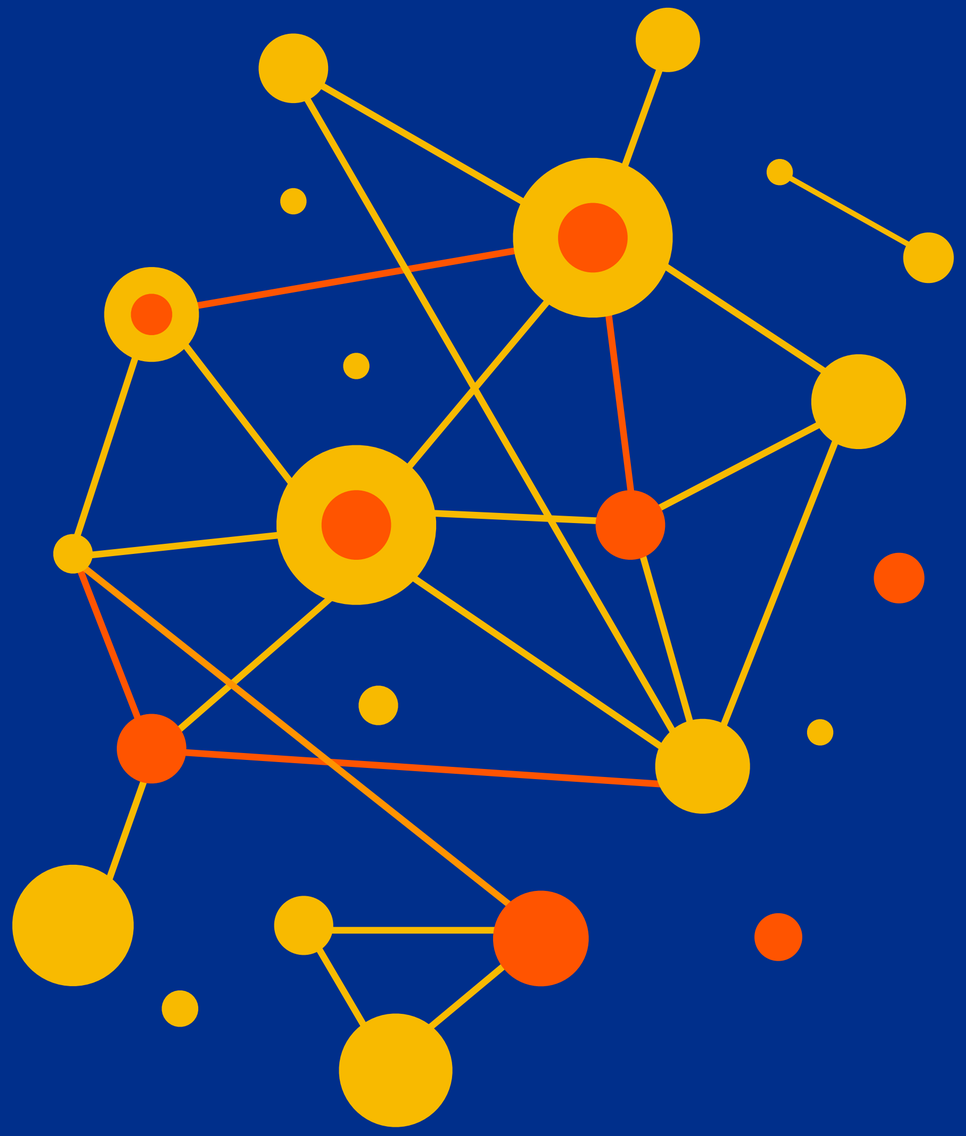


Electrostatic responses of dense electrolytes at electrified interfaces

STSP2026 | 11–15 October 2026, Guilin, China

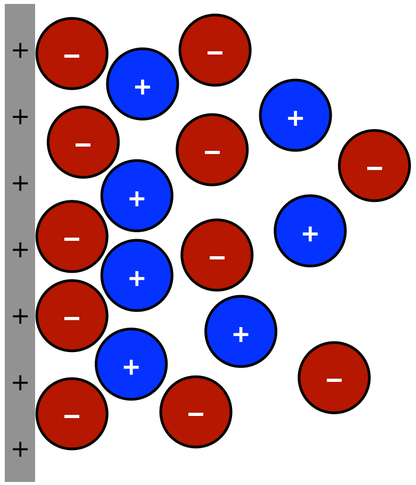
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SURANAREE UNIVERSITY OF TECHNOLOGY

