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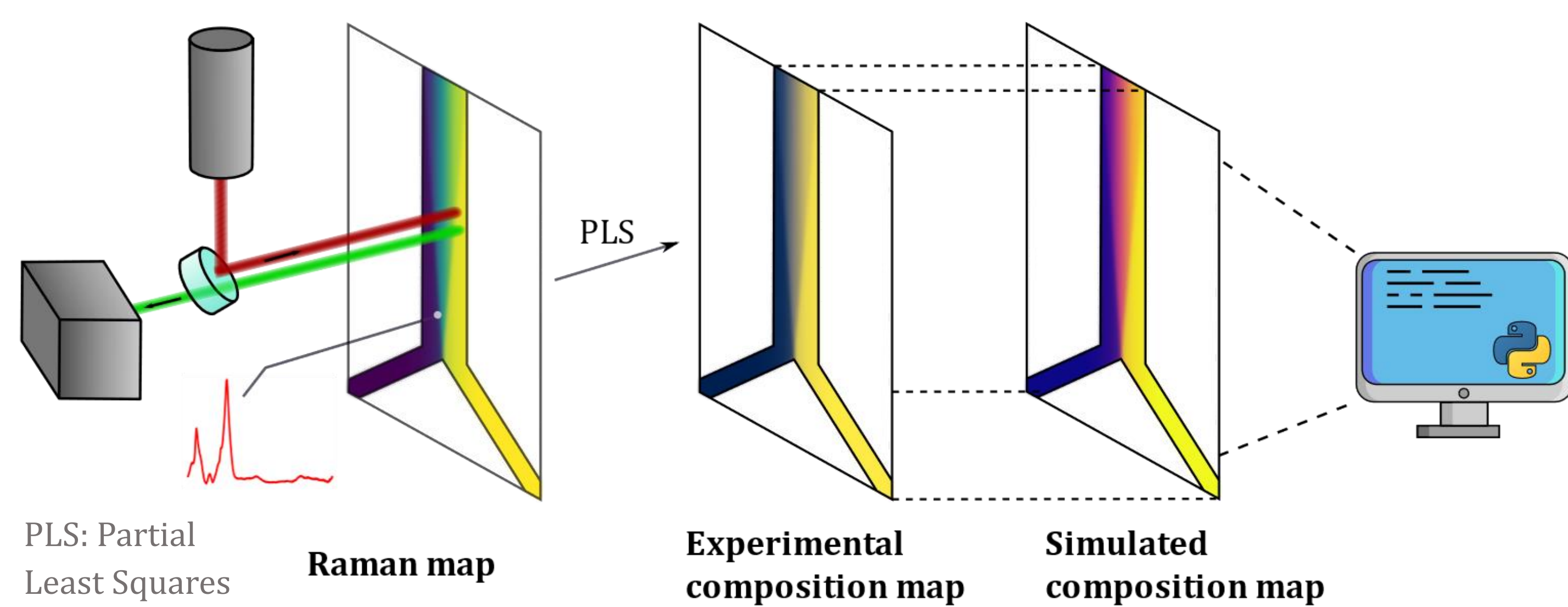
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Fick's law does not work for antisolvent crystallisation processes – what could we use instead?



1. Background

- **Mixing** impacts heavily on the outcome of antisolvent crystallisation processes [1]. Its poor understanding leads to unwanted phenomena such as **oiling out** and **unexpected polymorphs** – see **Figure 1(a)**.
- Even mixing between miscible liquids presents anomalies, such as the interface in **Figure 1(b)**.
- Standard mixing experimental studies fail to provide information-rich outputs, normally only reporting Fick's diffusion coefficient.
- A better-suited **mass transfer model** needs to be developed, and a **new standard** for reporting mixing data is needed to inform it.

