



Thermosensitive metal-chelating surfactants

Design, properties and uses in solvent free separation processes

C. Larpent

Objective : Thermo-Regulated Separation



Separation of Uranium (Nuclear Wastes Treatment, CEA)

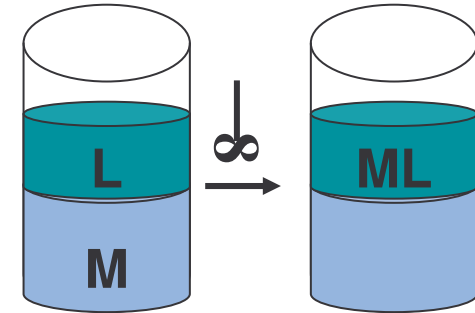
Extension : Separation of heavy metals

Extraction-Separation of metal ions from aqueous medium

- Classical liquid-liquid extraction

Lipophilic extractant + solvent

Drawbacks : Interfacial complexation, solvent

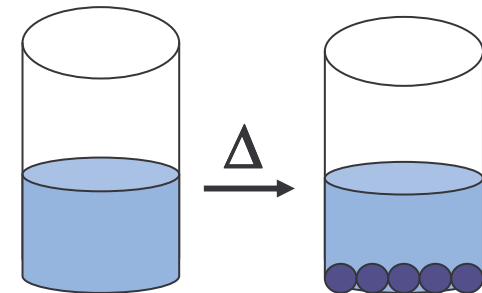


- Solvent-free alternative : Thermo-responsive systems

- No solvent

- Complexation in water (homogeneous)

- Separation induced
by an external stimulus (T)



- PNIPAM polymer derivatives



- PEG Derivatives (POE , POE-PPO)

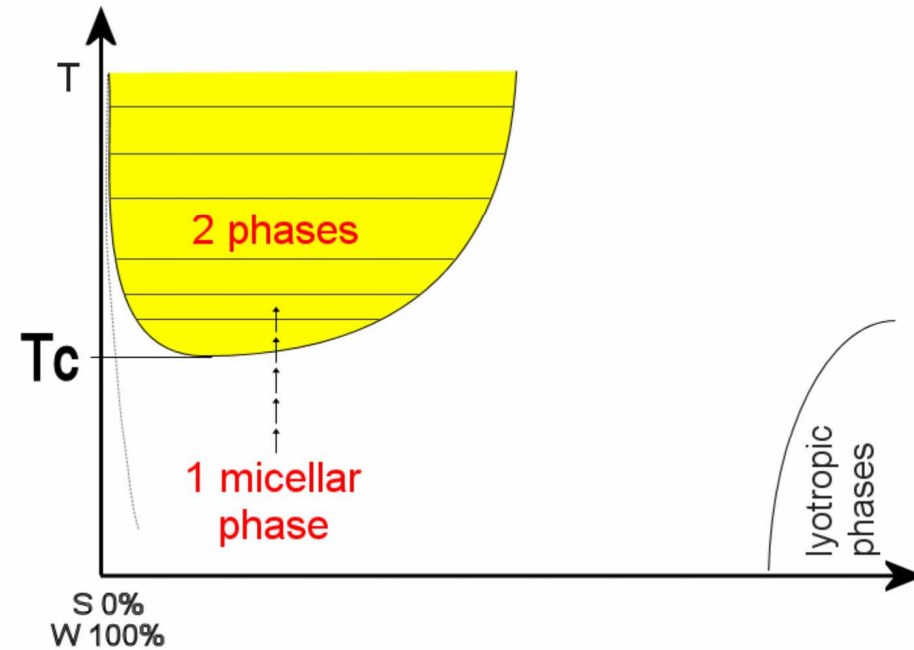
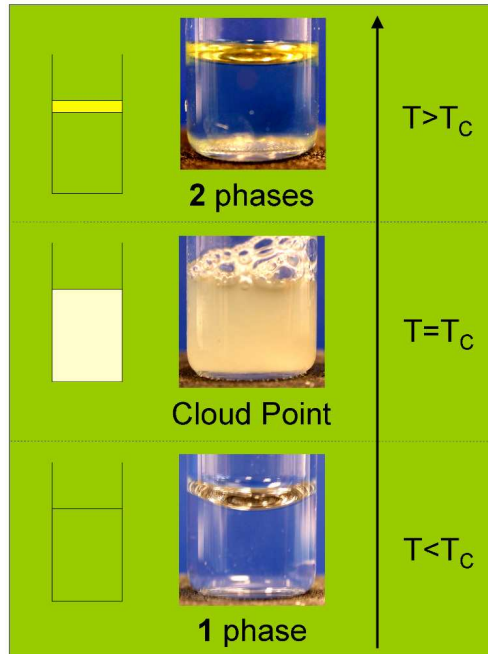
POE : Phase separation upon heating or addition of salts

Rogers et al.

