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INDUSTRIELS ET NATURELS



Experimental and modelling study of cyclopentane hydrates in the presence of salts

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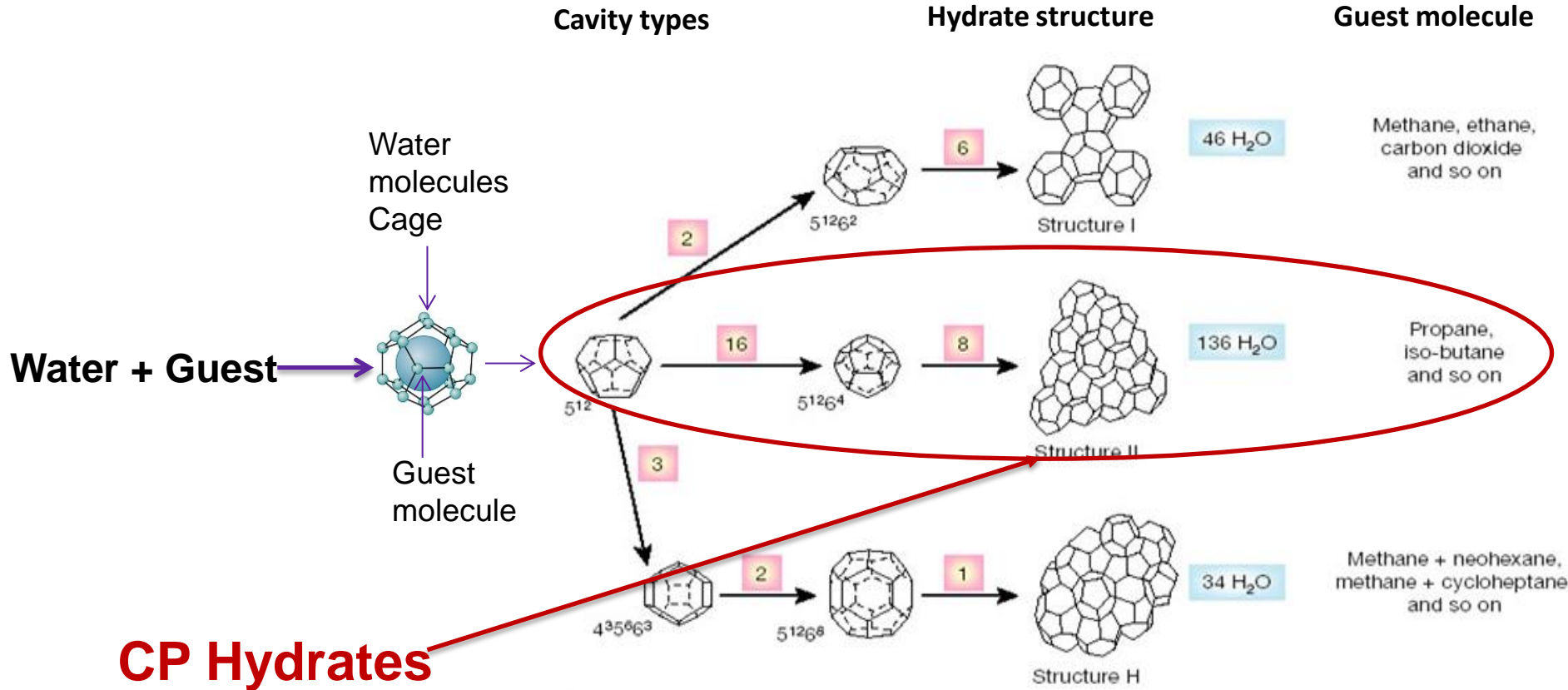
Baptiste BOUILLOT