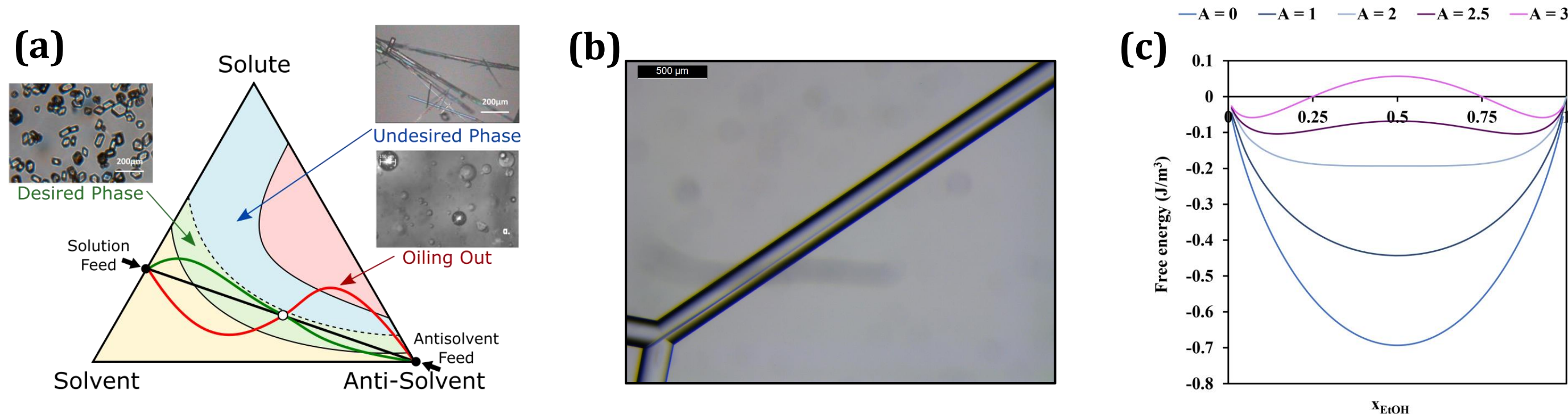


Figure 1. (a) Ternary phase diagram illustrating that the mixing path dictates the outputs. (b) Example of microfluidic mixing behaviour in a H₂O-50wt EtOH system, at 5 μ L/min. (c) Behaviour of the Margules model for different values of the parameter A [2].

Fick's diffusion law

$$\frac{\partial x_A}{\partial t} + \nabla(\mathbf{v}x_A) = -D_{AB} \cdot \nabla^2 x_A$$

- **Composition gradient** as the driving force
- **Ideal behavior**
- Not suitable for phase-changing systems

CaHiMaS phase-field model

$$\frac{\partial x_A}{\partial t} + \nabla(\mathbf{v}x_A) = \nabla[D_{AB} \cdot \nabla x_A] + \nabla[D_{AB}x_A \cdot \nabla[A(1-x_A)^2 - \epsilon^2 \nabla^2 x_A]]$$

- **Chemical potential gradient** as the driving force (Maxwell-Stefan)
- **Margules activity model**
- Interface free energy ($\epsilon^2 \nabla^2 x_A$)

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References: Please scan the QR on top.

2. Results and discussion

- **Figure 4** compares the performance of Fick's law and the CaHiMaS model for different values of A and ϵ , and with $D = 1600 \mu\text{m}^2/\text{s}$.