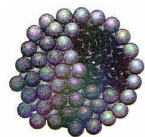
Non-Ionic surfactants : Cloud point

Non-Ionic Surfactants $C_iH_{2i+1}-O(CH_2CH_2O)_jH$ "C_iE_j"

Cloud Point (T_c)



Dehydration of the POE polar group



→
Micellar growth



→ → Phase Transition

T

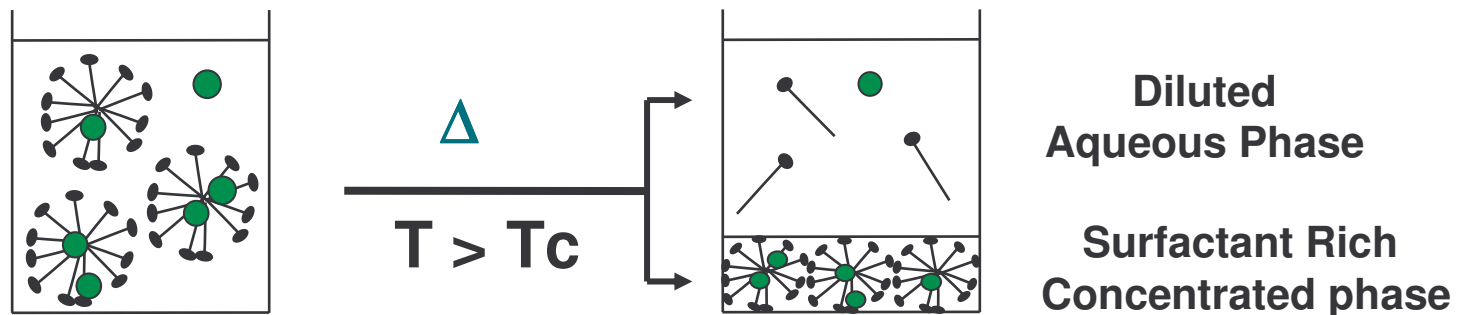


Thermo-Regulated Separation

Non-Ionic Surfactants $C_iH_{2i+1}-O(CH_2CH_2O)_jH$ "C_iE_j"

Cloud Point Extraction of Hydrophobic Solutes

Micellar solubilization



Numerous examples : organic pollutants, biomolecules ...
Analytical chemistry

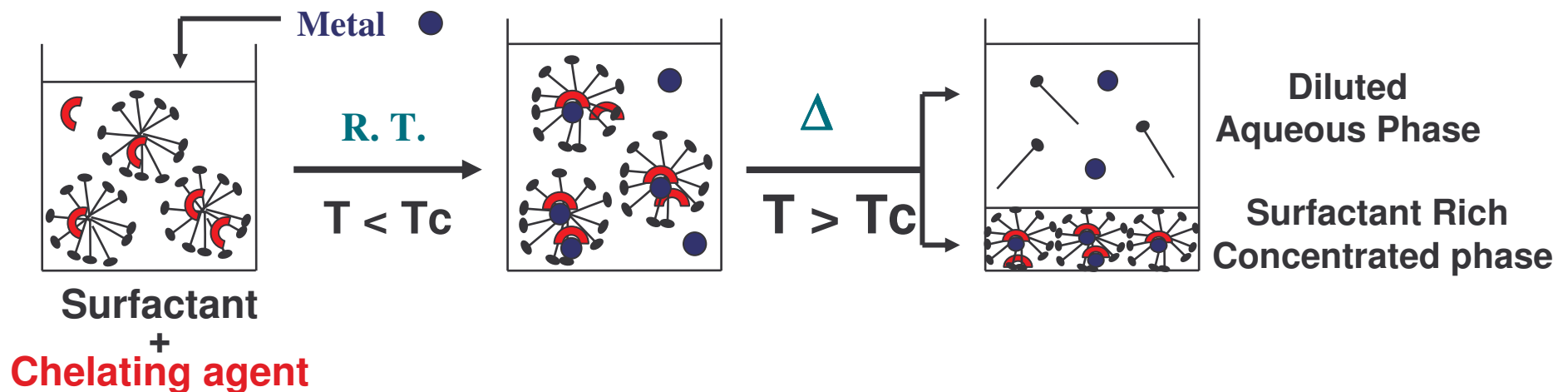
(Reviews : Hinze, 1993, Tani, 1997)

Thermo-Regulated Separation

Cloud Point Extraction of Metal Ions

Hydrophilic solute → Additional lipophilic chelating agent

Micellar solubilization of the metal chelate



Large excess of surfactant and chelating agent

Limitations

[Surfactant] \gg [Chelating agent] (>50/1)

[Chelating agent] \gg [M] (5/1 to 100/1)

Applications : Analytical Chemistry, Traces analysis

(Reviews : Hinze, 1993, Tani, 1997)

Thermosensitive Metal-Chelating Surfactants

Molecular Economy

Thermo-Regulated Extraction of U(VI)

