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Experimental determination and modelling of cyclopentane hydrates in presence of NaCl, KCl, CaCl₂, and NaCl-KCl

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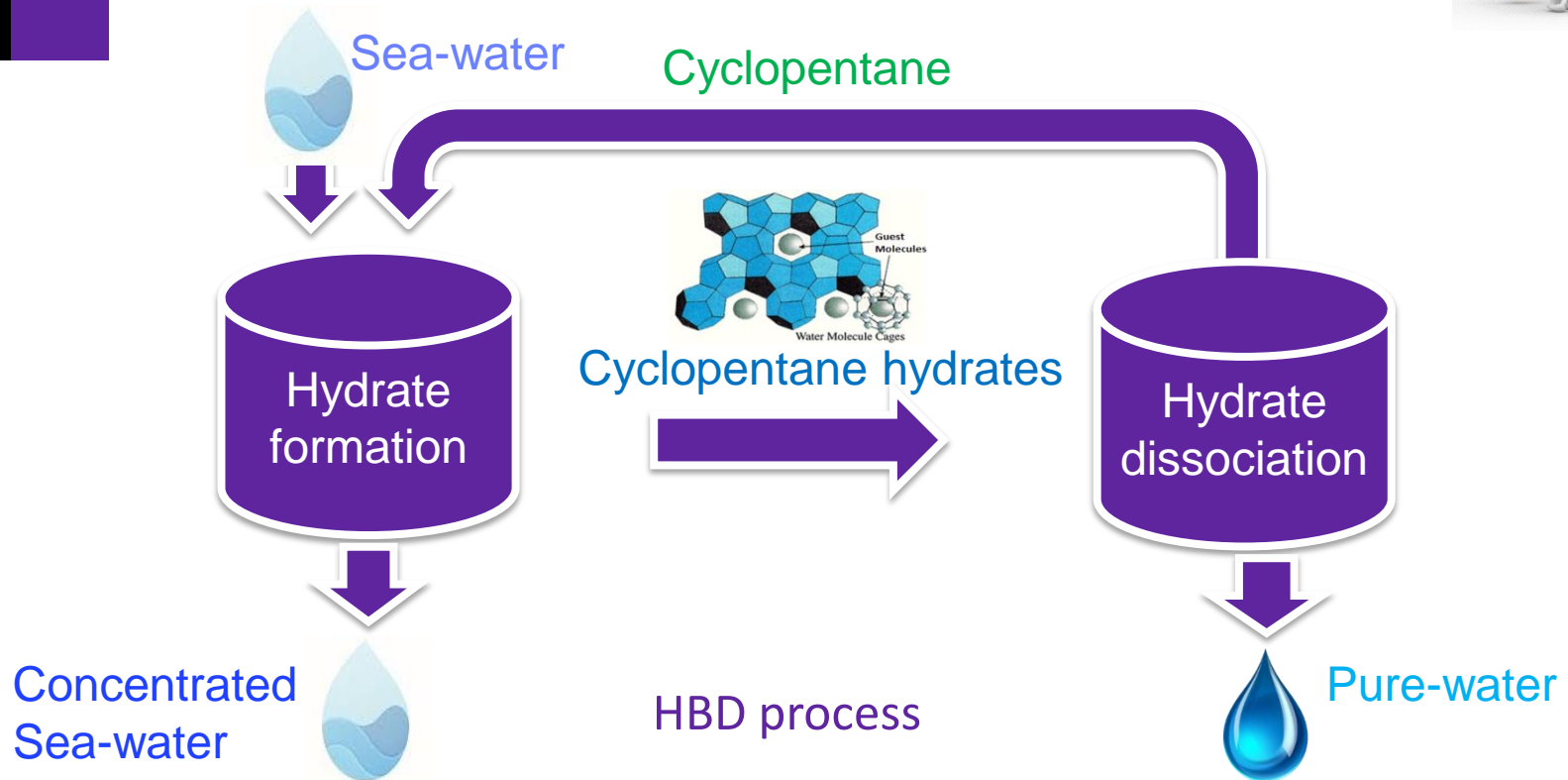
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Barcelona, 26/02/2018

- 1. Introduction and objective**
- 2. Experimental Methodology**
- 3. Experimental results**
- 4. Modelling**
- 5. Conclusions & Perspectives**

Hydrates can be used as a separation technique



Phase equilibria data in presence of diverse salts is needed.

