Ministero dell'Università e della Ricerca

FIS

POLITECNICO MILANO 1863 | DEPARTMENT OF ENERGY

Water as a tuning parameter for the thermophysical properties of aqueous ionic liquids

Alberto Arici[a], Felix Kexel[b], Nicolò Varallo[a], Michael Schlüter[b], Giorgio Besagni[a,c]

a *Department of Energy, Politecnico di Milano, Milan, Italy*
b *Hamburg University of Technology, Institute of Multiphase Flows, Hamburg, Germany*
c *Institute of Fluid Dynamics, Helmholtz-Zentrum Dresden – Rossendorf, Dresden, Germany*

XXIX Convegno AIPT | 25.09.2026

AURIGA project – The goals

AURIGA - Unveiling the RIddles of GAs-liquid fluid dynamics

Towards novel carbon dioxide absorption systems

General Goals



Formulate a **novel theory** to unveil some of the riddles (e.g., multi-scale connections) of **gas-liquid fluid dynamics** and apply the acquired perspective to develop a novel **ionic-liquid reactor** to absorb **carbon dioxide** from sour gas streams.

Specific Goals



1. Develop a **physical-based approach** to describe a-priori the flow patterns in **bubble columns**, including the relationships between local and global flow properties;
2. Set-up **experimental facilities** (small-scale and large-scale) to study the influence of **ionic liquids** on the local and the global fluid dynamics and to study the mass transfer in ***CO_2-IL* systems**;
3. Scaling-up towards the industrial scale.

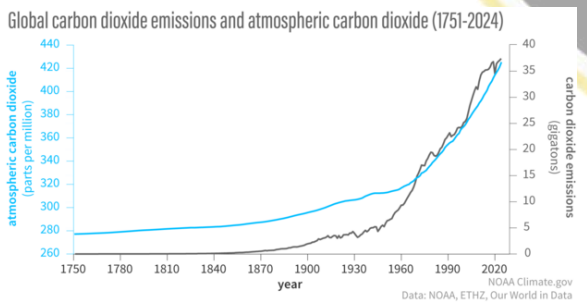
Motivation & Aim

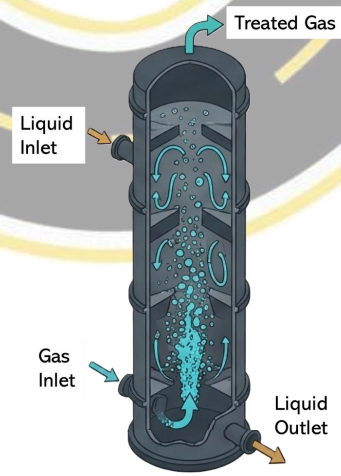
CO_2 emissions are a major climate challenge, requiring scalable capture solutions

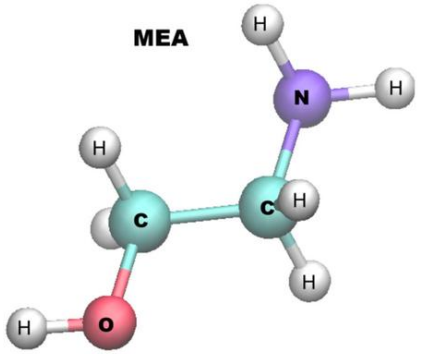
Chemical absorption in **gas-liquid processes** is the most mature technology for CO_2 capture

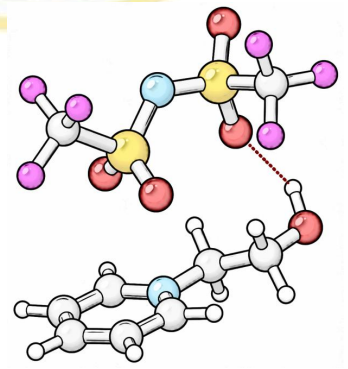
Conventional amine systems are effective but suffer from several **drawbacks**

Ionic liquids have emerged as promising alternative









[1] Nunes (2023), Enviroments
[2] Rochelle (2009), Science
[3] Hospital-benito et al. (2020), Chemical Engineering Journal