Surfactant Block

Chelating Block

Thermoreversibility



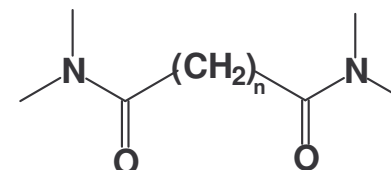
Nonionic Surfactant

Target : UO_2^{2+}



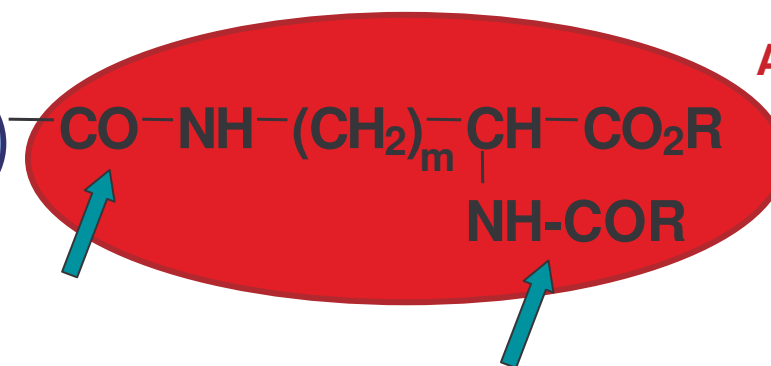
Diamide

Malonamide
Uranyle Ionophore



Nonionic
Surfactant

"C_iE_j" Block



Amino-acid Residue

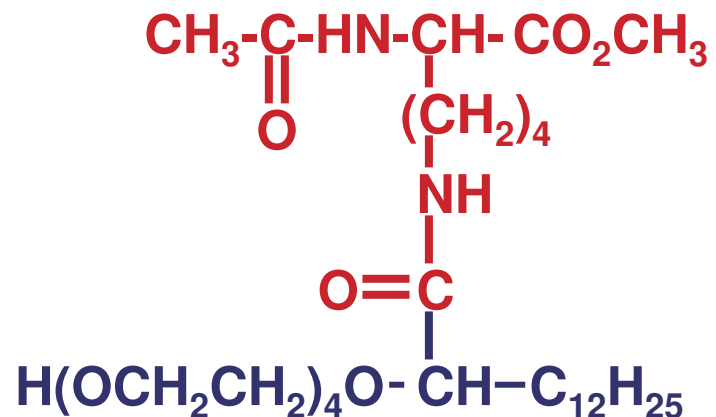
Diamide

Lysine Block

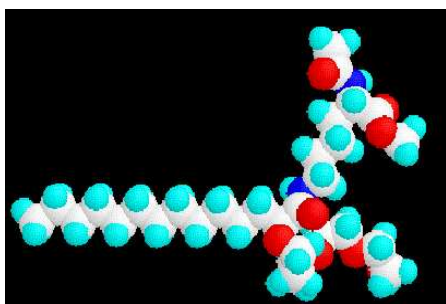
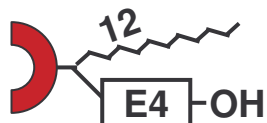
Synthesis, Properties, Use in CPE