Outline

- Introduction: electrified interfaces
- Electrical double layer (EDL) models
- Differential capacitance
- Dense ionic fluids
- Differential capacitance of ionic liquid systems
- Responses due to ion-size heterogeneity
- Deep eutectic solvents

What happens at electrified surfaces…



- When the surface is charged, ions in $\mathbf{E}$ field adjust themselves to screen the interface.
- Ion redistribution, in turn, affect $\mathbf{E}$ field. . . .until equilibrium is reached.
- This ion distribution next to charged surface is called "**electrical double layer (EDL)**."
- From Poisson's equation:

$$\nabla^2 V = -\frac{\rho(r)}{\epsilon}$$

  The electric potential (V) and ion distribution (ρ) must be determined "self-consistently."

- The "surface charge density" for planar electrode can be calculated from

$$\sigma_s = -\int_0^\infty \rho(x)\mathrm{d}x \qquad \text{with } V = 0 \text{ in bulk}$$

- We can define a measurable quantity that represents the response of surface charge to changes in electric potential → the "**differential capacitance**"

$$C_d(V) = \frac{\partial \sigma_s}{\partial V}$$

- A **"bridge"** between "theory" and "experiment."

Poisson-Boltzmann theory

- For ions under electrostatic potential field V at finite temperature $T \rightarrow$ Boltzmann distribution

$$\rho = \sum_i n_i^{\infty} z_i e \exp(-z_i eV/kT)$$

- This results in a non-linear **Poisson-Boltzmann** equation:

$$\nabla^2 V = -\frac{1}{\epsilon} \sum_i n_i^{\infty} z_i e \exp(-z_i eV/kT)$$

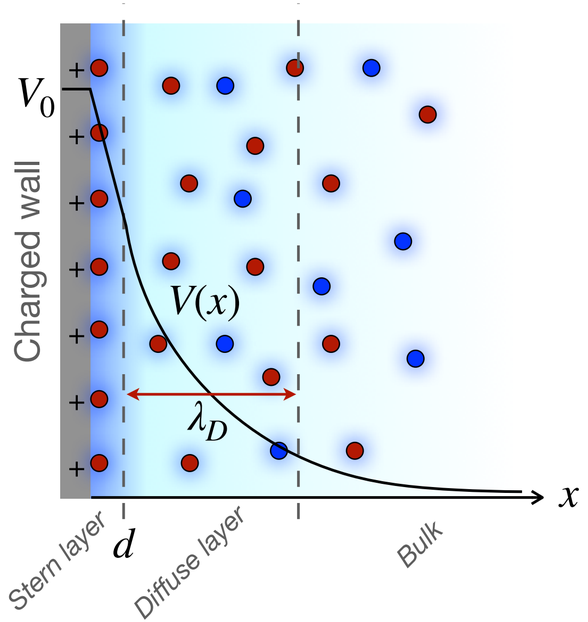
- For z:z electrolyte, the surface charge density is given by the Grahame equation

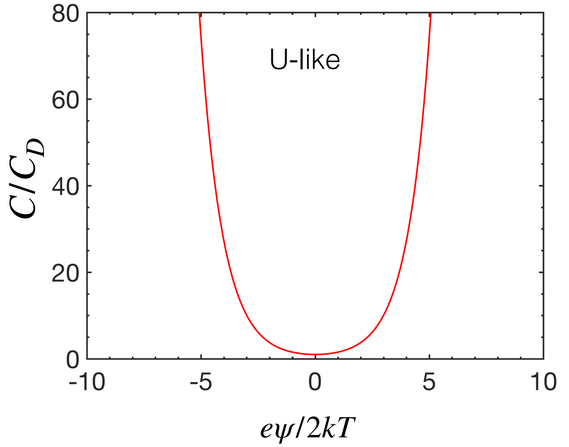
$$\sigma_s = \frac{2\epsilon kT}{ze\lambda_D} \sinh\left(\frac{zeV}{2kT}\right)$$

where $\lambda_D = \sqrt{\dfrac{\epsilon kT}{2z^2 e^2 n_0}}$ is the **Debye screening length**.