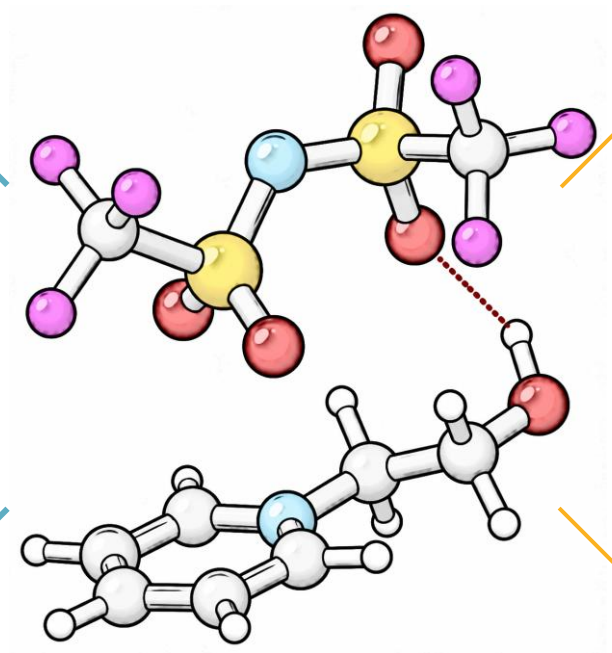
The Ionic Liquid Promise

Infinite Tunability

Over **10^{14} possible cation/anion combinations** allow precision engineering of viscosity, capacity and thermal properties

High stability

High thermal and chemical endurance allows for alternative **high-efficiency regeneration** strategies like flash desorption



Zero vapor pressure

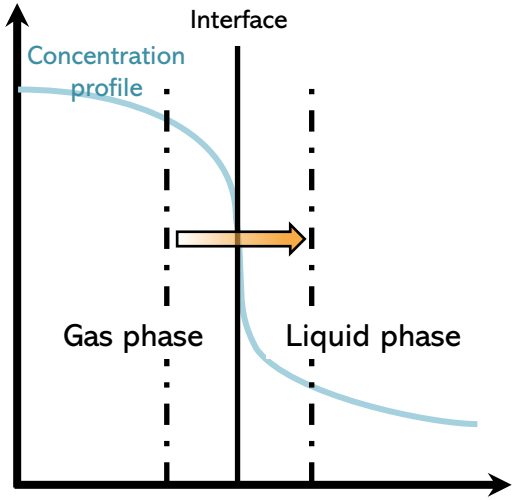
ILs do not evaporate eliminating **solvent losses** and atmospheric emission entirely

Selective affinity

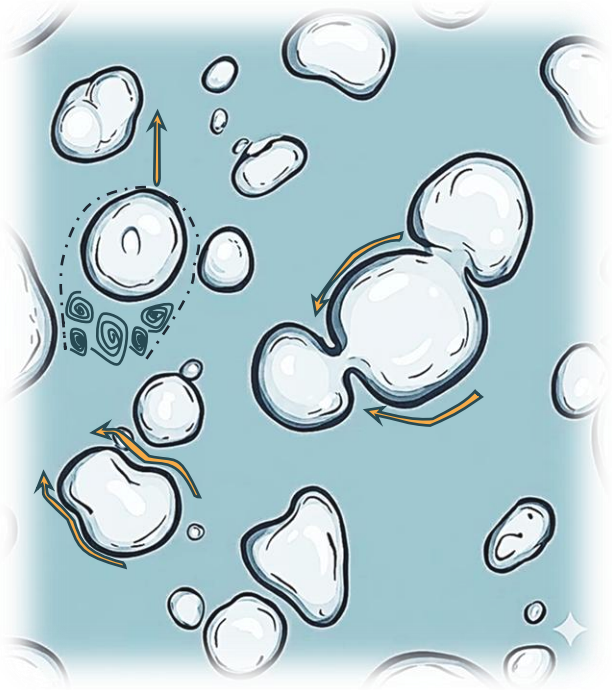
Exceptional physical and chemical **affinity for CO_2** over a lot of other gases

[3] Hospital-benito et al. (2020), Chemical Engineering Journal
[4] Chiappe et al. (2005), Journal or Physical Organic Chemistry
[5] Wasserceid et al (2002)