Jean-Michel HERRI

Nancy, 11/12/2017

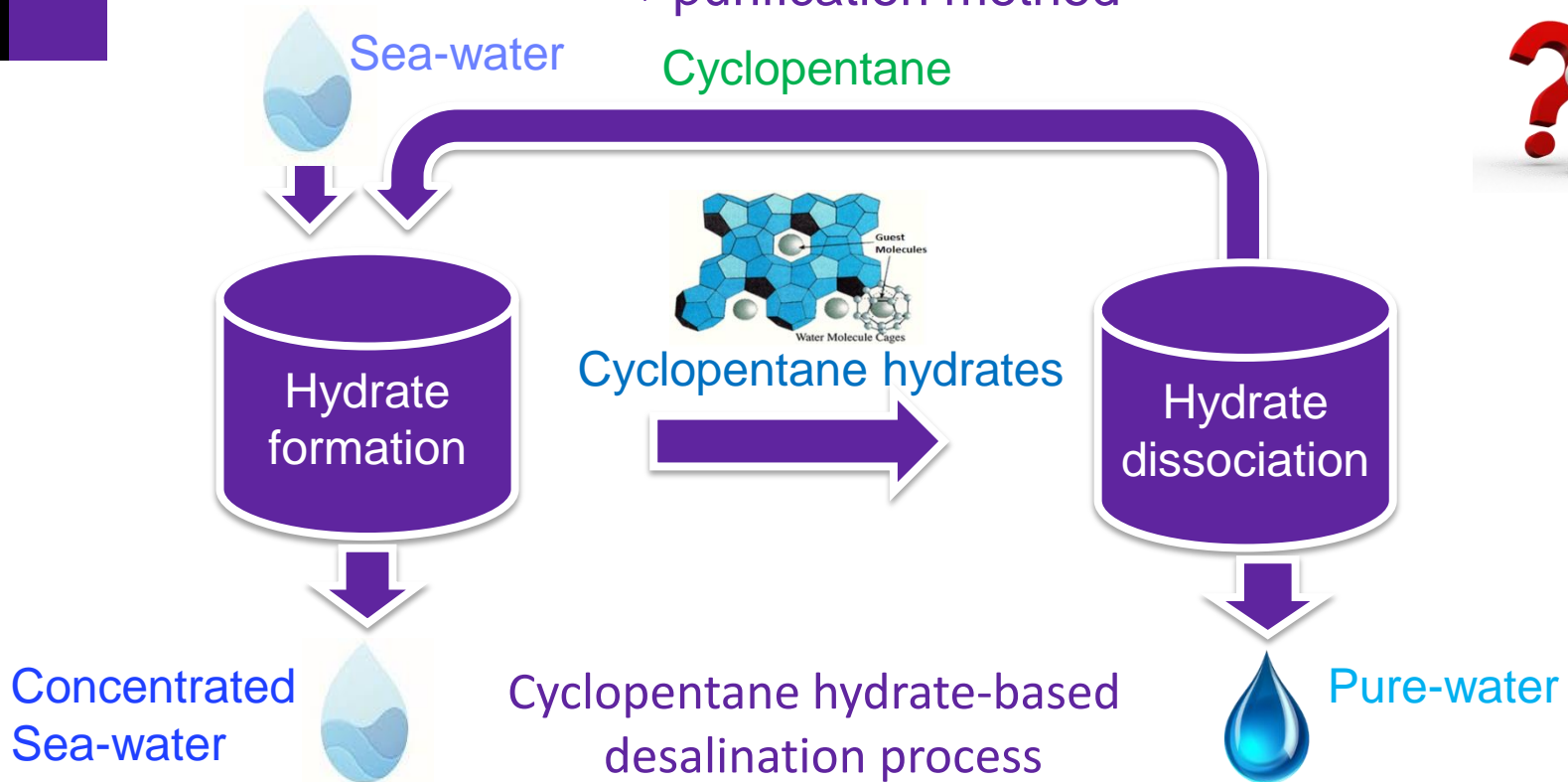
- 1. Introduction and objective**
- 2. Experimental Methodology**
- 3. Experimental results**
- 4. Modelling of cyclopentane hydrates**
- 5. Conclusions & Perspectives**

Introduction What are clathrate hydrates ?



The five cavity types and the three common unit crystals structures
 (E. Dendy Sloan and Jr, 2003)

Hydrates can be used to remove water from aqueous solution
→ purification method



Phase equilibria data in the presence of different salts is needed.

Objective

Experimental and modelling study of cyclopentane hydrates in NaCl, KCl, an equal-weight mixture NaCl-KCl, and CaCl₂

