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# Systematic computation of phase partition and solubilities in phase transfer catalytic processes

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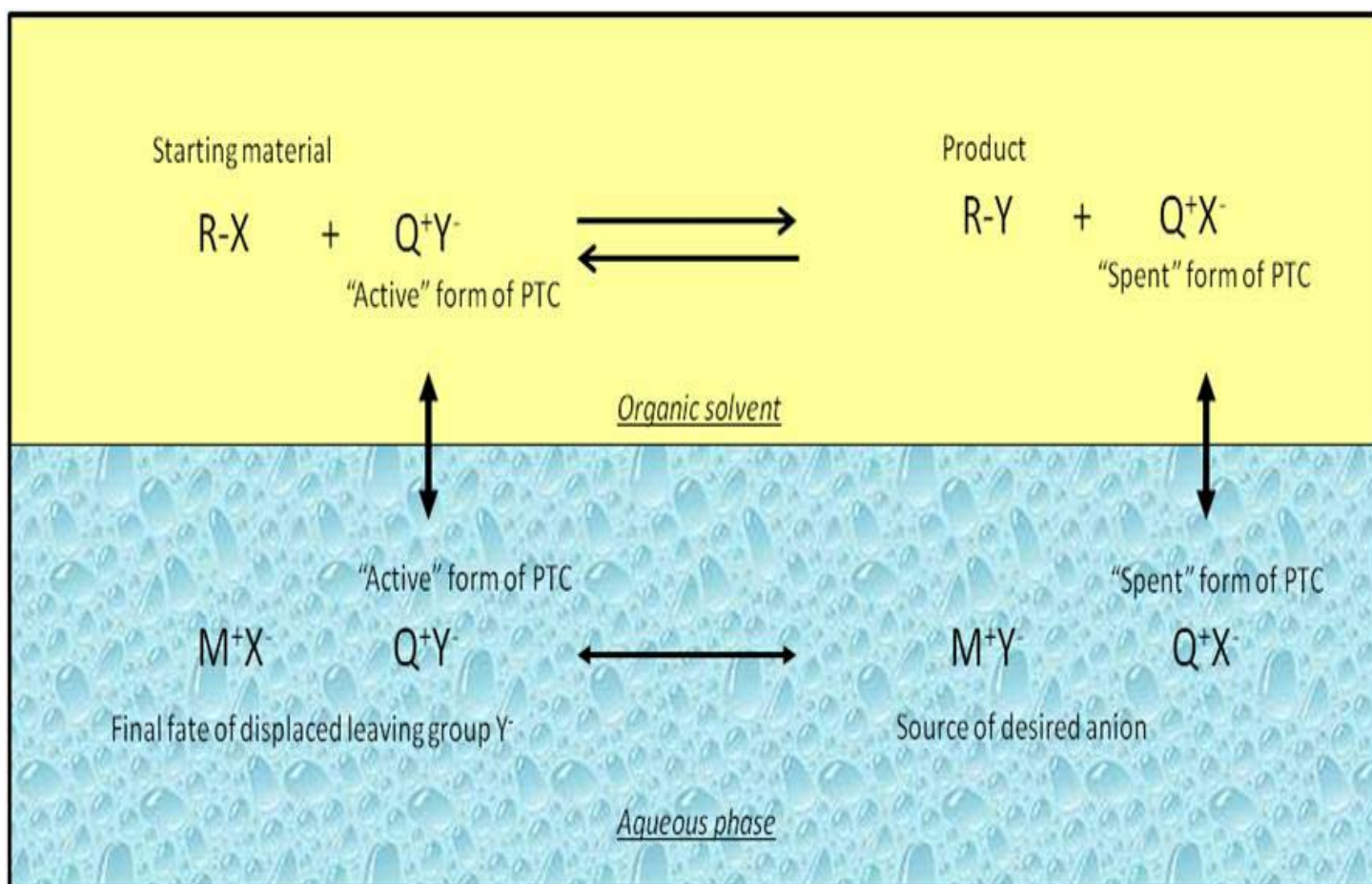
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## Abstract