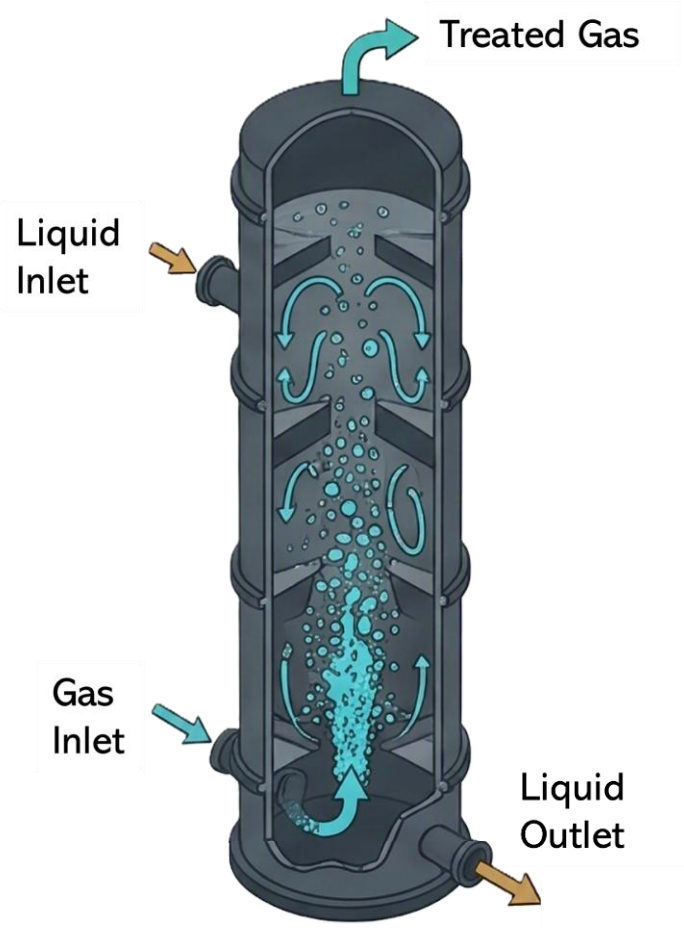
CO_2 Absorption: a multiscale problem



CO_2 solubility, diffusivity and chemical reaction



Liquid-film resistance, bubble size and interface renewal



Gas distribution, flow regime and k_La

Solvent properties affect reactor performance through coupled **molecular**, **interfacial** and **hydrodynamic mechanisms**.

[4] Besagni et al. (2018), ChemEngineering
[5] Zhang et al. (2014), AIChe Journal

Experimental matrix

Systems

[EMIM][OAc] + H_2O - hydrophilic, chemically enhanced uptake

[BMIM][BF_4] + H_2O - benchmark physical absorption

Compositions & temperature

13 compositions per system, ≈1–99 wt%
Three temperatures around ambient conditions

Properties & techniques

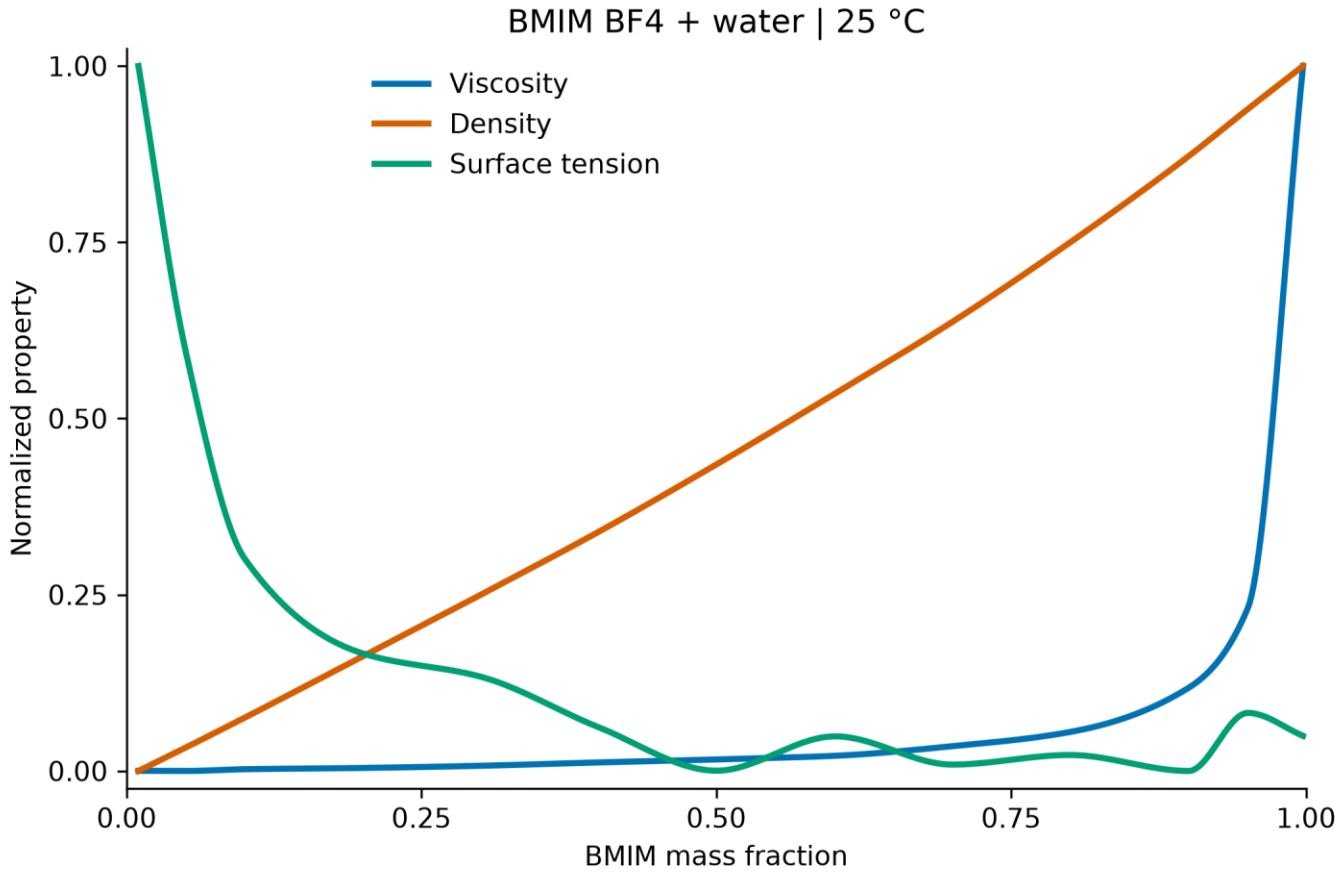
η — rotational rheometry
ρ — vibrating-tube density meter
σ — maximum bubble-pressure method