$\lambda_D \propto \dfrac{1}{\sqrt{c_0}}$ where c_0 is bulk molar concentration

- The differential capacitance $C = \dfrac{\partial \sigma_s}{\partial V} = C_D \cosh(zeV/2kT)$



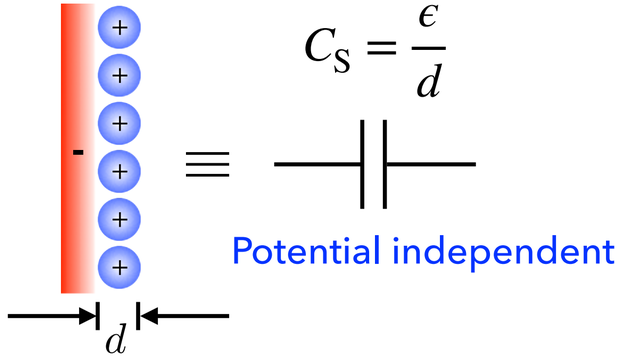


Electrical double layer (EDL) models

Helmholtz's model (1853):

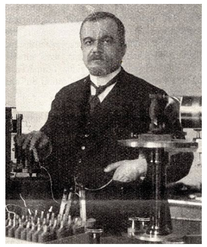


"The surface charge is neutralised by a molecular layer of counter-ions."

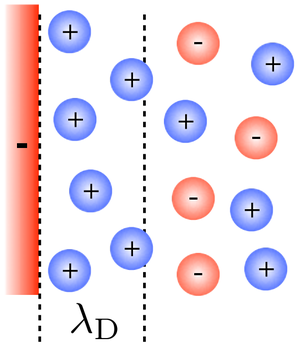


Gouy-Chapman's model (1910-1913):

"The ions exhibit thermal motion at $T > 0$ K."







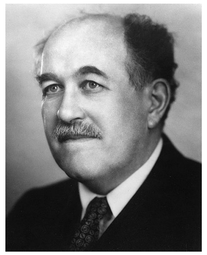
"Debye length"

$$C_{GC} = C_D \cosh(eV/2kT)$$

$$\lambda_D \propto c_0^{-1/2}$$

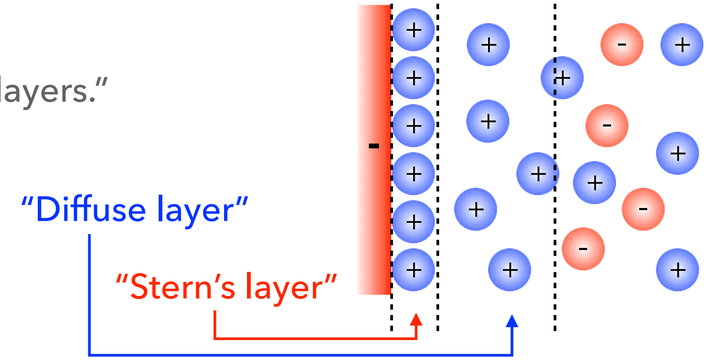
"Diffuse layer picture"

Stern's model (1924):



"A combination of compact and diffuse layers."

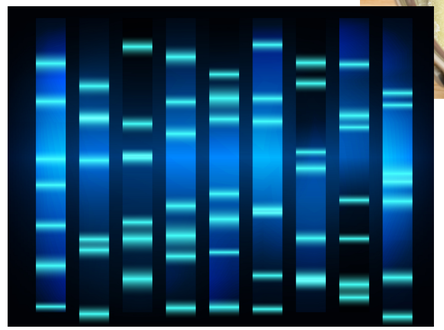
$$\frac{1}{C} = \frac{1}{C_S} + \frac{1}{C_{GC}}$$



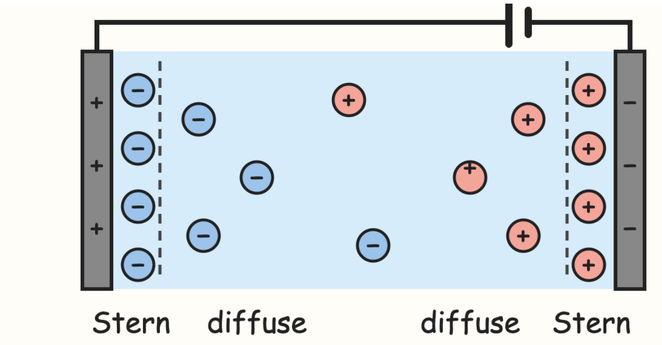
Colloid stability



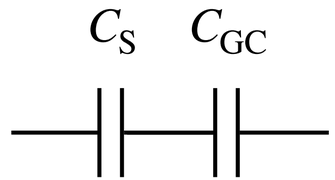
Electrokinetics



Electrochemical cell



Equivalent circuit



The breakdown of classical theory

- The classical Poisson-Boltzmann theory is based on key assumptions:

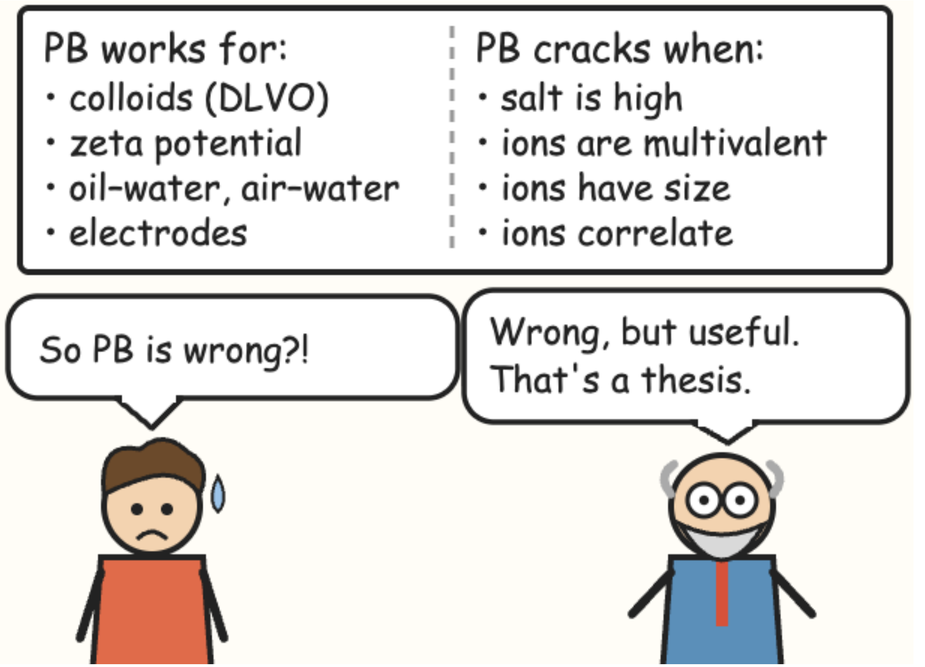
  - **Mean-field** → ions interact with the average field, correlation ignored

  - **Point ions** → no size effects

  - **Continuum solvent** → uniform dielectric value

  - **Purely electrostatics** → no special interactions

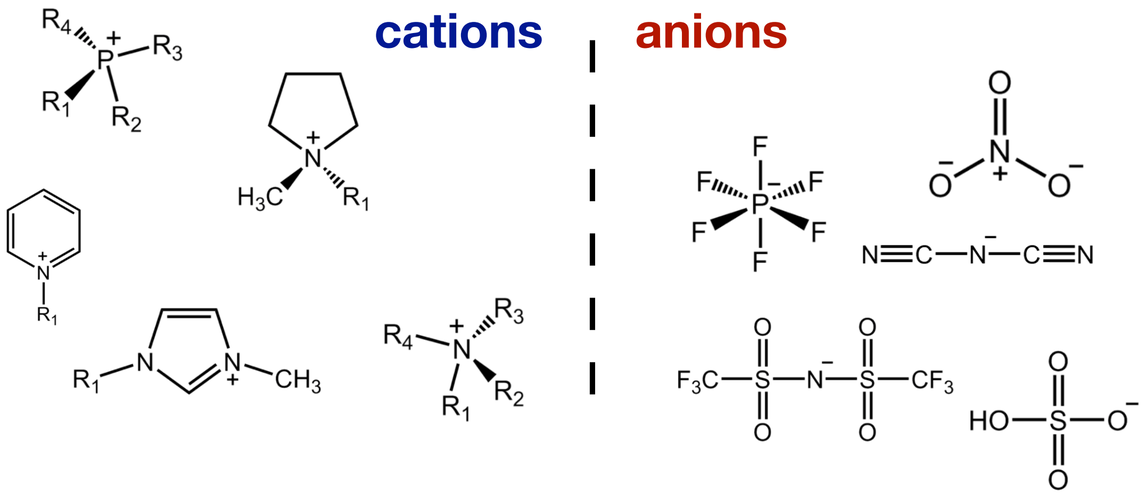
- These limit the validity to dilute electrolytes (< 0.1 M of monovalent at low surface potential)