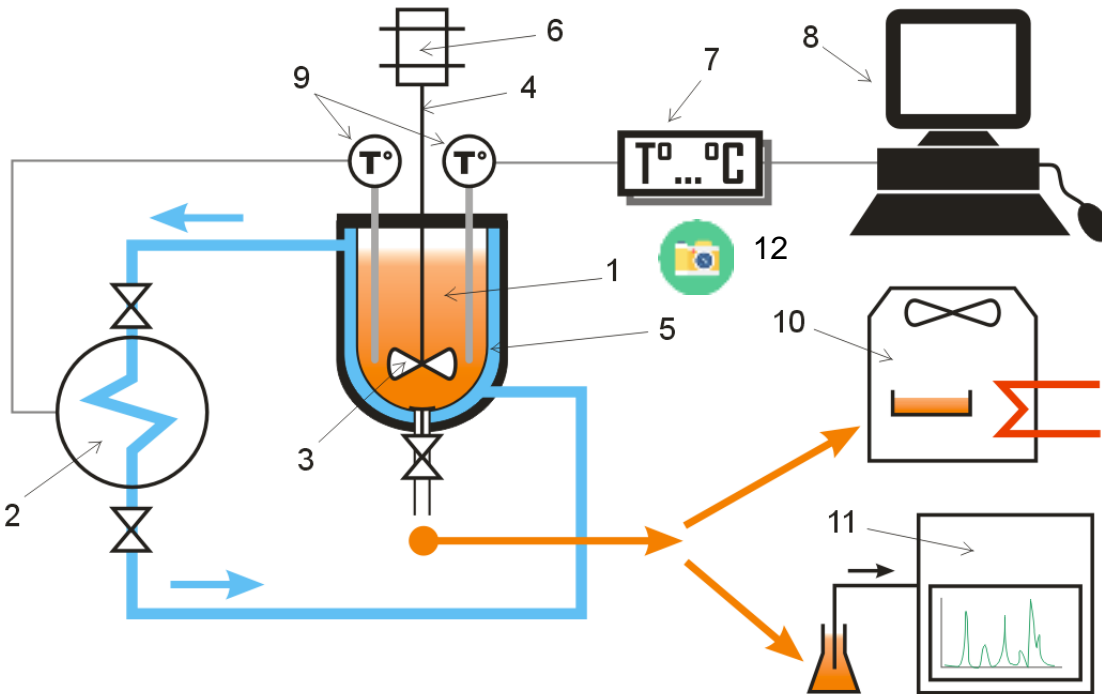
Objective



1. provide equilibrium data CPH in presence of salts
2. Model CPH

Experimental methodology

Equilibrium temperature measurement



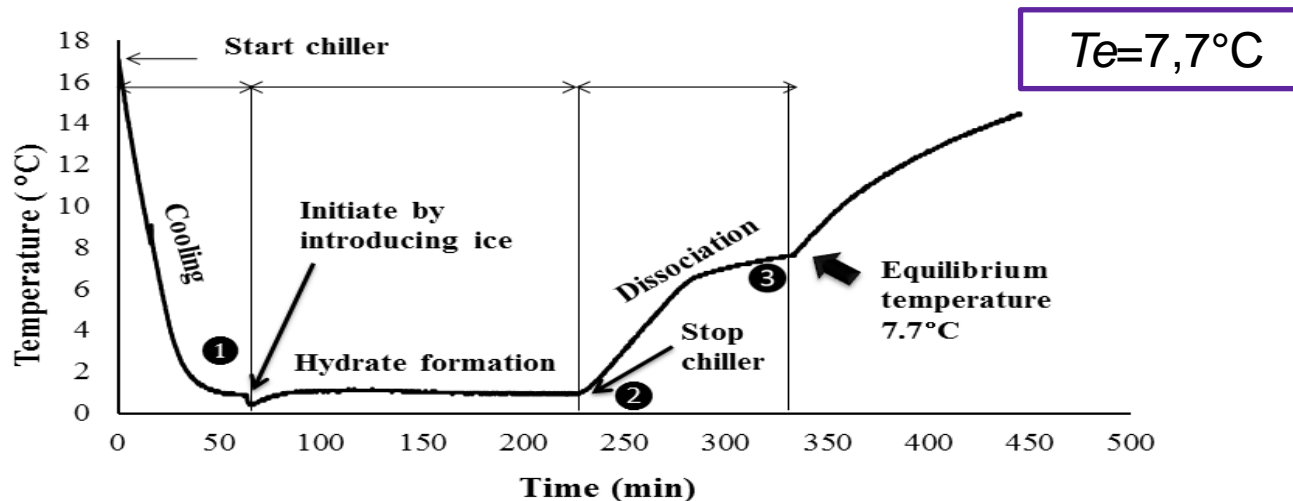
schematic diagram

1. Reactor
2. Cryostat
3. Impeller
4. Agitator
5. Cooling jacket
6. Motor
7. Temperature transmitter
8. Computer
9. Temperature probe
10. Drying oven
11. Ion chromatography
12. Camera