- The mixtures cover almost the entire composition range, not only the dilute limit.
- Each property was cross-checked against available literature data before correlating.
- Composition-dependent correlations: excess-property approaches for ρ and η, Szyszkowski–Langmuir for σ.

Two complementary ionic liquids, one common measurement protocol.

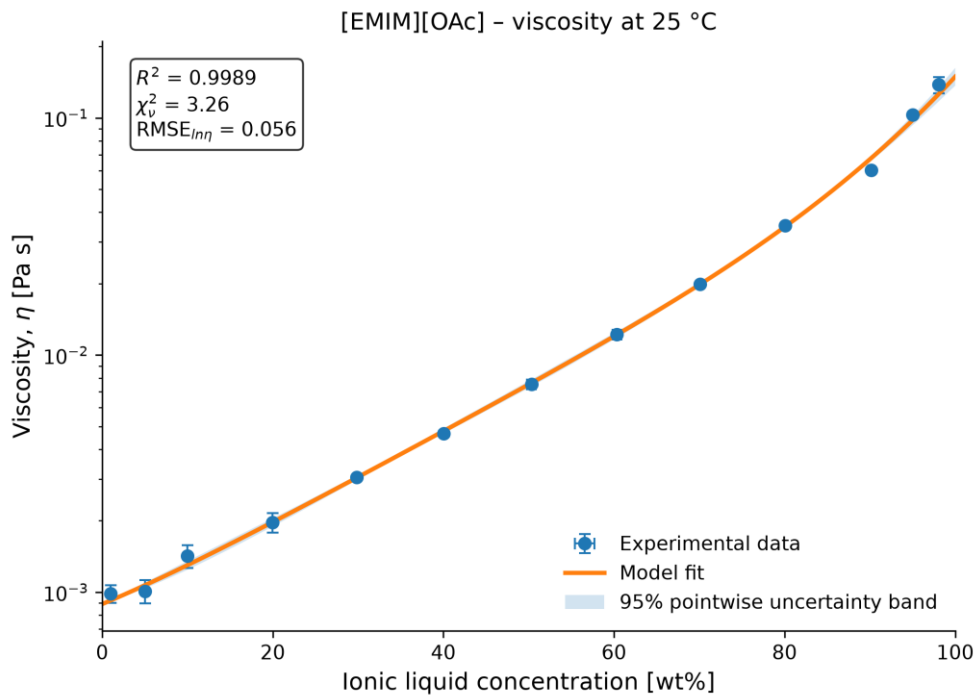
Same mixtures, three different clocks

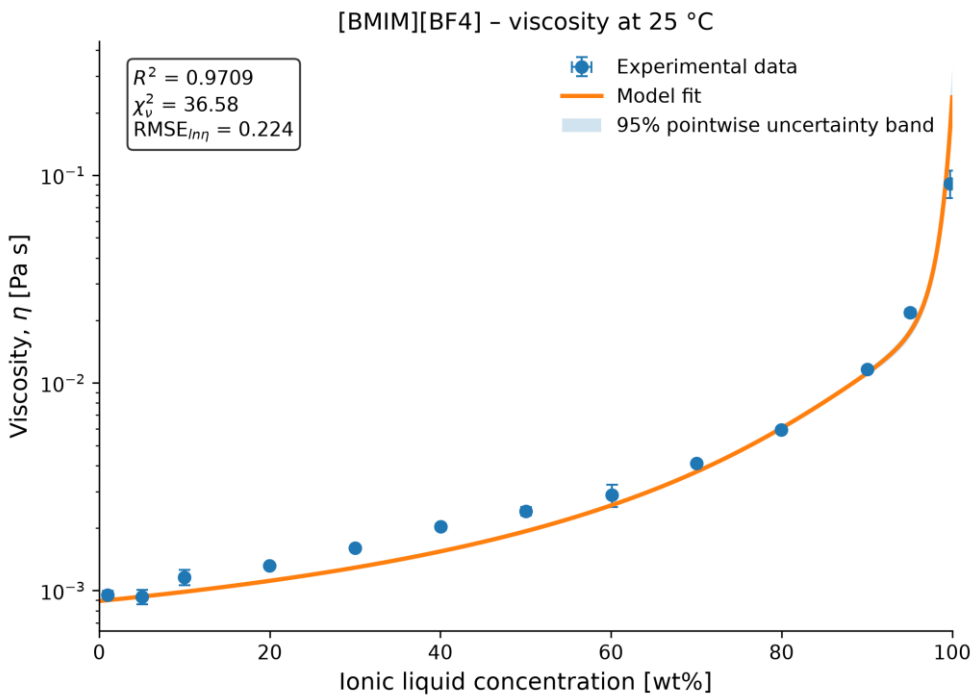
- σ moves first, in the dilute region; ρ moves roughly in step with mass mixing; ln η only moves at the IL-rich end.
- A measurement campaign stopped at 50 wt% would report σ and ρ correctly but miss essentially all of the viscosity transition.
- This is the reason to measure across almost the full range rather than a few "representative" points



the interesting physics for each property lives in a different window.