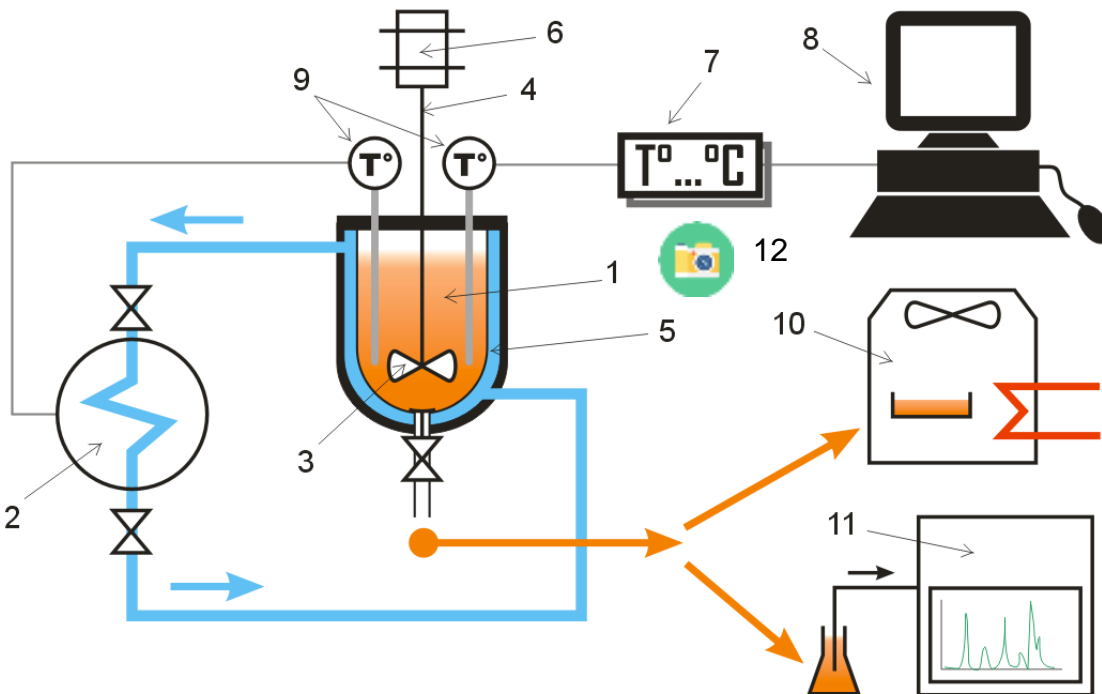


Outlines

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

Experimental methodology

Equilibrium temperature measurement



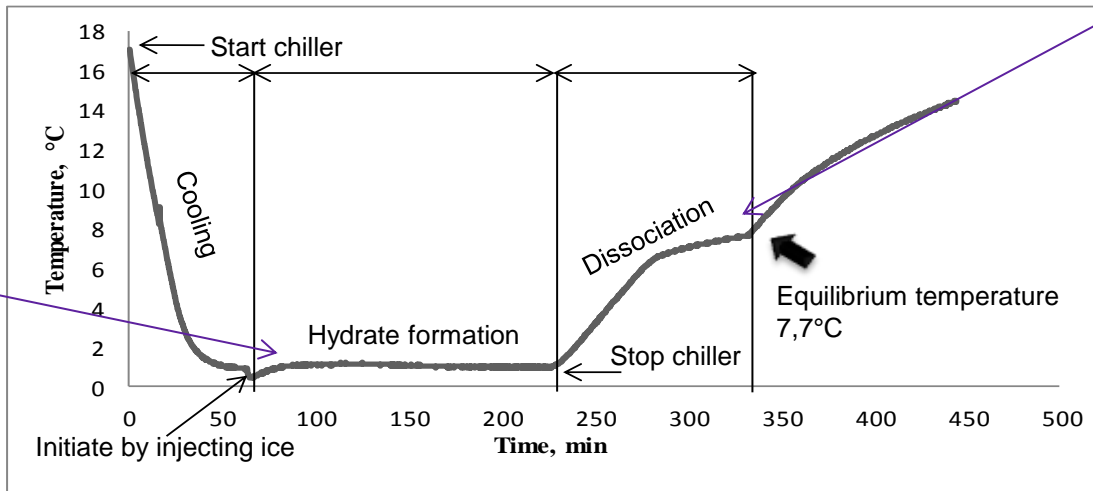
schematic diagram

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

Protocole: Two procedures



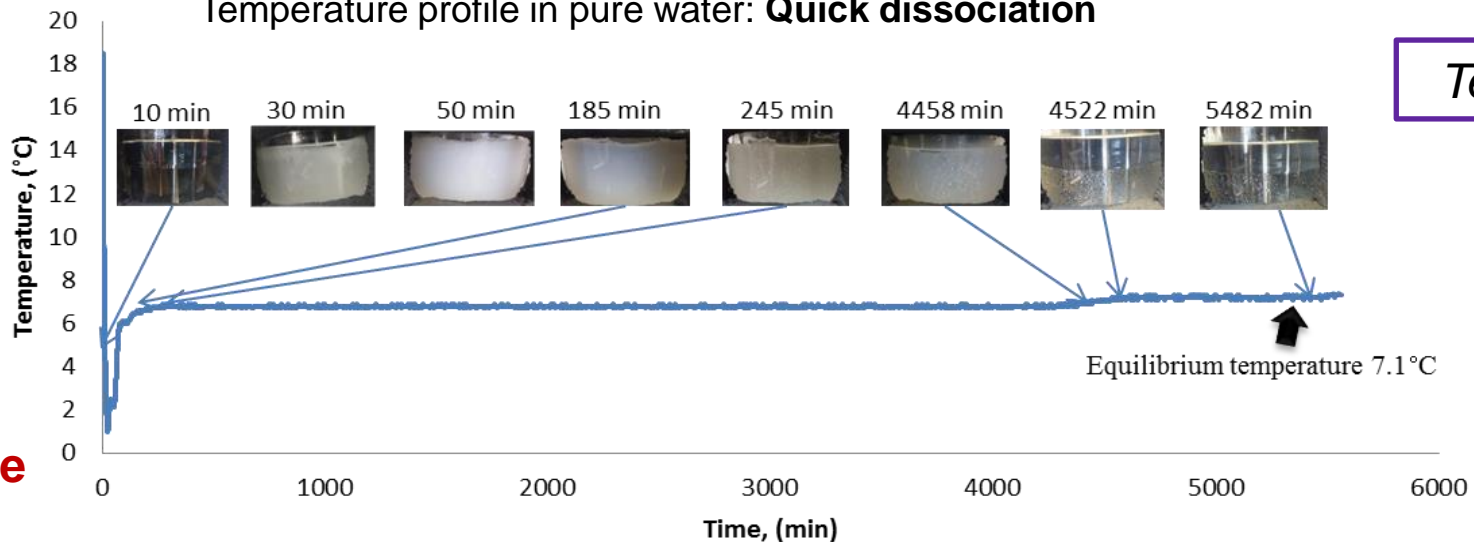
Endothermic process

$T_e = 7,7^\circ\text{C}$

Exothermic process

T Estimation

Temperature profile in pure water: Quick dissociation



$T_e = 7,1^\circ\text{C}$

T Accurate

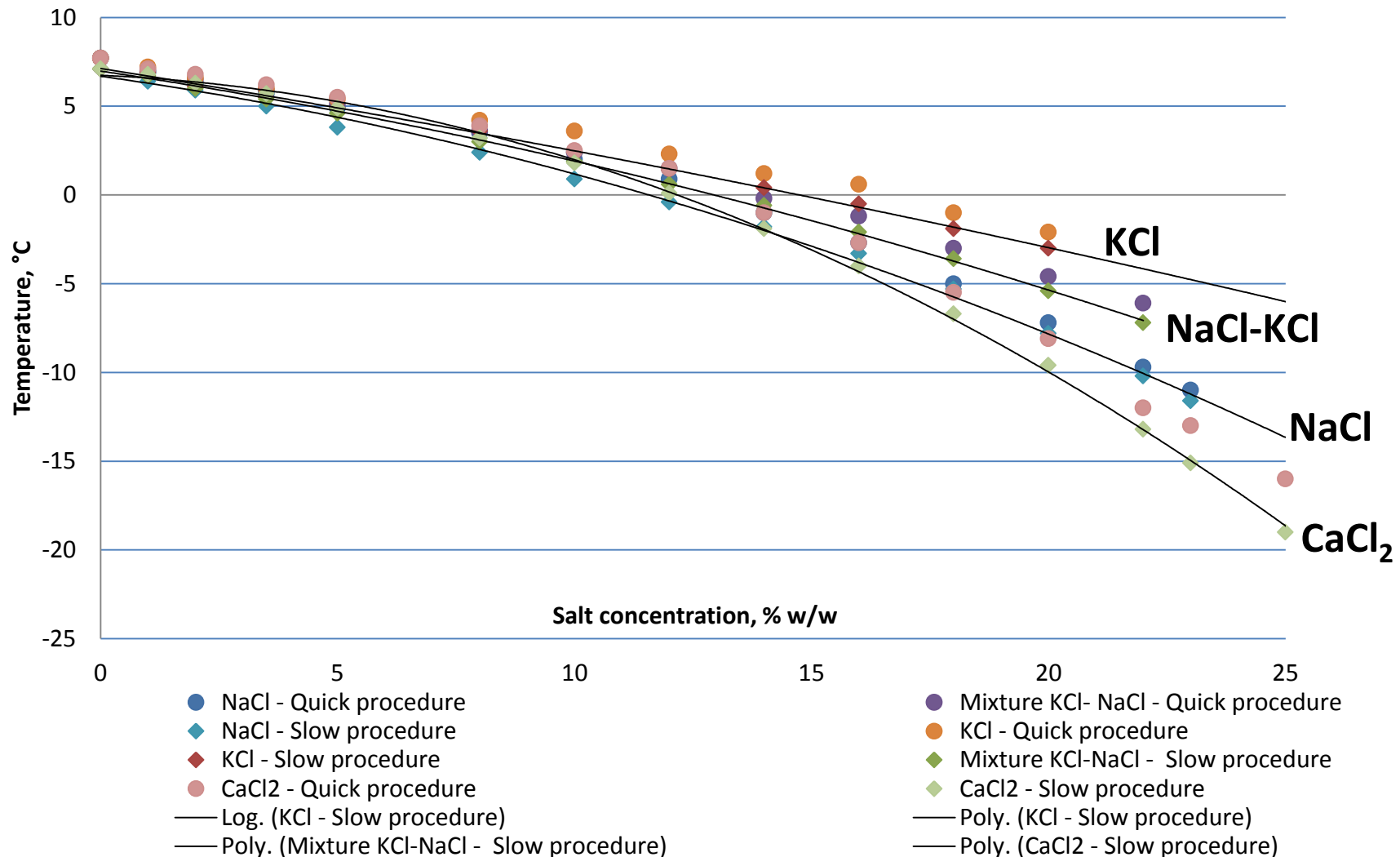
Temperature profile in pure water: Slow dissociation



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Equilibrium temperatures in the presence of salts



Equilibrium temperatures in the presence of NaCl, KCl, equi-mass mixture NaCl-KCl, and CaCl₂