Thermosensitive Metal-Chelating Surfactants

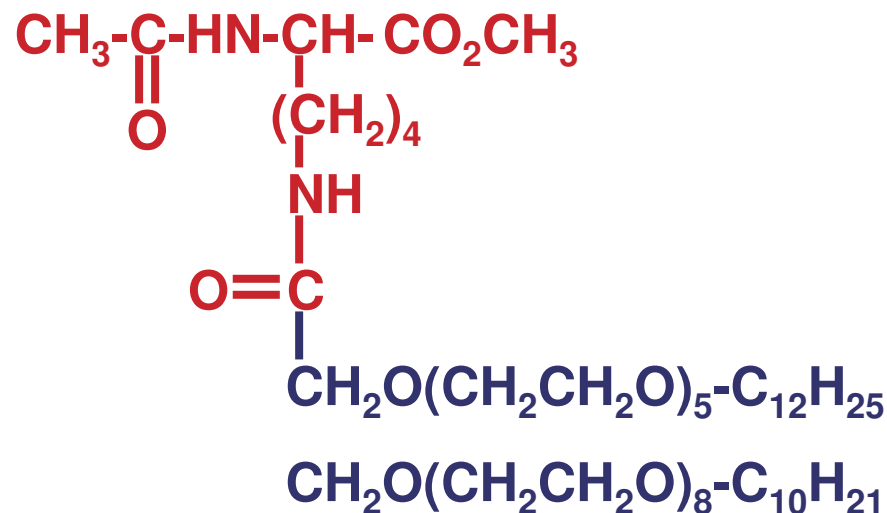
“Ramified“ Compounds
Lys-C_iE_j-OH



1 *L-C₁₂E₄OH*

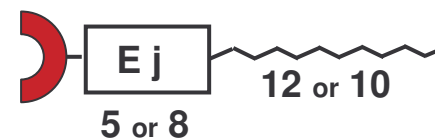


“Linear“ Compounds
Lys-O-C_iE_j



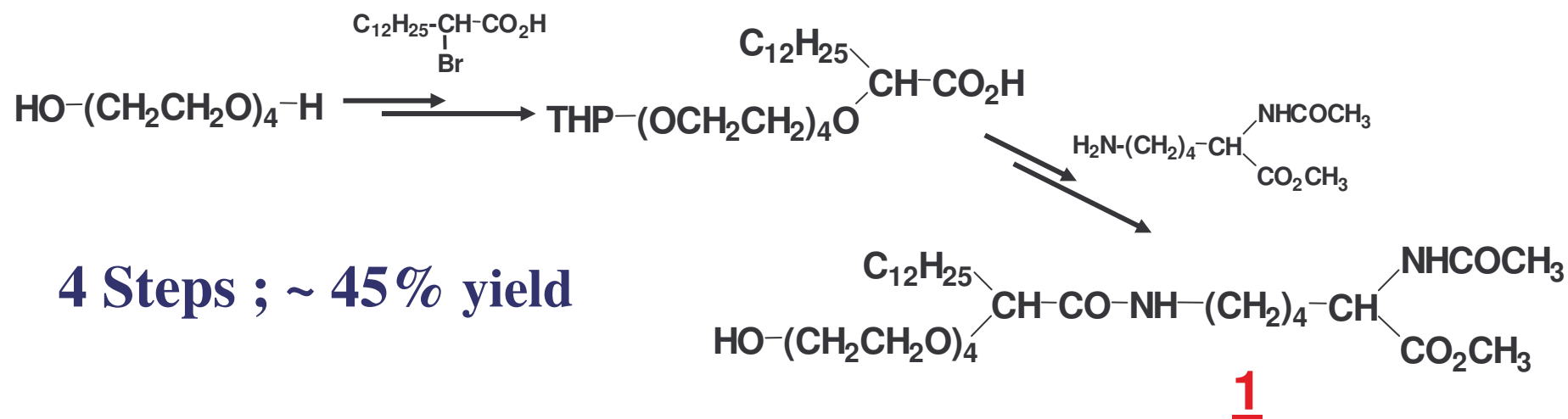