Phase transfer catalysis (PTC) is a general methodology applicable to a great variety of reactions in which inorganic anions react with organic compounds. In PTC, reactions are performed in heterogeneous two phase systems in which there is a negligible mutual solubility of the phases. One aqueous phase serves as a reservoir of reacting anions, whereas organic reactants are located in a second, organic phase. The key feature of this approach is the use of a catalytic amount of an organic soluble cation (often a quaternary ammonium cation) to induce solubilization of the reactive anion in the organic phase while trying to minimize the partition of the product anion. Therefore the determination of the solubility and the related equilibrium partitioning of the active and inactive form of the PT catalyst between the two phases is critical for the design of successful phase transfer catalytic processes.

## 1. Introduction

### PTC mechanism



- o Synthesis of organic molecules from two reactants located in immiscible phases (one organic phase and one aqueous phase)
- o A phase transfer catalyst added to transfer one reactant from its normal phase into a different phase where it encounters the second reactant

### Process insights

- o Mutual solubility between organic solvent and water
- o PTCs present in different aggregation status in the:
  - organic phase: PTCs dissociate into ions
  - aqueous phase: PTCs present as ion pairs
- o The active and the spent form of the catalyst distribute between the organic and the aqueous phase  $\rightarrow$  The ratio between the active and the spent form of the catalyst in the organic phase determines the extent of conversion of the organic reaction

Solubility model based calculations and partition between phases are critical for the development of PTC processes

## 2. Solubility calculations framework

### A. Decomposition into 4 binary systems

- Organic solvent - water
- Inorganic salt - water
- Organic solvent - PTC
- PTC - water



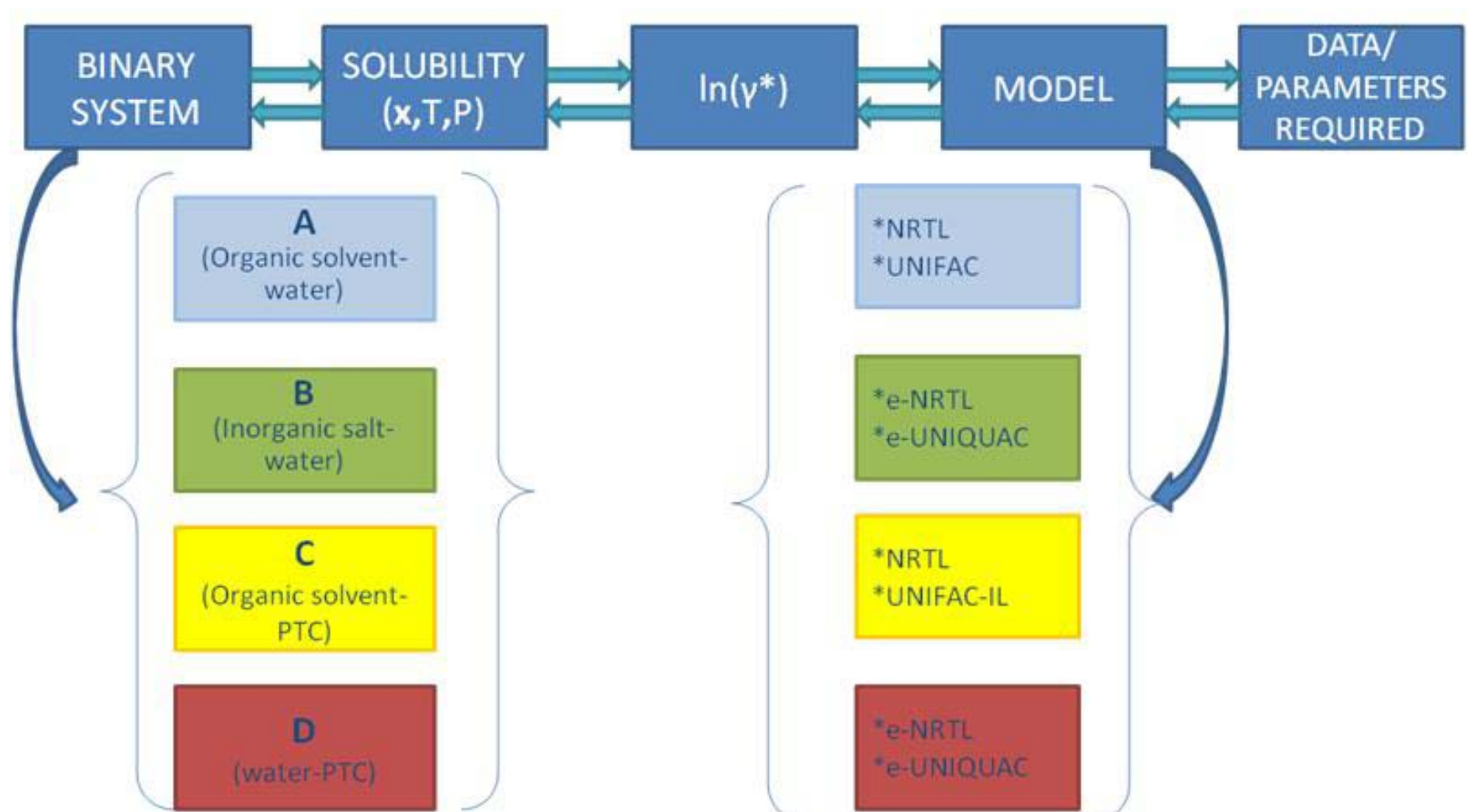
### B. Collection of experimental solubility data