Salinity, % w/w	T _{e-quick} in NaCl, °C	T _{e-slow} in NaCl, °C	T _e in NaCl, °C [9]	T _e in NaCl, °C [3]	T _{e-slow} in KCl, °C	T _{e-slow} in a mixture of NaCl-KCl, °C	T _{e-slow} in CaCl ₂ , °C
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 Kishimoto [3] and Zylyftari [9]

[3]. M. Kishimoto, Apr. 2012.
 [9]. G. Zylyftari, May 2013.



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4. **Modelling of cyclopentane hydrate**
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Modelling: Approach n°1

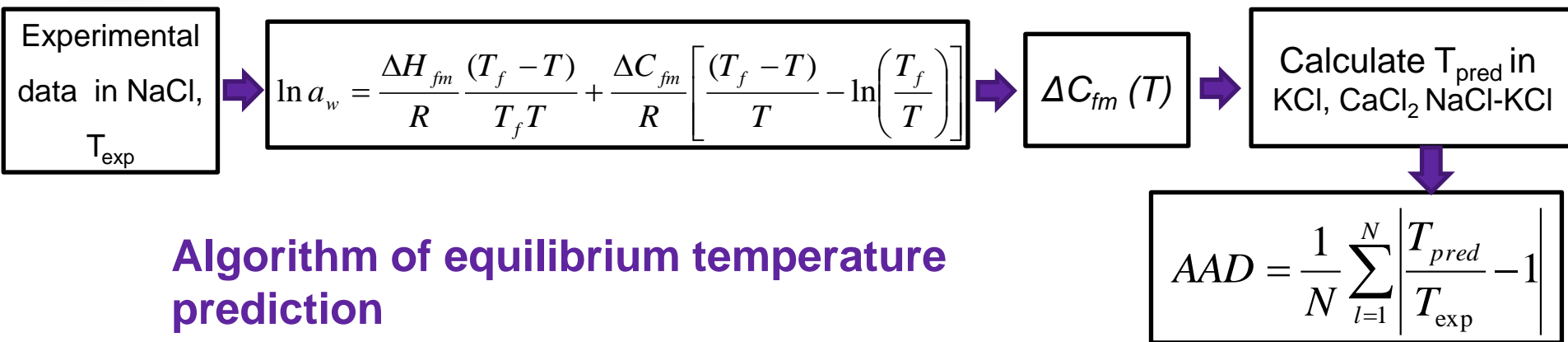
Standard SLE equation:

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

Geochemical model PHREEQC is used to predict water activity a_w



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



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)