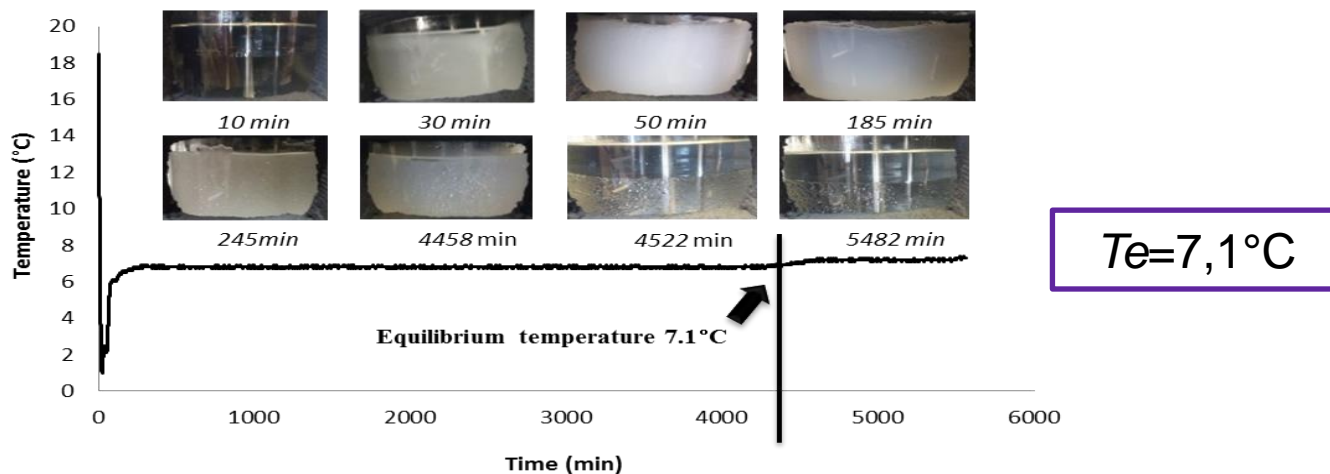


Actual system

Protocol: Two procedures

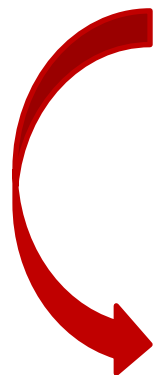


Temperature profile : Quick dissociation



Temperature profile : Slow dissociation

T Estimation



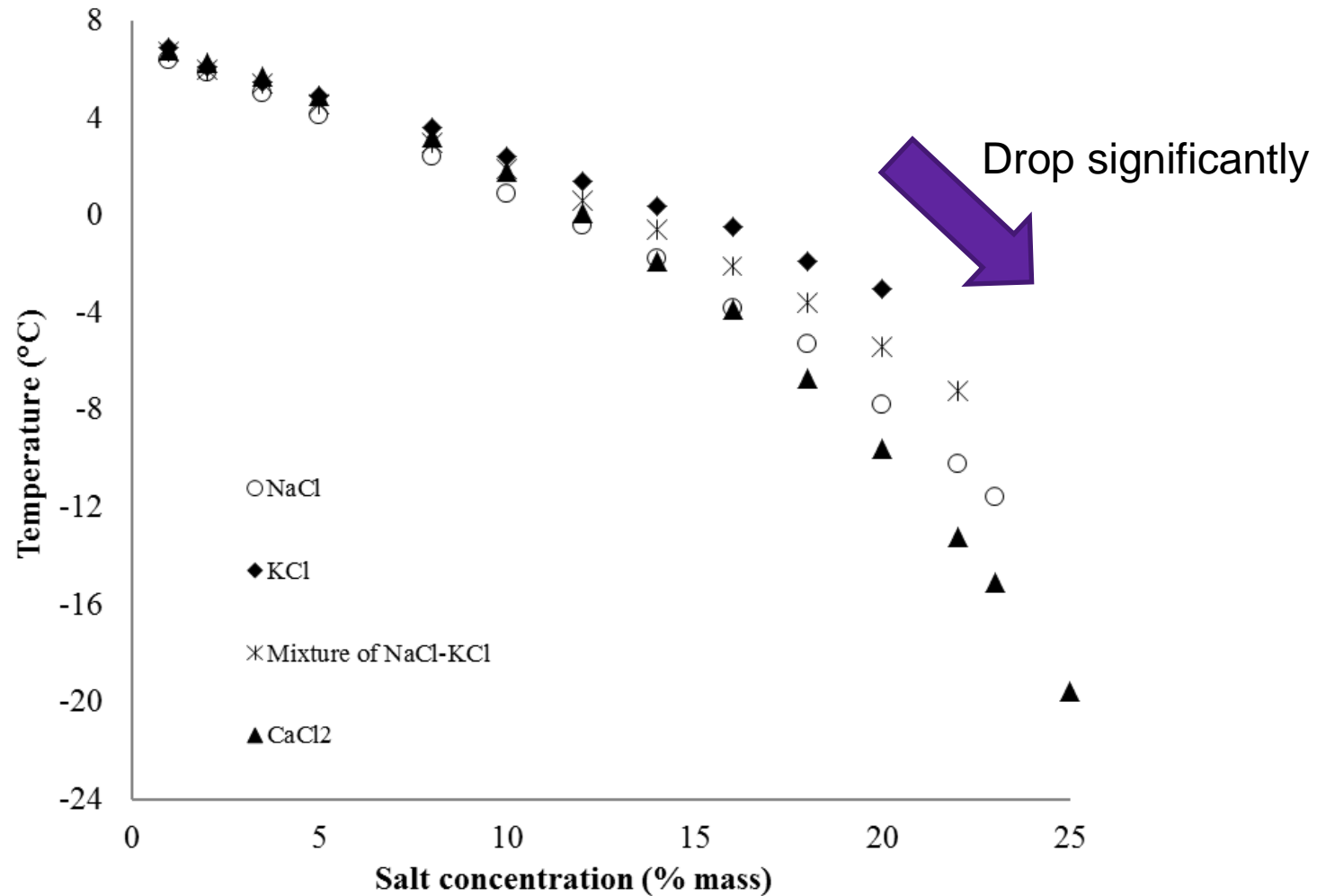
T Accurate



Outlines

1. Introduction and objective
2. Experimental Methodology
3. Experimental results
4. Modelling of cyclopentane hydrate
5. Conclusions & Perspectives

Equilibrium temperatures in the presence of salts



Equilibrium temperatures (°C) in presence of NaCl, KCl, NaCl-KCl, and CaCl₂

Salinity, % w/w	NaCl, quick	NaCl, slow	NaCl, [1]	NaCl [2]	KCl, slow	NaCl-KCl, slow	CaCl ₂ , slow
0	7.7	7.1	7.11	-	7.1	7.1	7.1
1	6.9	6.4	-	-	6.9	6.7	6.8
2	6.3	5.9	-	-	6.1	6.0	6.3
3.5	5.7	5	-	-	5.5	5.4	5.6
5	4.9	4.1	-	4.45	4.9	4.6	4.9
8	3.5	2.4	-	-	3.6	3.0	3,2
10	2	0.9	1.16	1.25	2.4	1.9	1.8
12	0.9	-0.4	-	-	1.4	0.6	0.1
14	-1	-1.8	-	-	0.4	-0,6	-1.9
16	-2.7	-3.8	-	-	-0.5	-2,1	-4
18	-5	-5.3	-	-	-1.9	-3,6	-6.7
20	-7.2	-7.8	-8.00	-	-3	-5,4	-9.6
22	-9.7	-10.2	-	-	-	-7,2	-13.2
23	-11	-11.6	-11.66	-	-	-	-15.1
25							-19.0

Our values in the presence of NaCl, 0%, 5%, 10%, 20% and 23% are very close to Zylyftari [1] and Kishimoto [2]

[1]. G. Zylyftari, May 2013.
[2]. M. Kishimoto, Apr. 2012.

