_{Tr} \sim 2$ kJ.mol^{-1} in DiPB

$\Delta\Delta G^{\circ}_{Complex} \sim 6.3$ kJ.mol$^{-1(3)}$

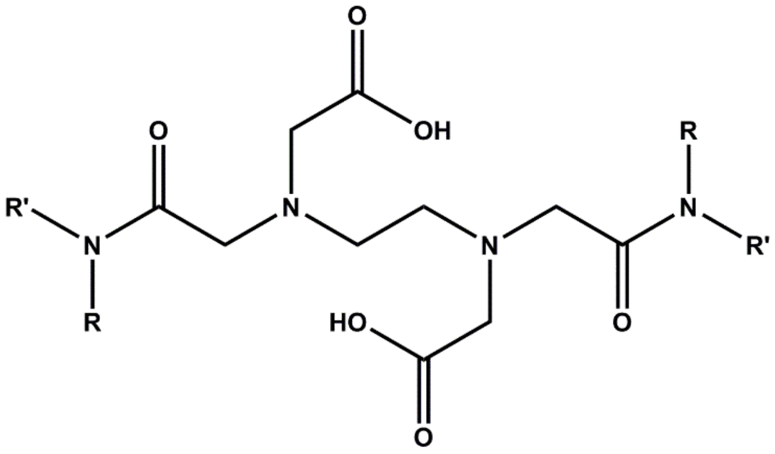
$SF_{Nd/Dy} \sim 1.4$
$\Rightarrow \Delta\Delta G^{\circ}_{Tr} \sim 0.84$ kJ.mol^{-1}
in DiPB

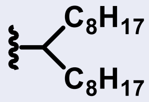
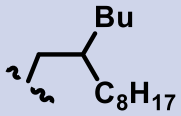
HCl or HNO$_3$ leachate

CONCLUSION & OUTLOOK

- ❑ **Promising and interesting properties that must be improved**
  - Solubility in *n*-dodecane must be adjusted to that expected (0.2 M)
  - Selectivity intra-Ln must be improved

- ❑ **Molecular tailoring**
  - Development of new lipophilic APCAs derivatives = first phase of E. Fauvel’s Ph. D.
    - ➢ Enhanced lipophilicity provided by branched alkyl chains
    - ➢ Systemic study with various topologies tuned at same carbon number



R	R’	Topology
-*n*-$C_{10}H_{21}$	-*n*-$C_{10}H_{21}$	Symetrical linear
	-*n*-Pr	Disymmetrical branched
	-*n*-Hex	Disymmetrical branched
Neodecyl	Neodecyl	Symetrical branched
2-Ethyloctyl	2-Ethyloctyl	Symetrical branched

-$C_{40}H_{84}$

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