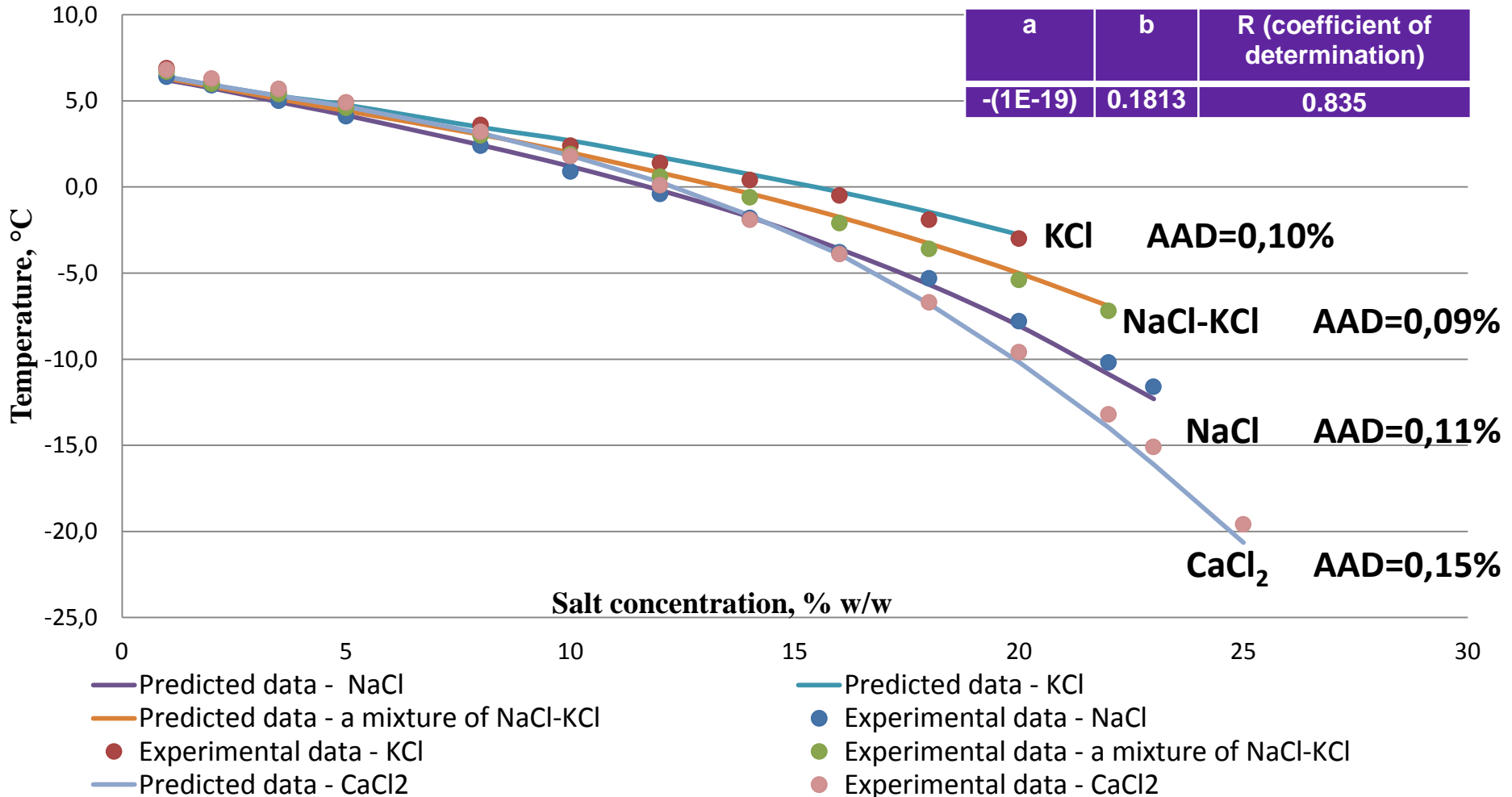
Approach n°3: correlation
 $\theta = \theta(a_w)$