Modelling: Approach n°1

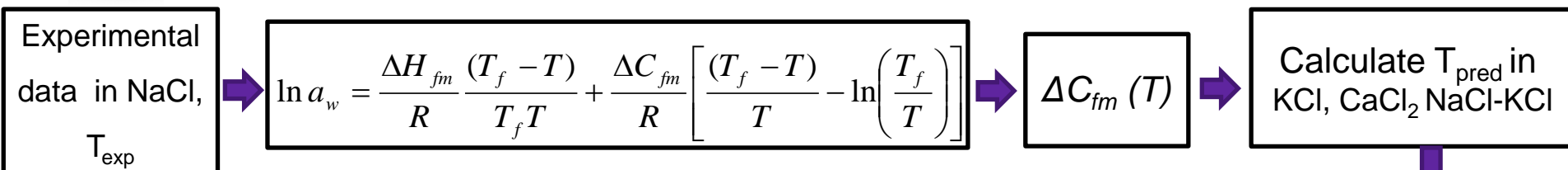
Standard SLE equation:

$$\ln a_w = \frac{\Delta H_{fm}}{R} \frac{(T_f - T)}{T_f T} + \frac{\Delta C_{fm}}{R} \left[\frac{(T_f - T)}{T} - \ln \left(\frac{T_f}{T} \right) \right]$$

Geochemical model PHREEQC predicts water activity a_w



No data for ΔC_{fm} in the literature for CPH



Algorithm of equilibrium temperature prediction

$$AAD = \frac{1}{N} \sum_{l=1}^N \left| \frac{T_{pred}}{T_{exp}} - 1 \right|$$

Approach n°2 & 3

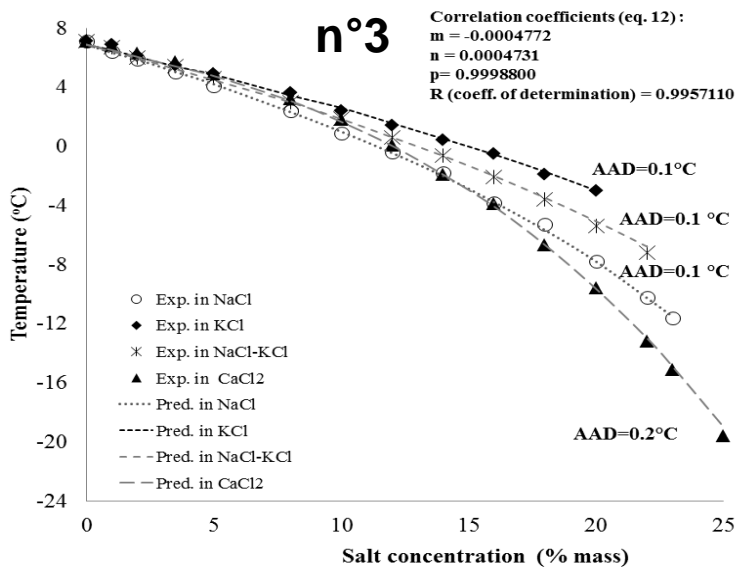
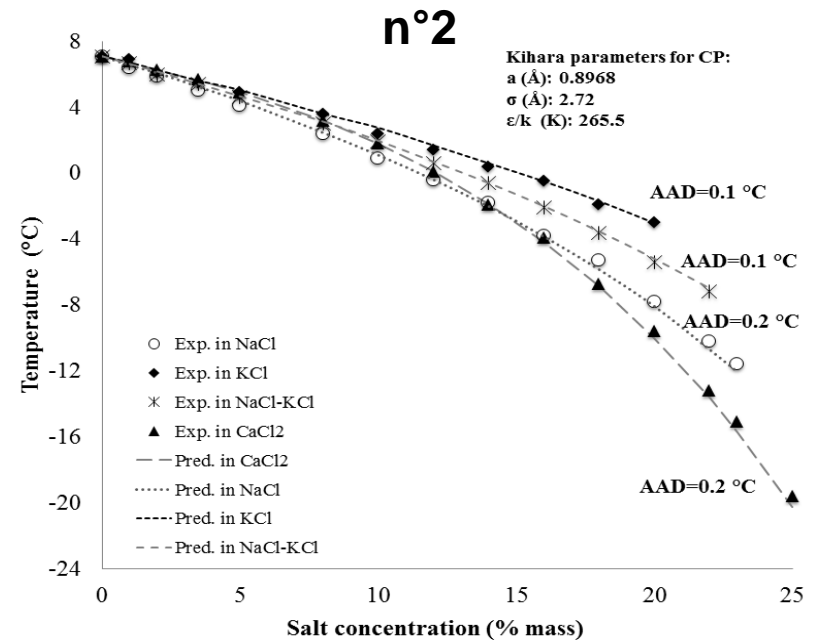
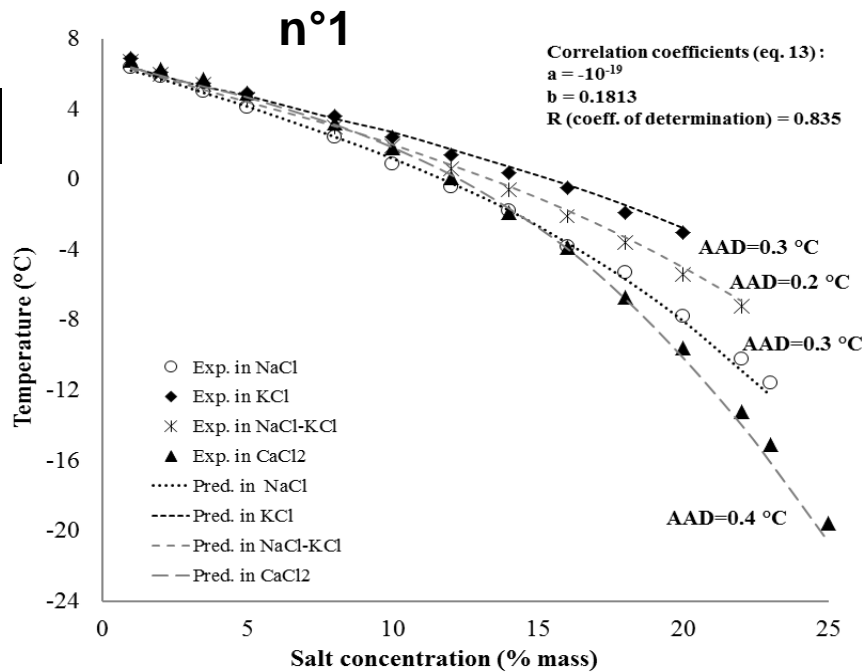
At thermodynamic equilibrium