Viscosity: where the mobility is won

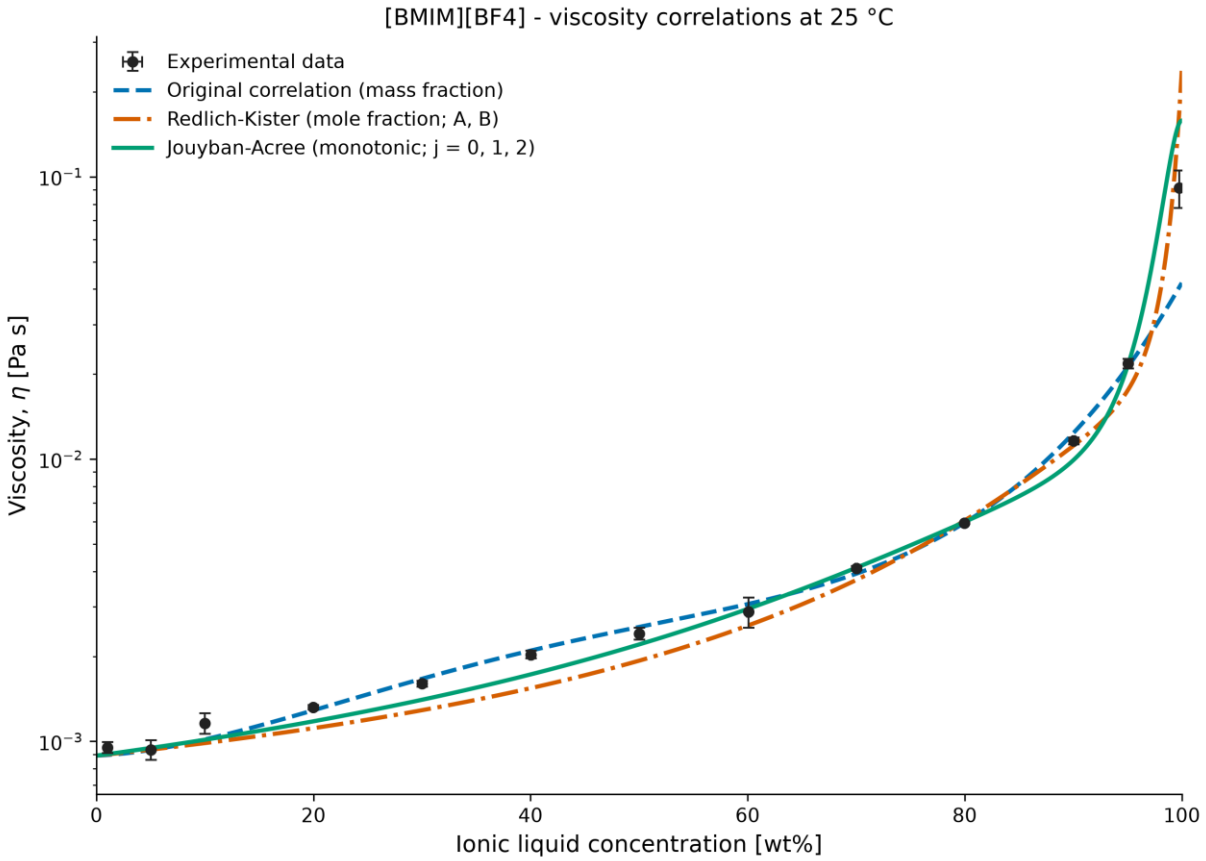




[BMIM][BF_4]: between 99.75 and 50 wt% (factor ≈ 38 decrease);
[EMIM][OAc]: 140 → 7 mPa·s (factor ≈ 20).
ln η is nearly exponential in wt% for [EMIM][OAc], strongly convex for [BMIM][BF_4].
At equal mass fraction [EMIM][OAc] stays ≈ 3× more viscous over the whole mid-range.

The first tens of wt% of water buy most of the mobility but the two ILs do not pay the same price.