Modelling results

Approach n°1

$$\Delta C_{mf} = F(T) = a \times \exp(b \times T)$$

a	b	R (coefficient of determination)
-(1E-19)	0.1813	0.835

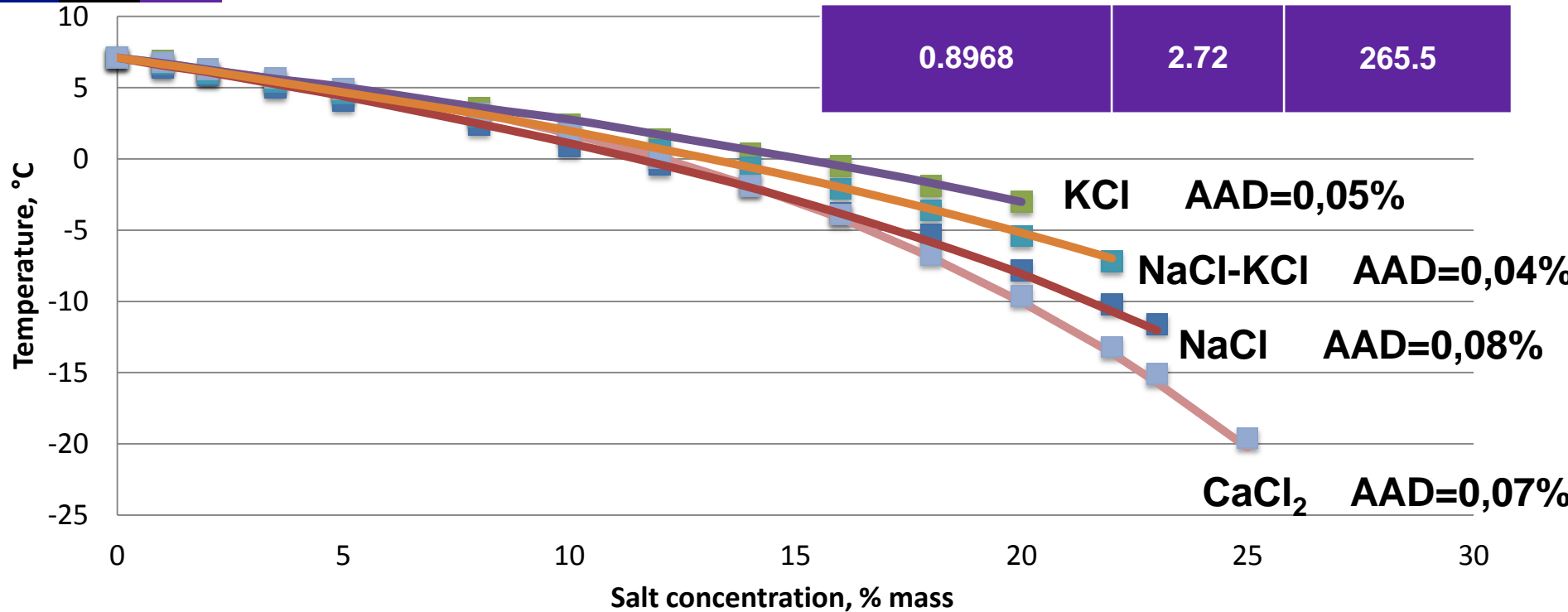


Predicted-equilibrium temperatures: **Approach n°1**

Approach n°2

Kihara parameters for CPH

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



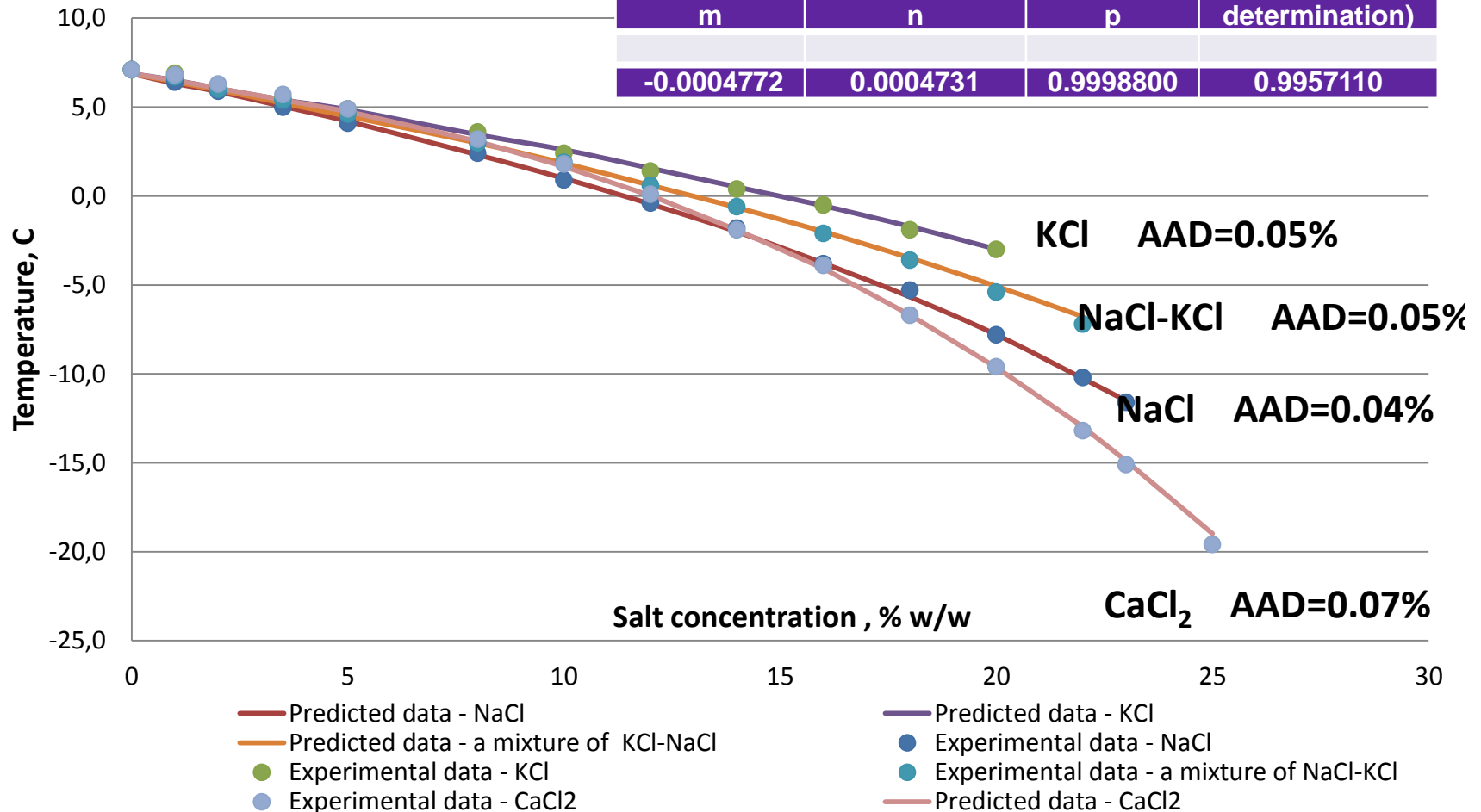
- Experimental data in NaCl
- Experimental data in KCl
- Experimental data in NaCl-KCl
- Experimental data in CaCl₂
- Predicted data in CaCl₂
- Predicted data in NaCl
- Predicted data in KCl
- Predicted data in NaCl-KCl