Statistical thermodynamics $\Delta\mu_w^{\beta-H} = \Delta\mu_w^{\beta-L}$ Gibbs-Duhem

$$\Delta\mu_w^{\beta-H} = -RT \sum_i v_i \ln(1 - \sum_j \theta_j^i)$$

Approach n°2: Kihara potential
Interaction potential (ϵ, σ, a)

Approach n°3: correlation
 $\theta = \theta(a_w)$



- All models are capable of predicting equilibrium

- n°3 is the most accurate and simplest method



Outlines

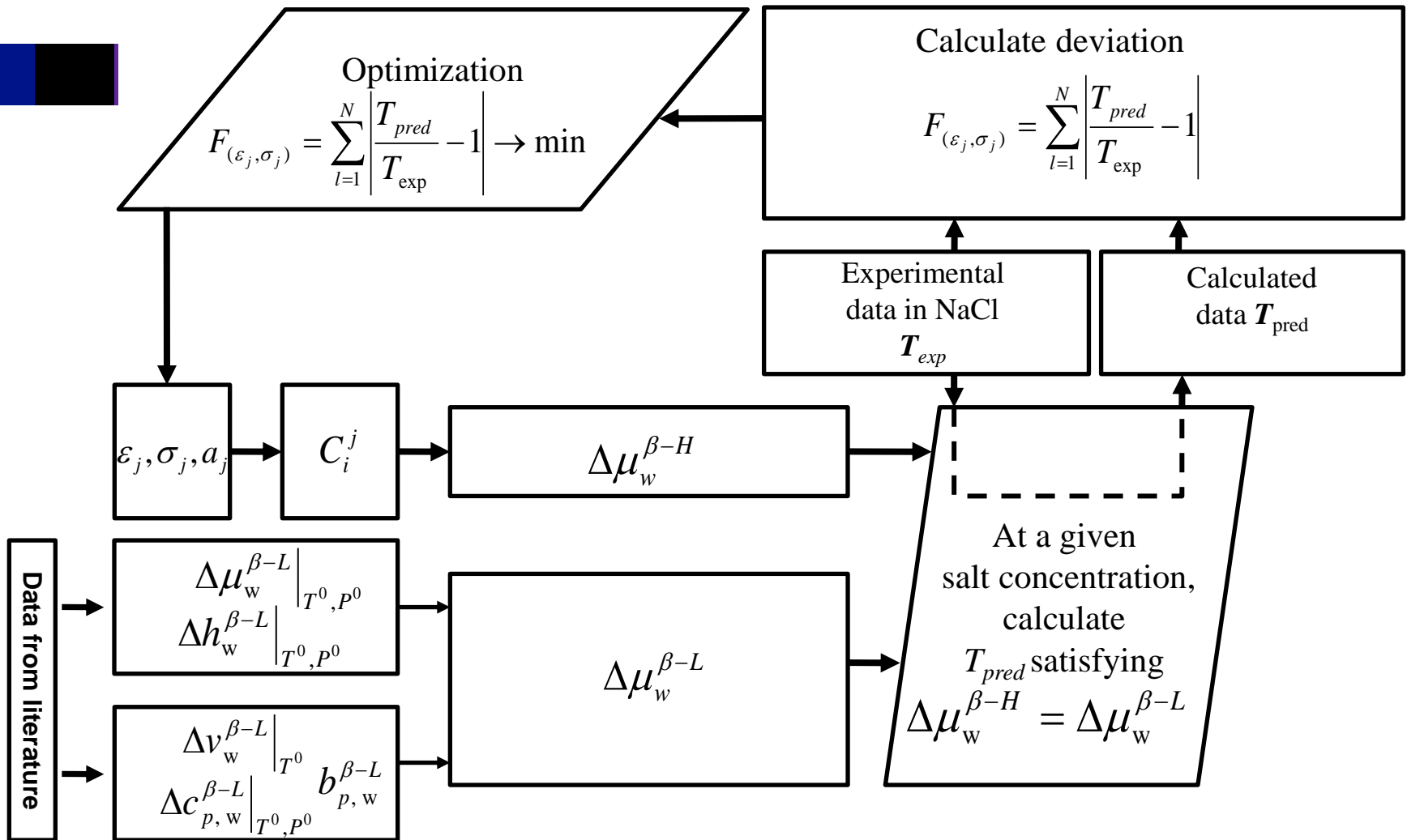
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Conclusions