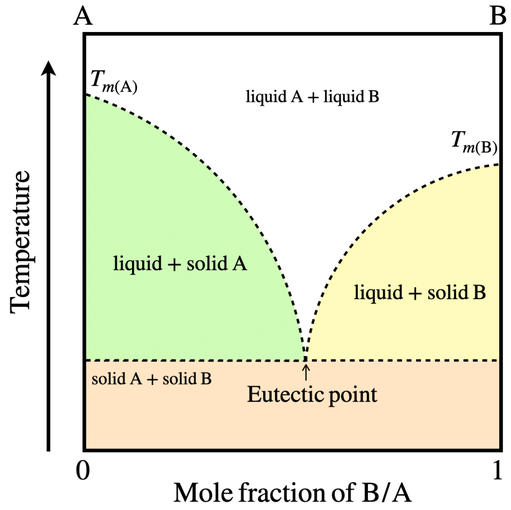
Dense ionic fluids

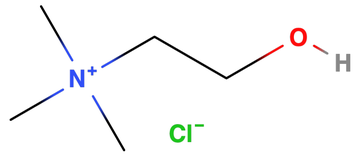
- Charged molecules (ions) interacting through Coulomb forces & other intermolecular interactions (e.g. H-bonds, van der Waals forces, etc.)
- Bulky ions with (usually) asymmetric molecular geometry
- Strongly correlated ions
- Non-aqueous electrolytes that form liquid phase at "room temperature" → mostly dense liquid salts/ concentrated electrolyte
- Exhibit unconventional behaviour, not captured by classical theory

Ionic liquids (ILs)

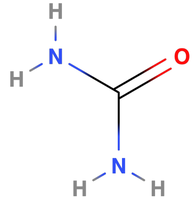


Deep eutectic solvents (DESs)





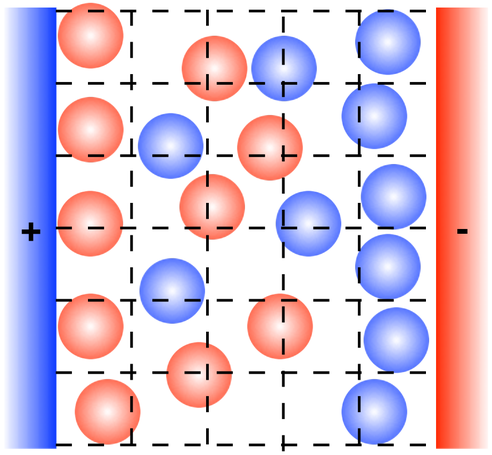
Choline chloride (ChCl)



Urea

Ionic liquids: Lattice-gas model

- Lattice-gas model (Goodwin-Kornyshev): free energy → minimised w.r.t. no. ions →distribution → PB equation → C_d



System's free energy

$$F = \boxed{eV(N_+ - N_-)} + \boxed{A_+N_+^2 + A_-N_-^2 + BN_+N_-} - \boxed{kT \ln \frac{N!}{(N - N_+ - N_-)!N_+!N_-!}}$$

Electrostatic **Ion-ion correlation** **Entropic**

At equilibrium

$$C = \tilde{C}_0 \frac{\cosh(\alpha u/2)}{1 + 2\gamma \sinh^2(\alpha u/2)} \sqrt{\frac{2\gamma \sinh^2(\alpha u/2)}{\ln[1 + 2\gamma \sinh^2(\alpha u/2)]}}$$

$$u = eV/kT$$

$$\tilde{C}_0 = \sqrt{\alpha}\frac{\epsilon}{\lambda_D}$$

"Packing parameter" (ion size & geometry)