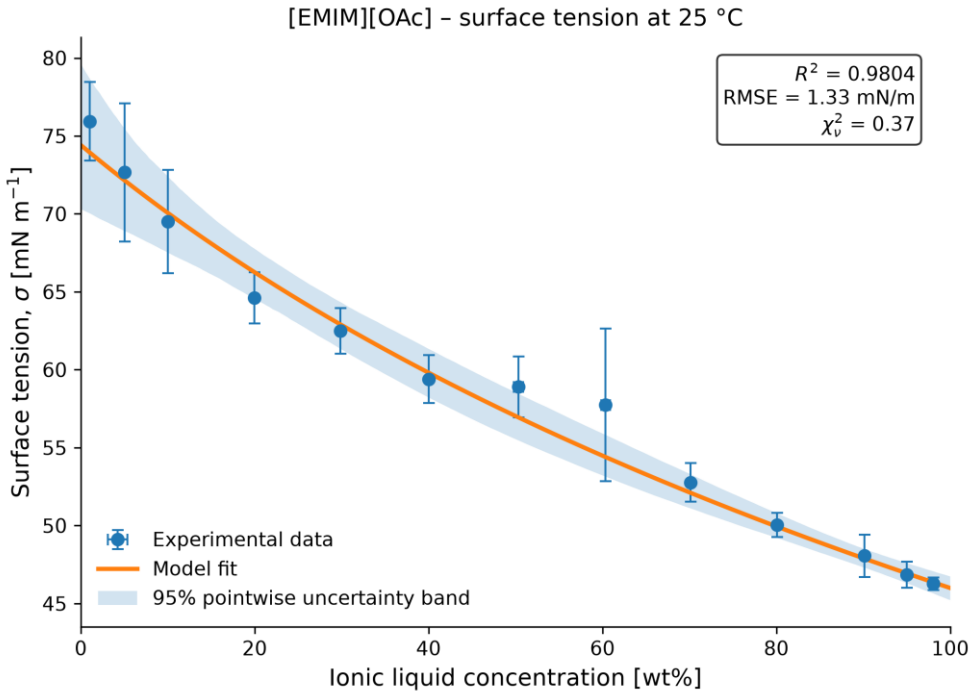
Why composition representation matters

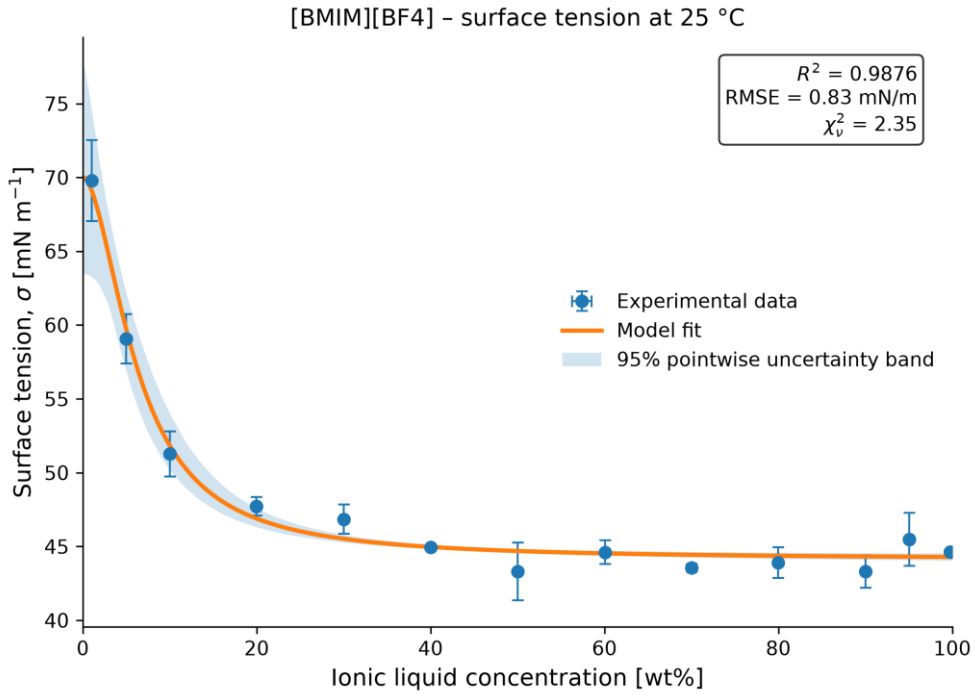


- 50 wt% IL = 7.4 mol% [BMIM][BF_4] (9.6 mol% [EMIM][OAc]): "half ionic liquid by mass" is a dilute solution by mole.
- The last sample, 99.75 wt%, still contains 3 mol% water.
- Same data, three models — extrapolated pure-IL viscosity: 0.041 / 0.166 / 0.154 Pa·s against 0.091 Pa·s measured.
- Jouyban–Acree wins on RMSE(ln η) — 0.172 vs 0.232 — but loses on the weighted χ^2_ν — 16.3 vs 6.0: the log-space winner violates the error bars exactly where they are tightest.

The correlation you choose moves the extrapolated pure-IL viscosity by a factor ≈ 4