Binary System	Number of systems studied	Number of data points
A (Organic solvent-water) LLE data	9	494
B (Inorganic salt-water) SLE data - Experimental mean activity coefficient data	10	271
C (Organic solvent-PTC) SLE data	172	251
D (water-PTC) SLE data - Experimental mean activity coefficient data	43	89

### C. Development+identification of the model for each binary subsystem:

- model for mixture  $\gamma^{LLE}$  and  $\gamma^{SLE}$  are needed
- parameters of constitutive models for  $\gamma$  calculations are needed

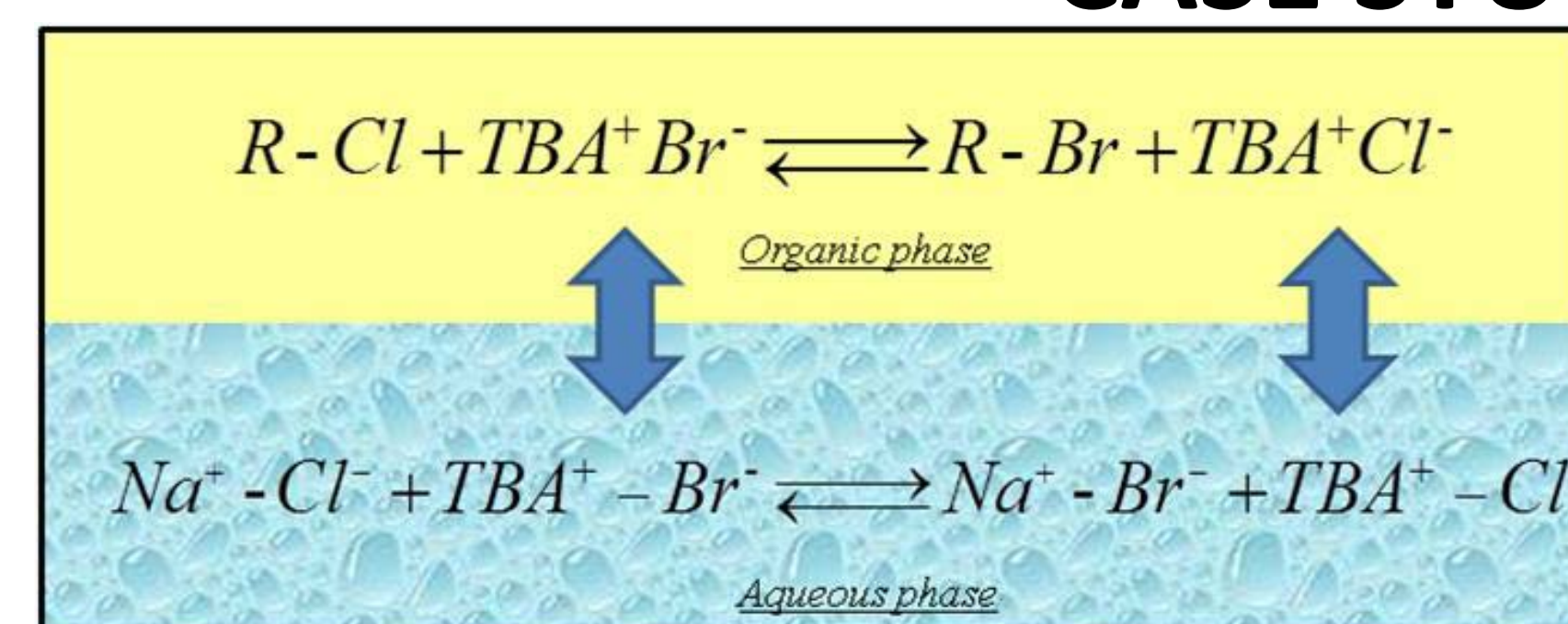
### Constitutive models



### Equilibrium models

A (Organic solvent-water) LLE	$x_i^{org} \gamma_i^{org} = x_i^{aq} \gamma_i^{aq}$
B (Inorganic salt-water) SLE	$x_i \gamma_i = \exp\left(\frac{\Delta H_i}{RT_s} \left(1 - \frac{T_s}{T}\right) + A + B \frac{1}{T}\right)$