Predicted-equilibrium temperatures: **Approach n°2**

Approach n°3

$$\theta = F(a_w) = m \times (a_w^2) + n \times (a_w) + p$$

m	n	p	R (coefficient of determination)
-0.0004772	0.0004731	0.9998800	0.9957110



Predicted-equilibrium temperatures: **Approach n°3**



Outlines

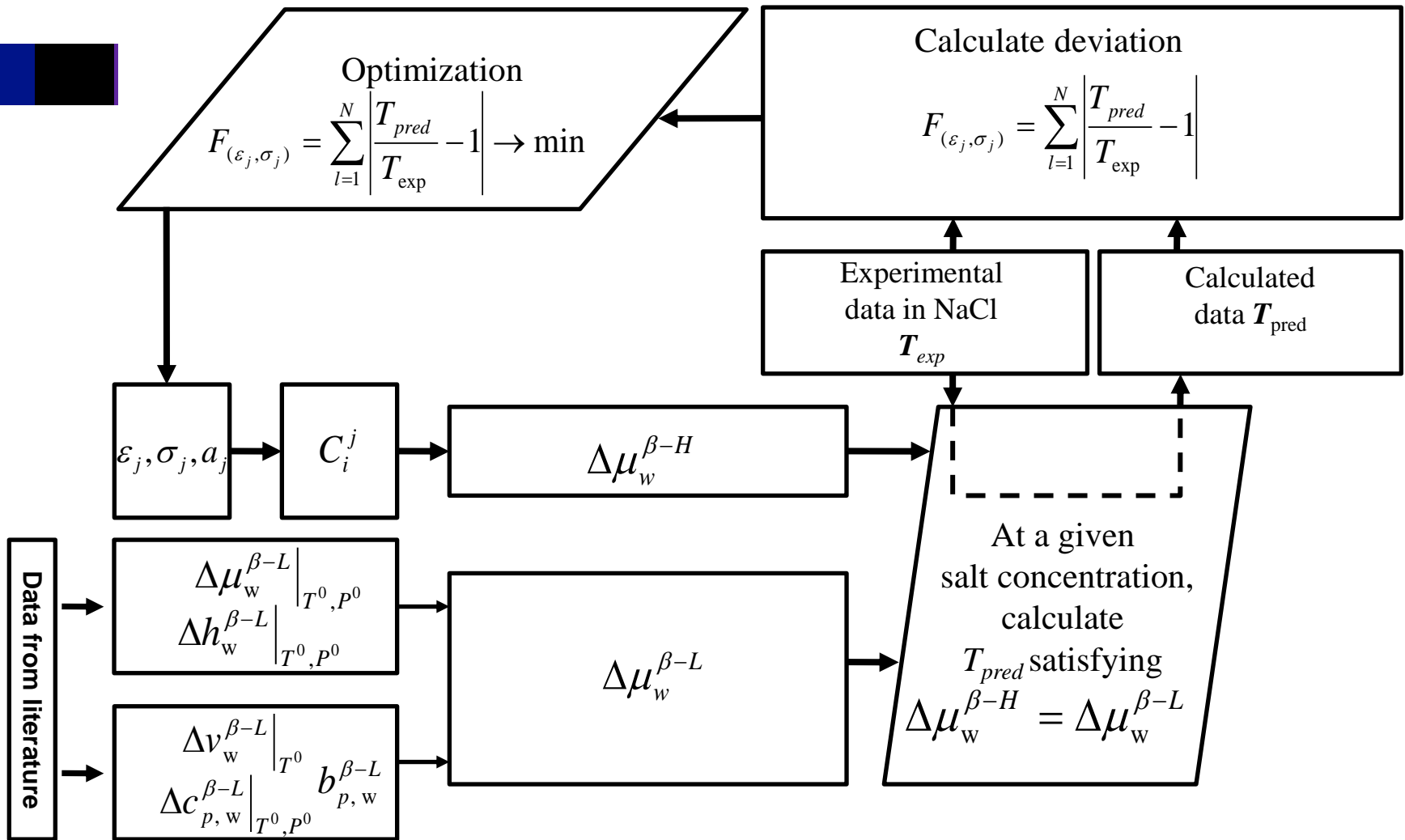
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Conclusions

- ❖ **The Equilibrium temperatures in the presence of NaCl, KCl, mixture NaCl-KCl, and CaCl₂ were determined following the quick and the slow procedures:**
 - The Equilibrium temperatures drop strongly with increasing of salt concentration
 - Slow dissociation provided accurate data
- ❖ **Accurate thermodynamic predictions : AAD ≤ 0.15%**
 - Occupancy based approaches are better