Surface tension: two interfacial regimes

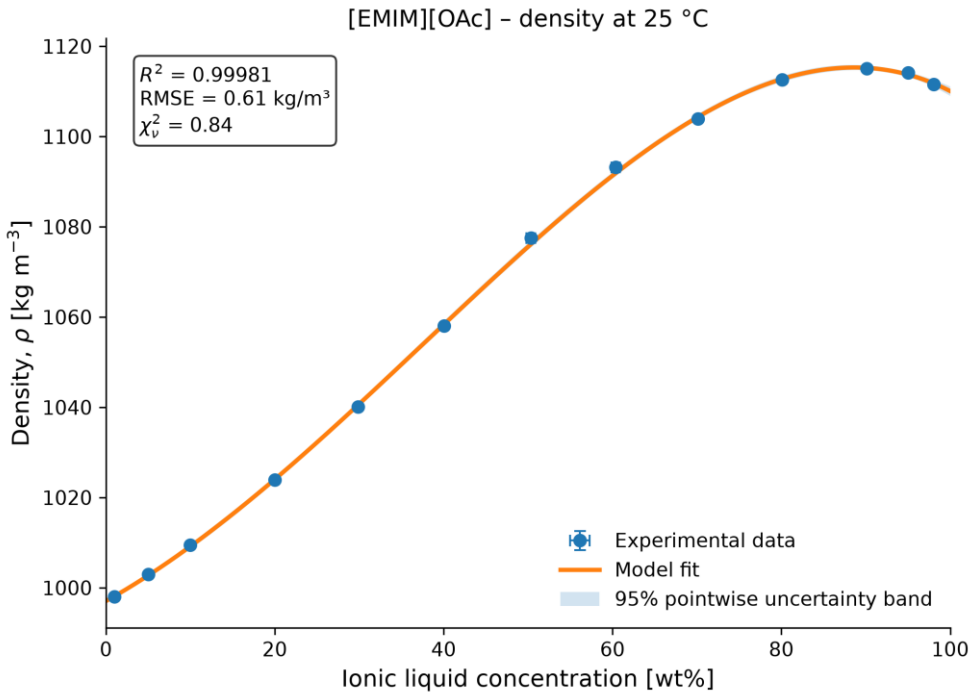


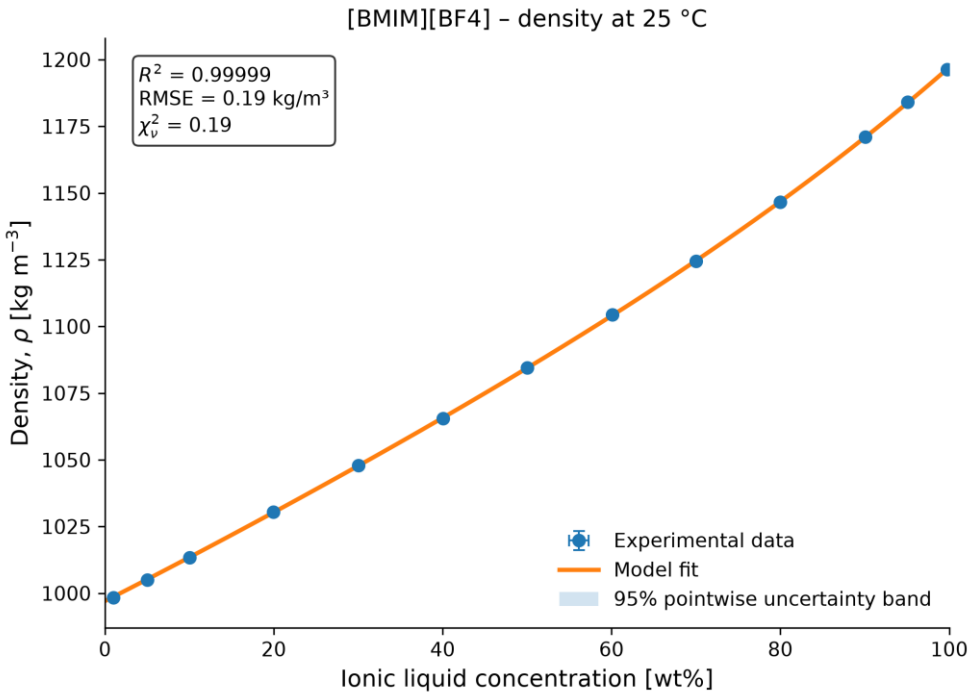


- [EMIM][OAc]: 76 → 46 mN·m^{-1} spread over the whole range, no plateau → near-ideal interfacial mixing.
- [BMIM][BF$_4$]: 70 → 47 mN·m^{-1} within 20 wt%, then a plateau at ≈ 44 mN·m^{-1} → Langmuir-type saturation.
- **At 10 wt% [BMIM][BF$_4$]: 73% of the total σ reduction, for only +30% viscosity over pure water.**

Bulk and interface do not respond to water on the same scale for [BMIM][BF$_4$]

Density and excess molar volume





- Density is resolved to RMSE ≤ 0.6 kg·m^{-3}: precise enough to extract the excess molar volume V^E.
- [EMIM][OAc] shows a density maximum near 88 wt%: the mixture is denser than either pure component.
- Preliminary: $V^E \approx -1.2$ cm³·mol^{-1} for [EMIM][OAc] at an IL mole fraction ≈ 0.5, against ≈ 0 for [BMIM][BF$_4$].

V^E values preliminary — to be recomputed from the raw density data and the pure-component values.

Density is the property reporting most directly on ion–water association.

One composition axis, three different scales

Property (w_{50})	[BMIM][BF_4]	[EMIM][OAc]
σ - interface	≈ 5 wt%	≈ 33 wt%
ρ - bulk packing	≈ 56 wt%	≈ 39 wt%
ln η - molecular mobility	≈ 88 wt%	≈ 59 wt%

w_{50} = composition at which half of the total change between water and pure IL is reached.

Indicative values — to be recomputed directly from the fitted correlations.

Reading the table

[BMIM][BF_4] decouples its properties over almost the entire axis: 5 → 88 wt%.

[EMIM][OAc] moves as a block: 33 → 59 wt%.

Order is the same, interface first, packing next, mobility last, but the spread is not.