2 *L-C₁₂E₅*

3 *L-C₁₀E₈*



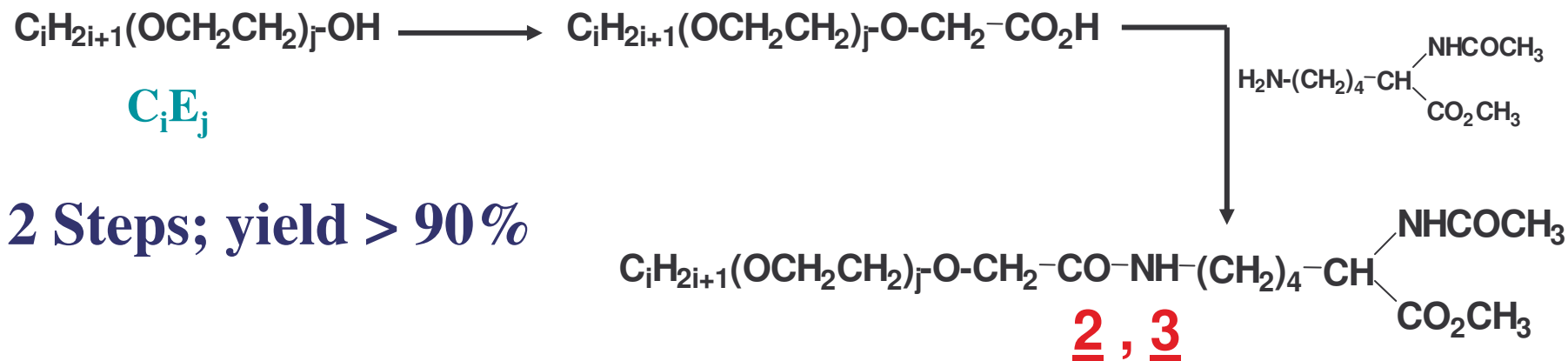
Synthesis

"Ramified" Compounds : LC_iE_jOH



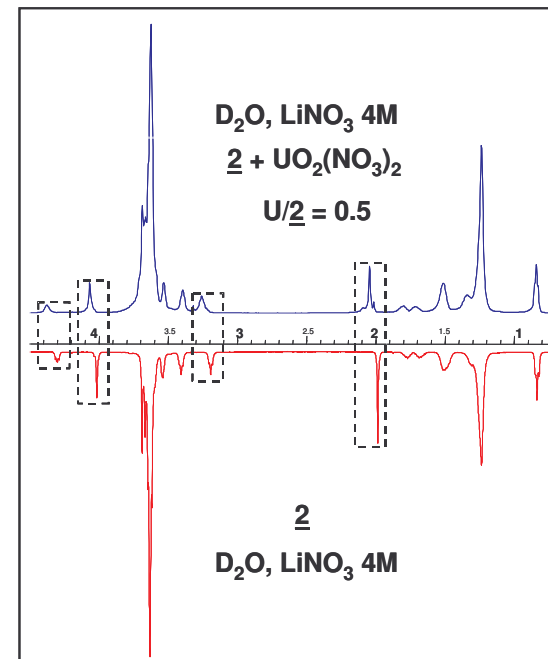
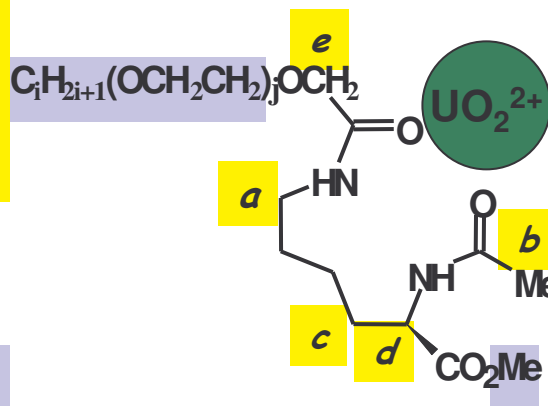
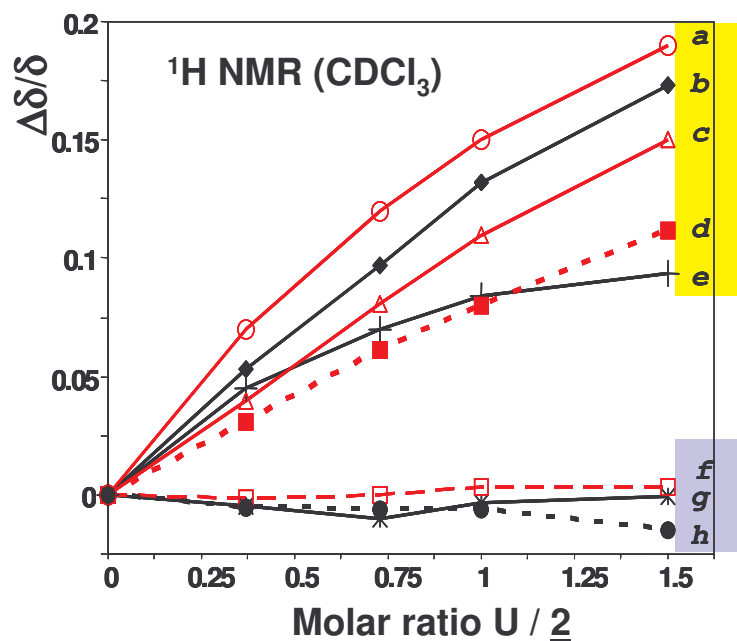
4 Steps ; ~ 45% yield