C (Organic solvent-PTC) SLE	$x_i \gamma_i = \exp\left(\frac{\Delta H_i}{RT_s} \left(1 - \frac{T_s}{T}\right) + \frac{\Delta H_{i,org}}{RT_s} \left(1 - \frac{T_s}{T}\right) + \frac{\Delta H_{i,aq}}{RT_s} \left(1 - \frac{T_s}{T}\right) + \frac{\Delta C_p}{R} \left(\ln \frac{T_s}{T} - 1\right)\right)$
D (water-PTC) SLE	$x_i \gamma_i = \exp\left(\frac{\Delta H_i}{RT_s} \left(1 - \frac{T_s}{T}\right) + \frac{\Delta H_{i,org}}{RT_s} \left(1 - \frac{T_s}{T}\right) + \frac{\Delta H_{i,aq}}{RT_s} \left(1 - \frac{T_s}{T}\right) + \frac{\Delta C_p}{R} \left(\ln \frac{T_s}{T} - 1\right)\right)$

## 3. Application of the methodology to an industrial CASE STUDY



### Production of benzyl bromide

- R - Cl = Benzyl Chloride
- R - Br = Benzyl Bromide
- TBA<sup>+</sup> Br<sup>-</sup> = Active catalyst
- TBA<sup>+</sup> Cl<sup>-</sup> = Inactive catalyst
- organic solvent = Toluene