Water is a property-tuning variable; the characteristic composition range depends on both the property and the ionic liquid.

What this means for CO_2 mass transfer

Measured here

η, ρ, σ of aqueous IL mixtures

Correlations over the full composition range

Two distinct thermophysical fingerprints

Next step - Taylor bubbles

k_L from CO_2 bubble shrinkage

Three capillary diameters

Same mixtures, controlled interface

Target - bubble column

Gas holdup and interfacial area

Flow regime transition

k_La at reactor scale

Open question: does a mixture with water-like viscosity and IL-like interfacial behaviour actually transfer better?

Take-home messages

1 — Water is a lever

Small water additions change IL transport properties by orders of magnitude, without the drawbacks of an organic co-solvent.

2 — Properties decouple

Interface, packing and mobility respond over different composition ranges, so they can be tuned separately.

3 — The two ILs differ

[BMIM][BF_4] is surface-active and strongly decoupled; [EMIM][OAc] responds as a block, with clear ion–water association.

Next: connect these thermophysical fingerprints to measured CO_2 mass-transfer performance.

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Thank you for the attention!

Acknowledgment

This work has been financed by the Italian Ministry of University and Research (Ministero dell'Università e della Ricerca) within the FIS2 call. In particular, This work has been conducted within the AURIGA ("Unveiling the RIddles of GAs liquid fluid dynamics: towards novel carbon dioxide absorption systems") project. Project number FIS-2023-00204, CUP D53C25000730001, funded within the FIS2 call (Decreto Direttoriale n. 1236 del 1-08-2023).

Contatti

alberto.arici@polimi.it

LinkedIn