- ❖ **Equilibrium temperatures CPH with NaCl, KCl, CaCl₂ or NaCl-KCl present were determined**
- ❖ **Accurate thermodynamic predictions : Occupancy correlation is the best**

PERSPECTIVES: ADD GAS MOLECULES

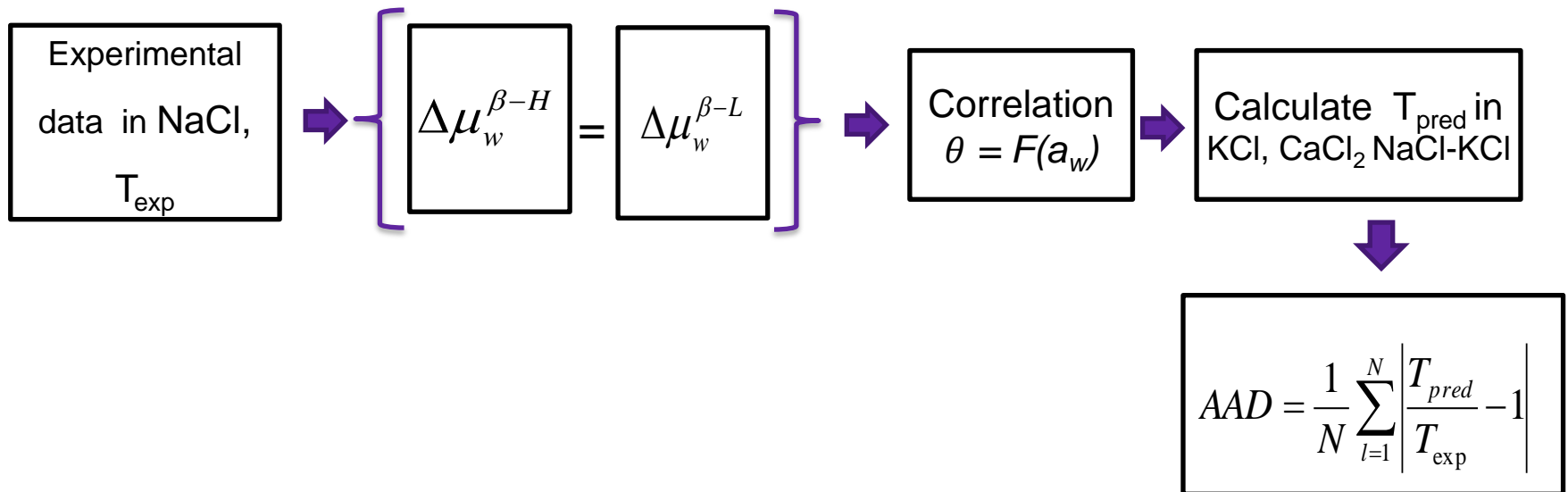
**Thank you very much for your
attention!!!**