PERSPECTIVES: ADD GAS MOLECULES

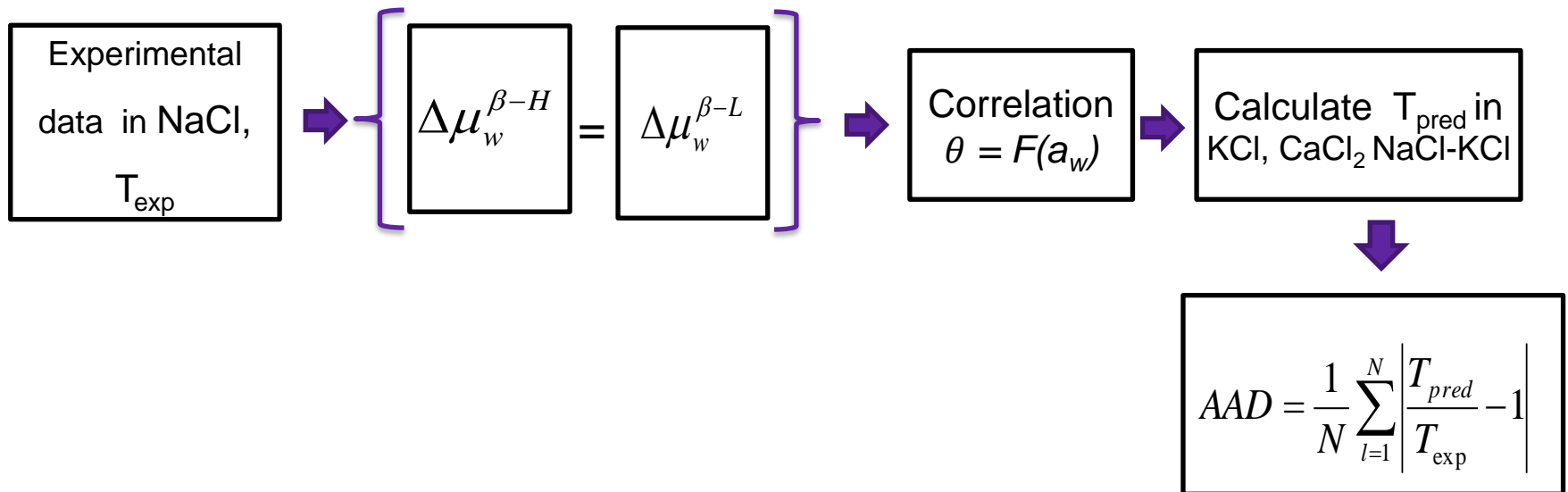
**Thank you very much for your
attention!!!**



Procedure to optimize the Kihara parameters approach n°2

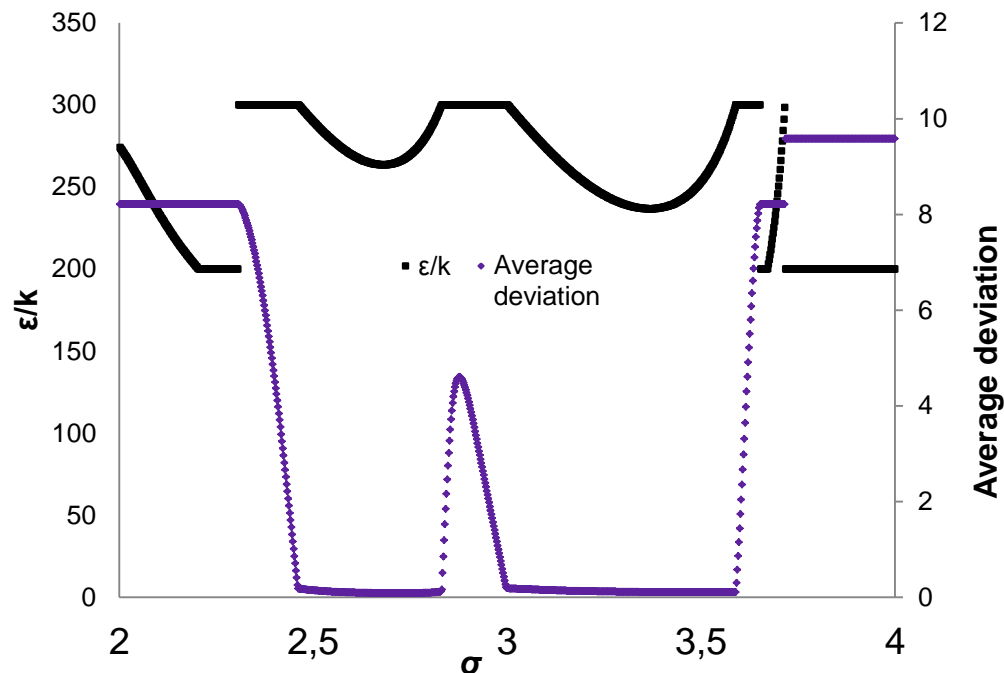
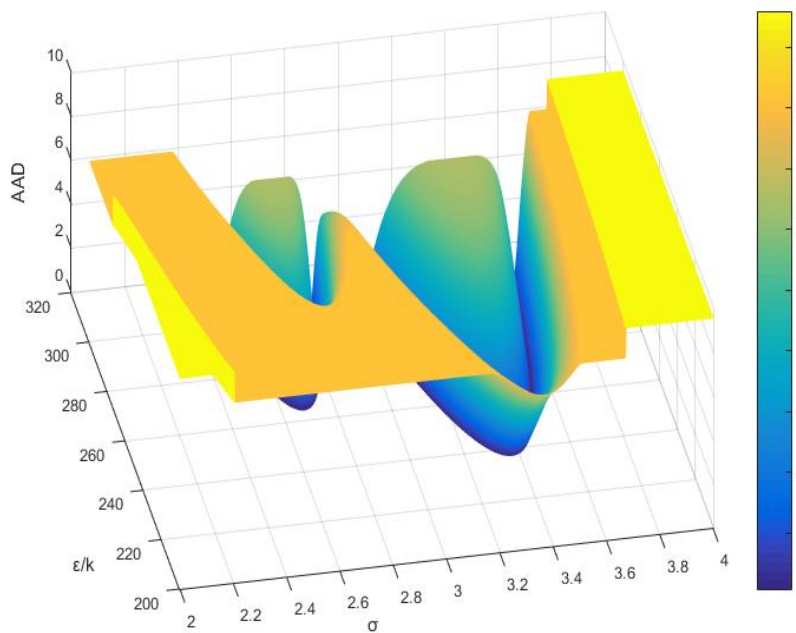
Approach n°3 - Correlation $\theta = F(a_w)$

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