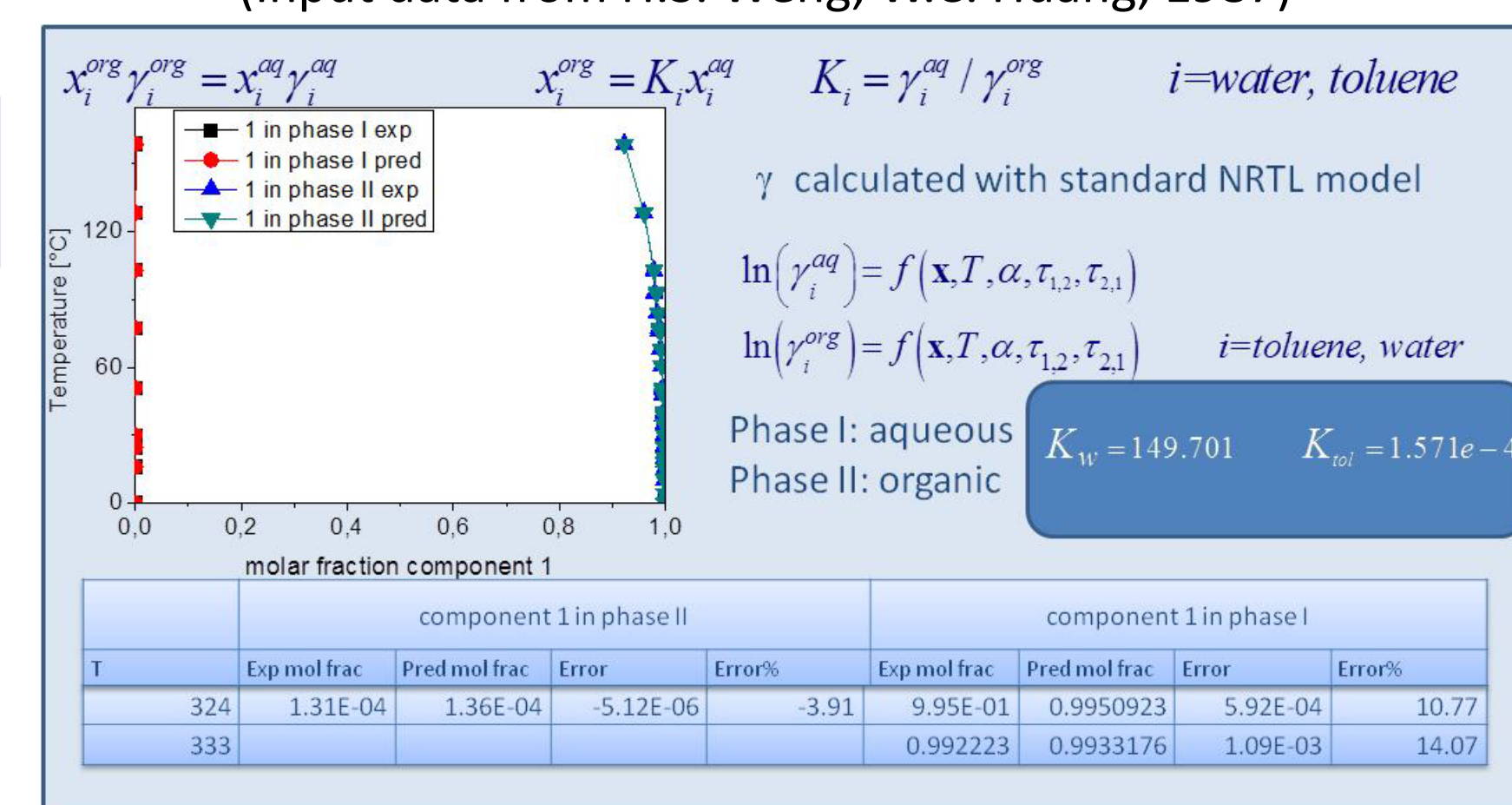
4 components/species distribute (are in equilibrium) between the two phases: toluene, water, active and inactive catalysts

An equilibrium relation can be written for each of them  $x_i^I \gamma_i^I = x_i^{II} \gamma_i^{II}$  or  $x_i^I = K_i x_i^{II}$  with  $K_i$ : partition coefficient