Procedure to optimize the Kihara parameters approach n°2

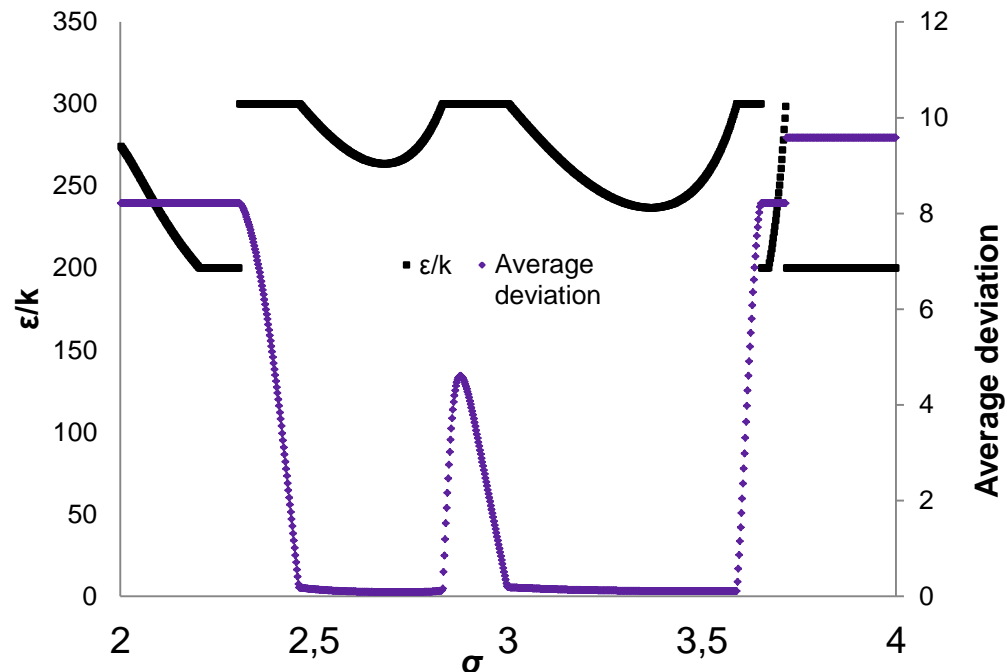
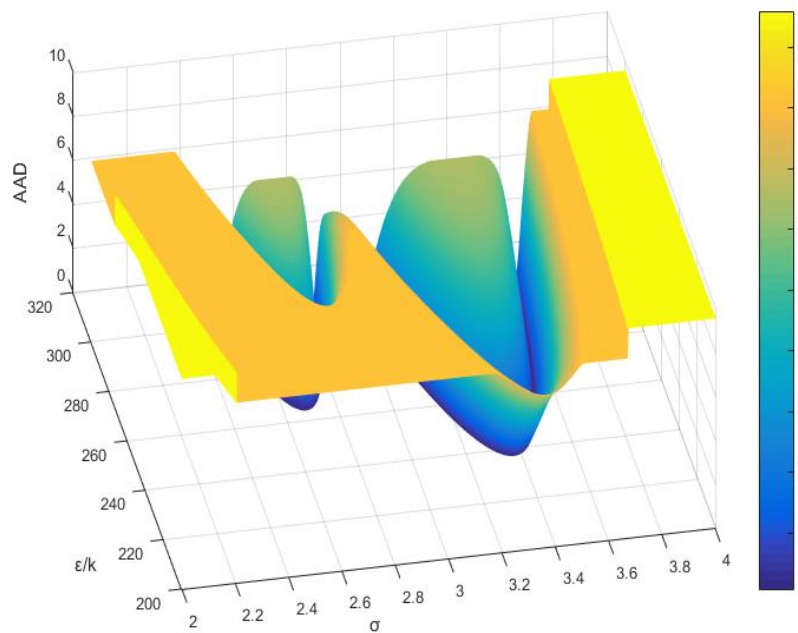
Approach n°3 - Correlation $\theta = F(a_w)$

As in the approach n°2, the **van de Waals and Platteeuw** model is used to describe the hydrate phase. The new correlation $\theta = F(a_w)$ is obtained



Algorithm of equilibrium temperature prediction: **Approach n°3**

Approach n°2



Typical form of the deviation between the predicted and the experimental data

ε/k versus σ at the minimum deviation with experimental data

Kihara parameters for cyclopentane hydrate

a (10^{-10} m)	σ (10^{-10} m)	ε/k
0.8968	2.72	265.5