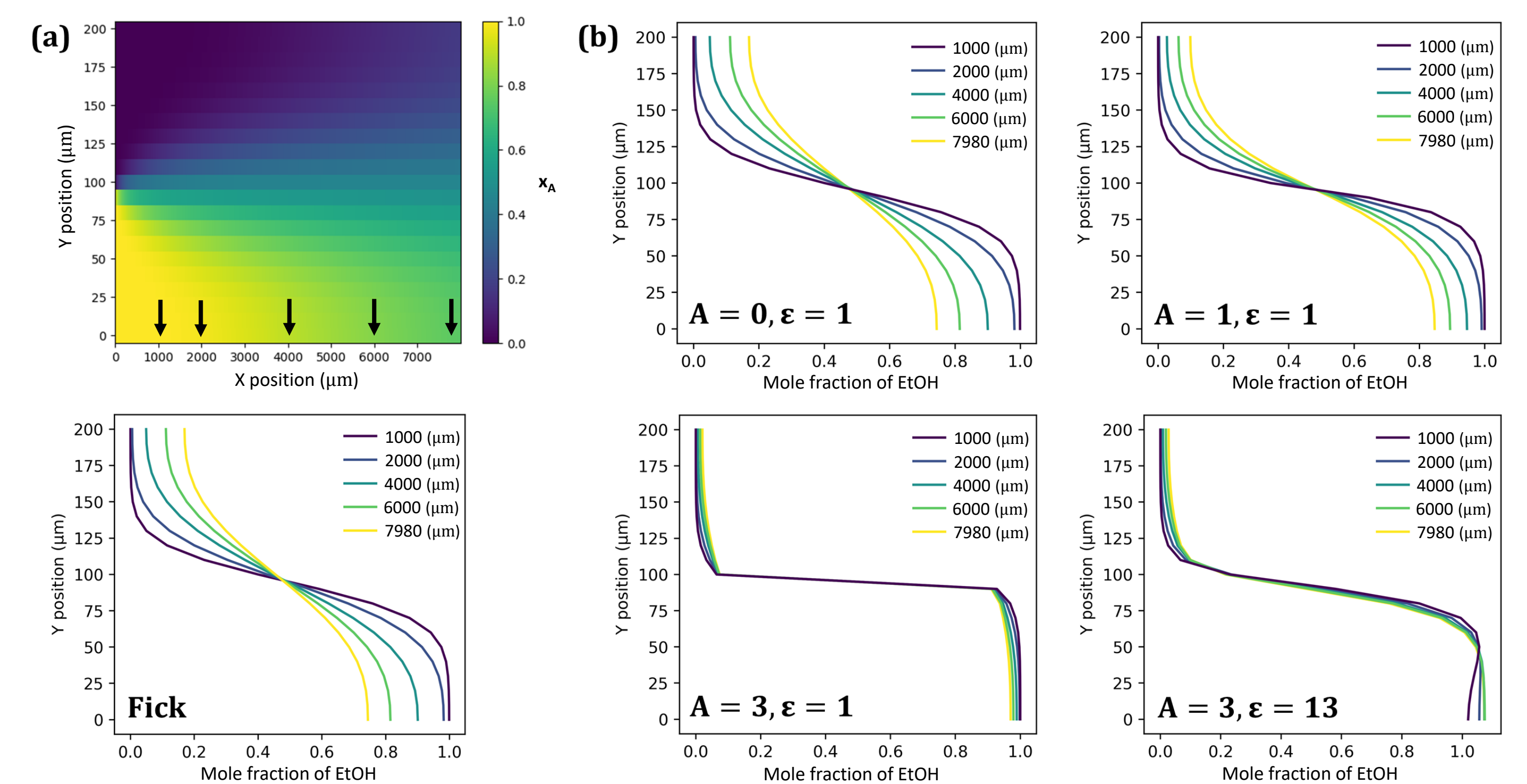


Figure 4. Performance comparison between both models. (a) **Fick's law** – top: example of steady state mixing map, obtained with Fick's law; bottom and (b): composition profiles at the points indicated in the mixing map for Fick and CaHiMaS, respectively.

- From **Figure 1(c)**, when $A < 2$ the final system will be homogeneous, and when $A > 2$ the system will phase split.
- For **higher ϵ** , the interface will be more diffuse.
- A preliminary **optimization** was carried out as shown in Figure 5, fitting Fick's law to an experimental glycine-H₂O map. Its objective was to **find the value of D** that better reproduced this map.
- Theoretical D: **920 $\mu\text{m}^2/\text{s}$** [3]; optimised D: **877 $\mu\text{m}^2/\text{s}$** (error <5%).

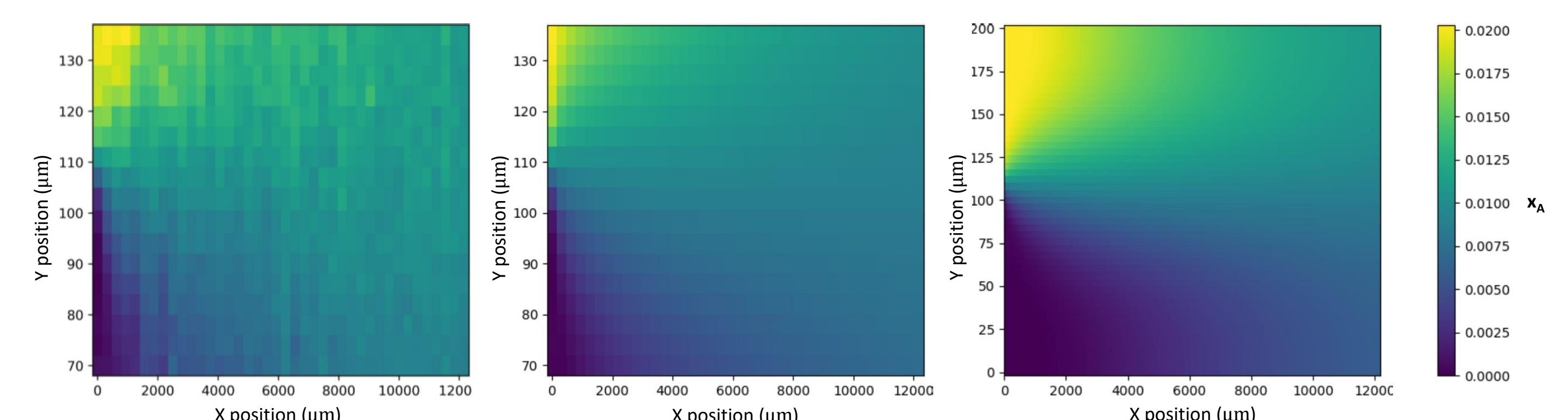


Figure 5. Preliminary optimization results. **Left:** Glycine-H₂O experimental composition map. **Centre, right:** Interpolated and original simulation composition maps, respectively.

3. Conclusions

- CaHiMaS is able to **reproduce nonideal mass transfer better** than Fick's diffusion law.
- The proposed optimization routine can be used to **inform mass transfer models** from experimental results.