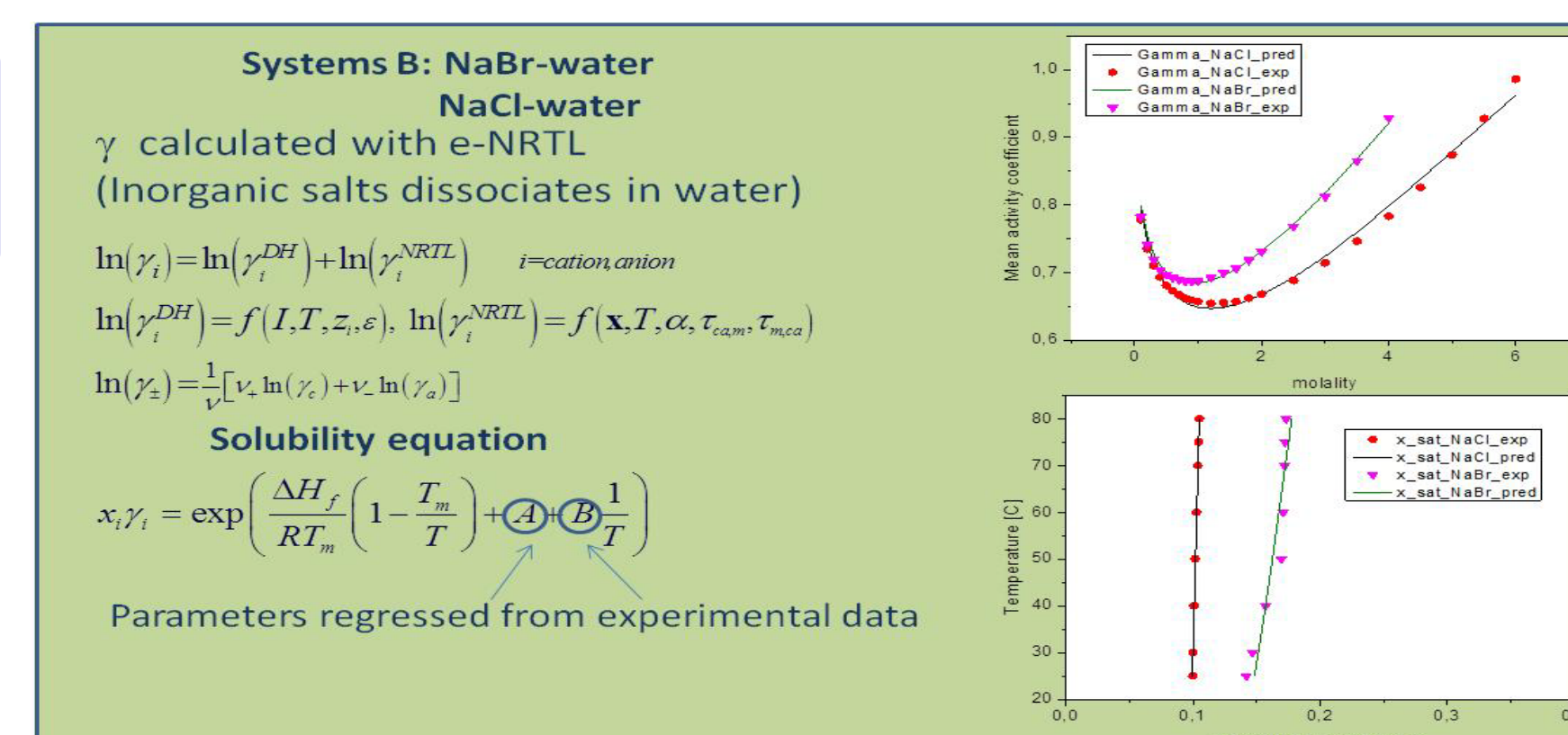
### Example of calculations:

(Input data from H.S. Weng, W.C. Huang, 1987)