"Linear" Compounds: $L-C_iE_j$

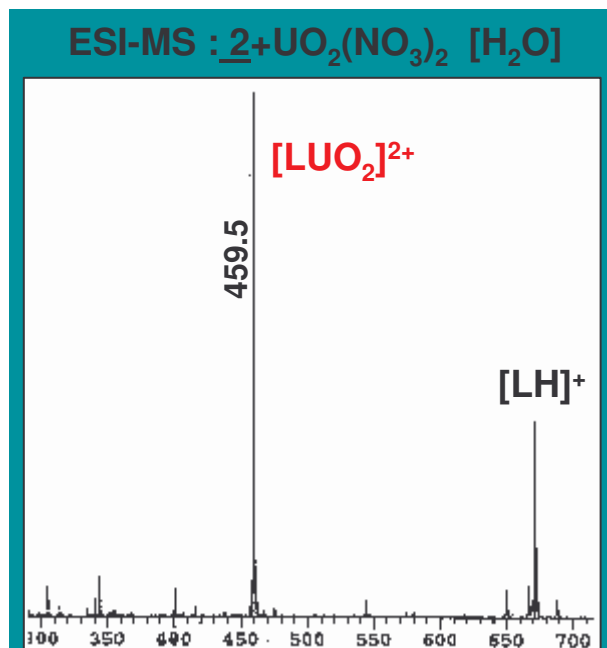


2 Steps; yield > 90%

Binding Properties / Uranyle Nitrate



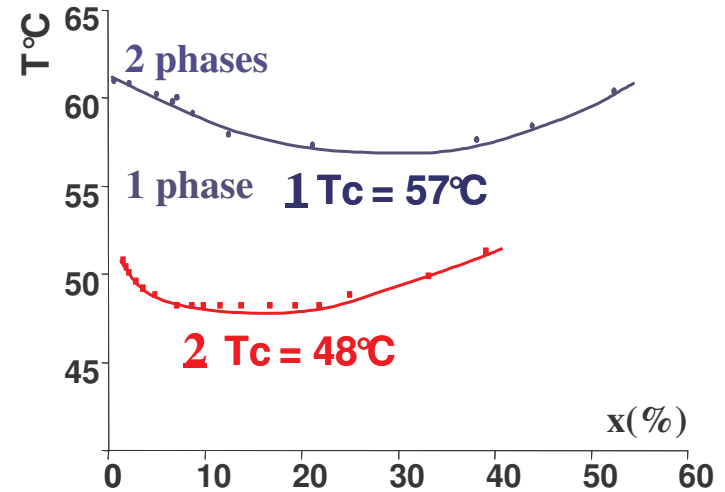
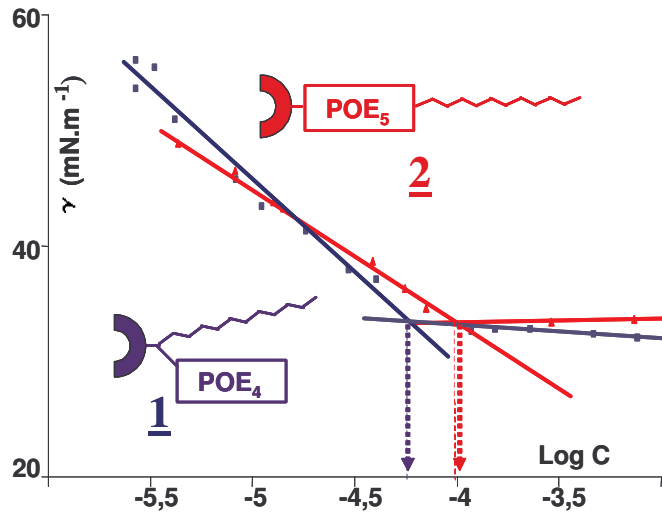
- Low complexation rate in pure water
- High complexation rate in the presence of nitrate anions (LiNO₃ 4M)



Neutral dinitrato 1/1 Complex



Surfactant Behavior & Thermoreversibility

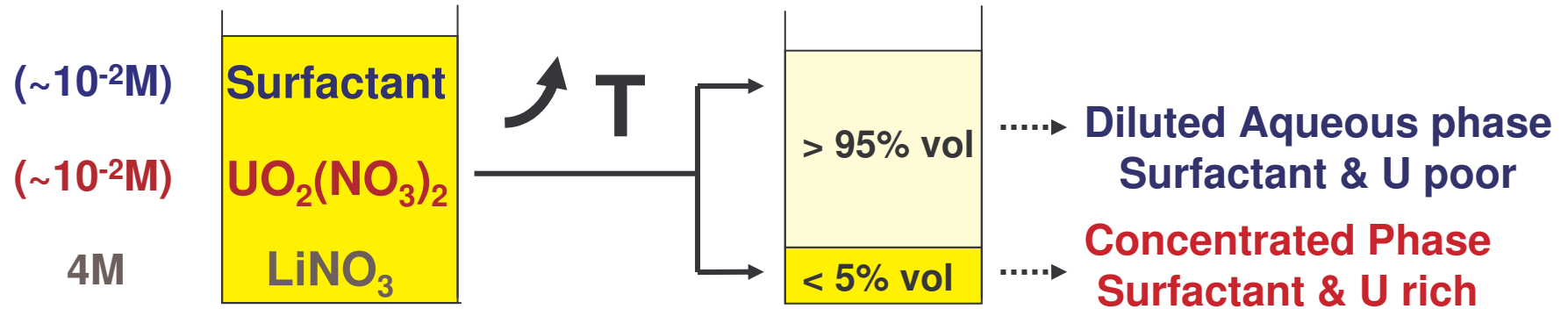



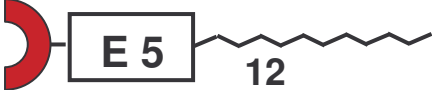
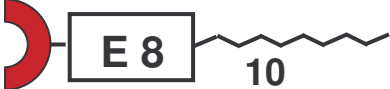
	<u>1</u>	<u>2</u>	<u>3</u>	$C_{12}E_4$	$C_{12}E_5$	$C_{10}E_8$
	$L-C_{12}E_4OH$	$L-C_{12}E_5$	$L-C_{10}E_8$			
cmc (mM)	0.08	0.1	0.8	0.1	0.1	1
Tc (°C)	57°C	48°C	71°C	6°C	32°C	84°C
N_{ag}	40	68	36	<i>Spherical Micelles</i>		

Langmuir 2004, 20, 4840

Classical Nonionic Surfactant Behavior
Tc controlled by the POE polar group

Thermo-Regulated Extraction of Uranyl Nitrate



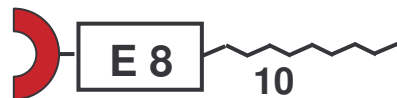
	T _c	% U extracted	n U ext./Surf
 <u>1</u>	25 °C	45%	0.27
 <u>2</u>	23 °C	46%	0.22
 <u>3</u>	52 °C	63%	0.28
C ₁₂ E ₅ or C ₁₂ E ₅ + Lys	26 °C	<5%	< 0.05