### System A: Toluene-water



### System B: NaCl-water NaBr-water

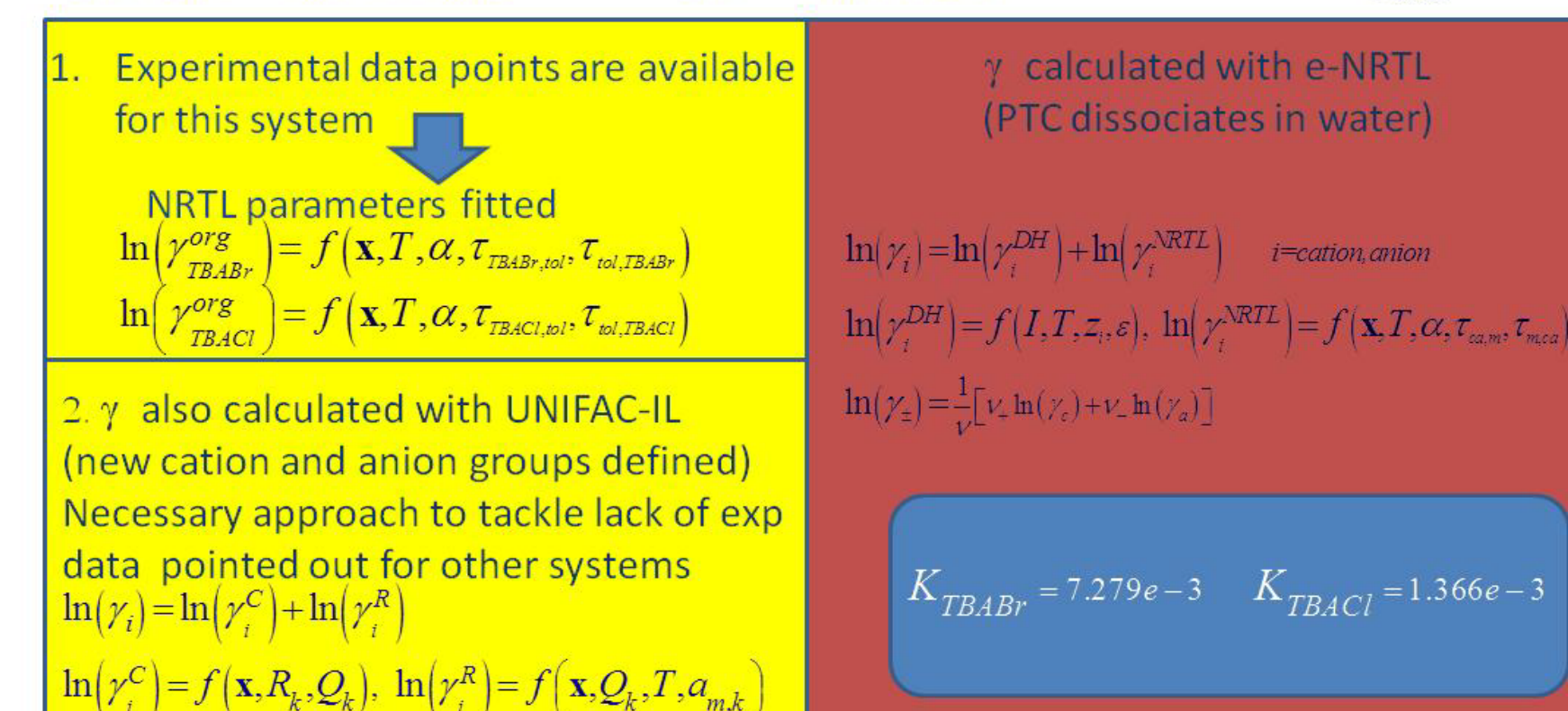


### Active and inactive PTC partition between water and organic phases

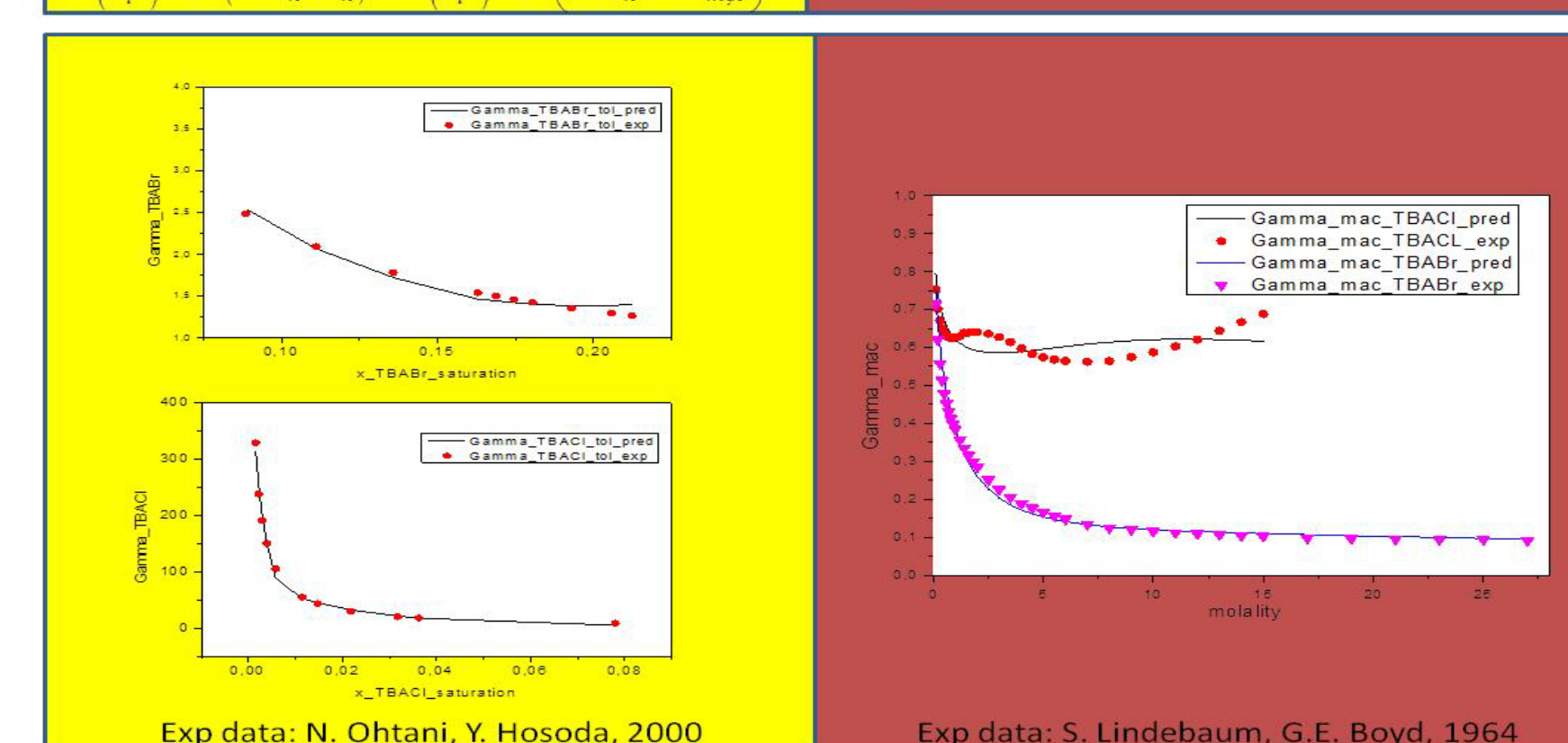
$$x_{TBA^+ Br^-}^{org} \gamma_{TBA^+ Br^-}^{org} = x_{TBA^+ Br^-}^{aq} \gamma_{TBA^+ Br^-}^{aq} \quad x_{TBA^+ Cl^-}^{org} \gamma_{TBA^+ Cl^-}^{org} = x_{TBA^+ Cl^-}^{aq} \gamma_{TBA^+ Cl^-}^{aq}$$

$$K_{TBA^+ Br^-} = \frac{\gamma_{TBA^+ Br^-}^{org}}{\gamma_{TBA^+ Br^-}^{aq}} \quad K_{TBA^+ Cl^-} = \frac{\gamma_{TBA^+ Cl^-}^{org}}{\gamma_{TBA^+ Cl^-}^{aq}}$$

### System C: TBABr-toluene TBACl-toluene



### System D: TBABr-water TBACl-water



## 4. Conclusions

A reliable thermodynamic framework for the calculation of solubilities and phase partition in phase transfer catalytic processes has been developed and illustrated through an industrial case study:

- o The system has been decomposed into binary subsystems
- o The appropriate thermodynamic models have been developed/selected for each subsystem
- o A database of solubility data has been built and used to regress parameters model and validate the modelling approach
- o The partition coefficient of the component/species which distribute between the two phases has been readily calculated

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