[Surf.] = 0.04 M

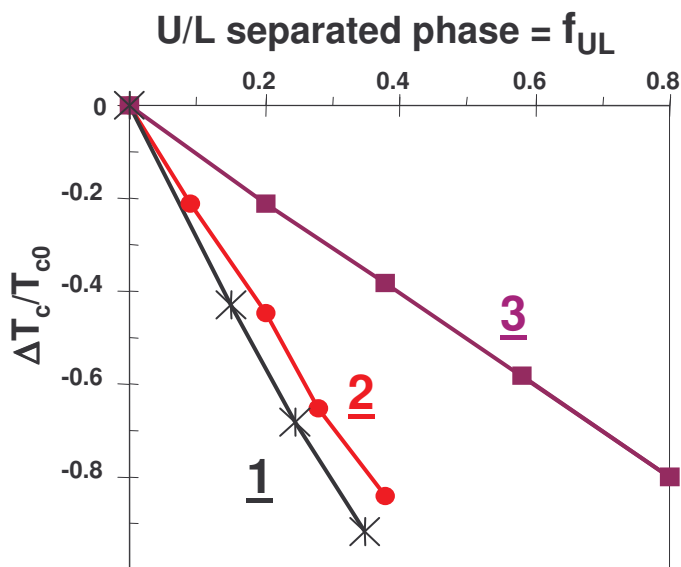
U/L = 0.5

- High Efficiency
- Di-Block Structure
- Modulation of T_c (C_iE_j block)

Thermo-Regulated Extraction of Uranyl Nitrate



	U/Surf	T_c	% U ext.	U ext./Surf
<u>3</u>	1/4	63 °C	69%	0.17
Surf : 40mM	1/2	47 °C	63%	0.32
4M LiNO ₃	3/4	35 °C	53%	0.40
	1/1	23 °C	47%	0.47



➤ **High efficiency (~ 0.5 U/ surf.)**

➤ **Decrease of the Cloud Point**

$$T_c = f(U \text{ ext.})$$

$$\text{Slope} = f(C_i E_j \text{ block})$$

Mixed micelles : surf + 1/2 U-Complex

Thermo-Regulated Extraction of Uranyl Nitrate

Influence of the Concentration of Lithium Nitrate (i.e. Complexation Rate)

[2] = 0.04 M

U / 2 = 0.5

LiNO₃ (Mol/L)

0

1

2

3

4

% U ext.

0

9

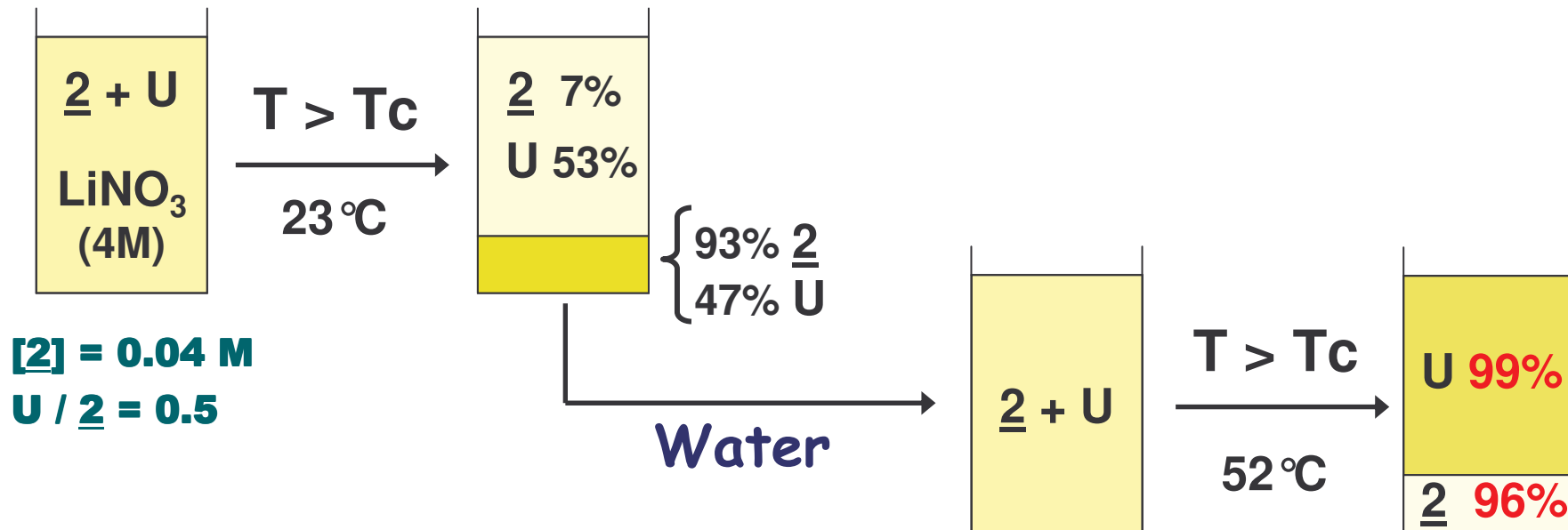
19

34

42



Separation / Recovery



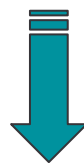
Thermosensitive Metal-Chelating Surfactants

Di-Block Structure

Nonionic Surfactant Behavior
Thermosensitive



Metal Binding Ability



Tunable Properties

Solvent-Free Thermo-Regulated Separation

Molecular Economy

Classical Cloud Point Extraction of UO_2^{2+}

Surfactant (Triton X114, 0.25-2 wt %) + Chelating agent (PAN or 8-HQ)

100 - 1000 mol / U

5 - 10 mol / U

Chelating thermosensitive surfactants

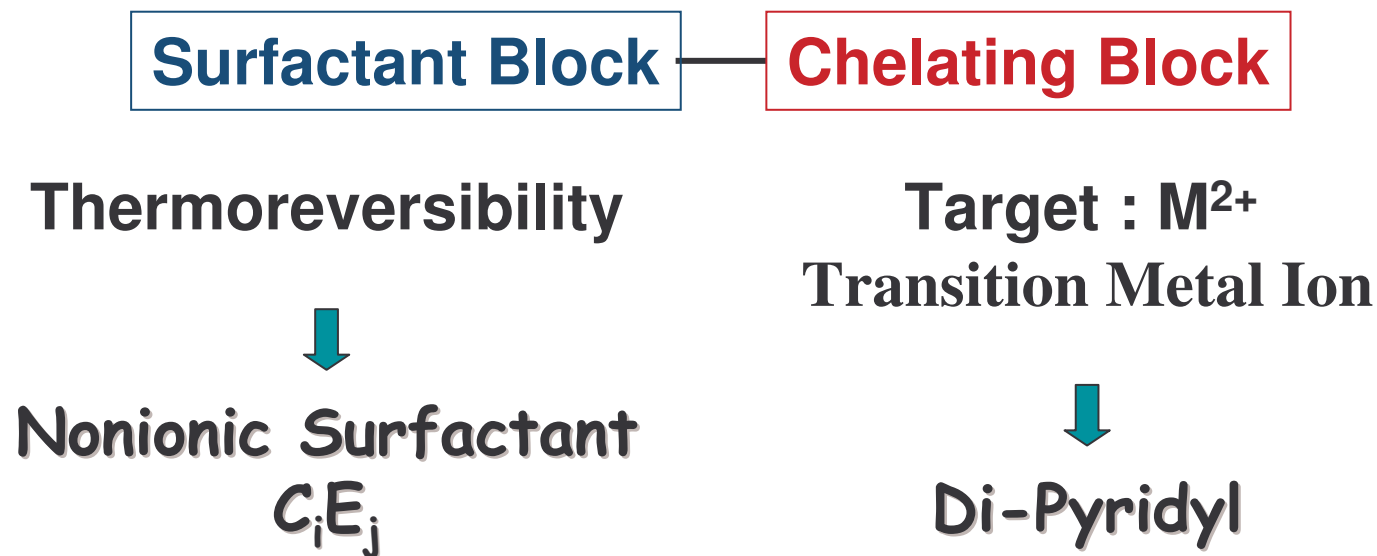
1 - 4 mol / U

Thermosensitive Metal-Chelating Surfactants

Extensions

Separation of other metal cations (Cu^{II} , Pb^{II} , Cd^{II} , Hg^{II} ..)

Choice of the chelating group



Thermosensitive Metal-Chelating Surfactants

➤ Libraries of functional surfactants

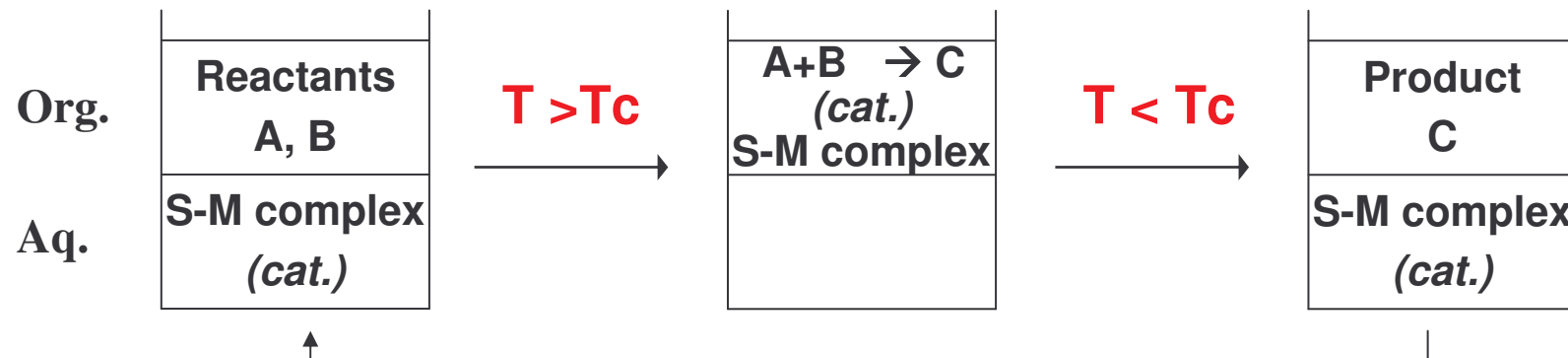
Modulable Cloud Points & Metal binding affinity

Surfactant unit

Chelating unit

General & Tunable Solvent-Free Separation Processes

➤ Other application : Thermo-regulated Catalysis





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