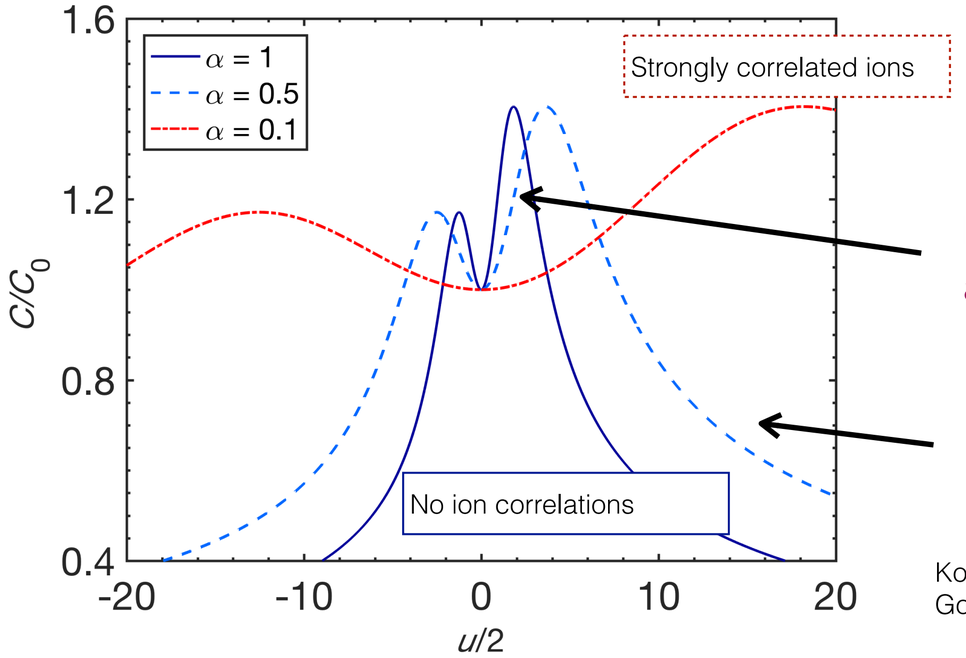
$$\gamma_\pm = N_\pm/N$$

$$\gamma(u) = \gamma_- + \frac{\gamma_+ - \gamma_-}{1 + \exp(\alpha u)}$$

$\gamma = 0, \alpha = 1$ U-shape (GC model)

$0 < \gamma \leq 1/3$ camel-shape

$1/3 < \gamma \leq 1$ bell-shape



Phenomenological correlation factor

$$0 < \alpha \leqslant 1$$

Different height → cation-anion asymmetry

Monotonically decreasing at high potential → "Crowding effect"

Kornyshev **2007**

Goodwin, Z. A. *et al. Electrochim. Acta.*, **2017**

Ionic liquids: Measurement

- Direct measurement of surface charge using electrochemical technique → **Multi-step chronoamperometry**

  - charge density/step: $q_i = \int j(t)dt \rightarrow \sigma(V) = \sum_i q_i$ where $j(t) = a_1 \exp(-t/\tau_1) + a_2 \exp(-t/\tau_2) + b$

  - differential capacitance: $C_d = \partial\sigma/\partial V$

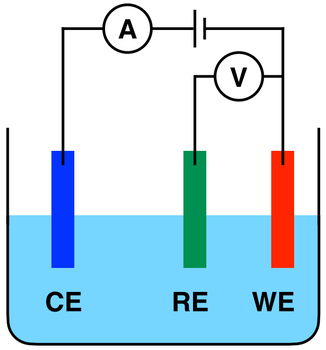
- Four different ionic liquids, Pt WE

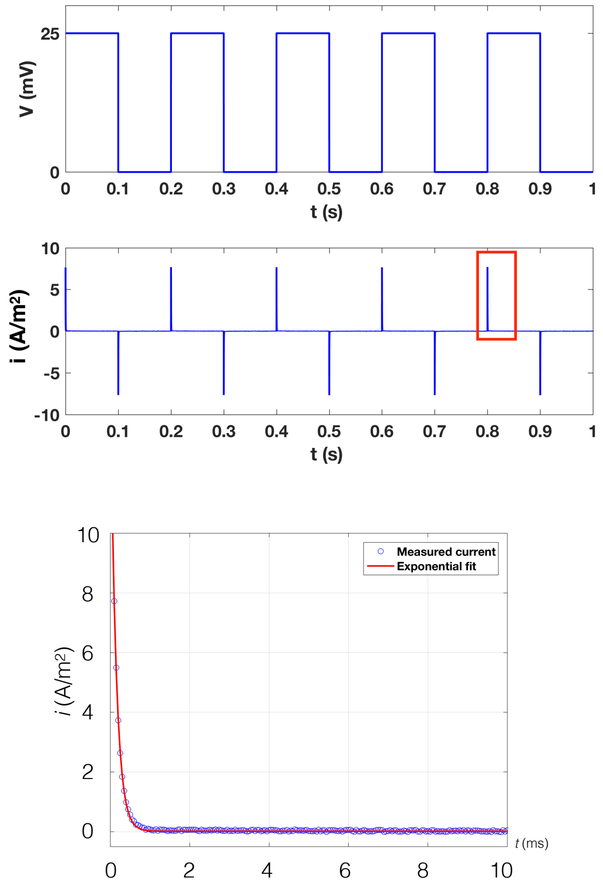
  [C4mpyr][NTf_2]

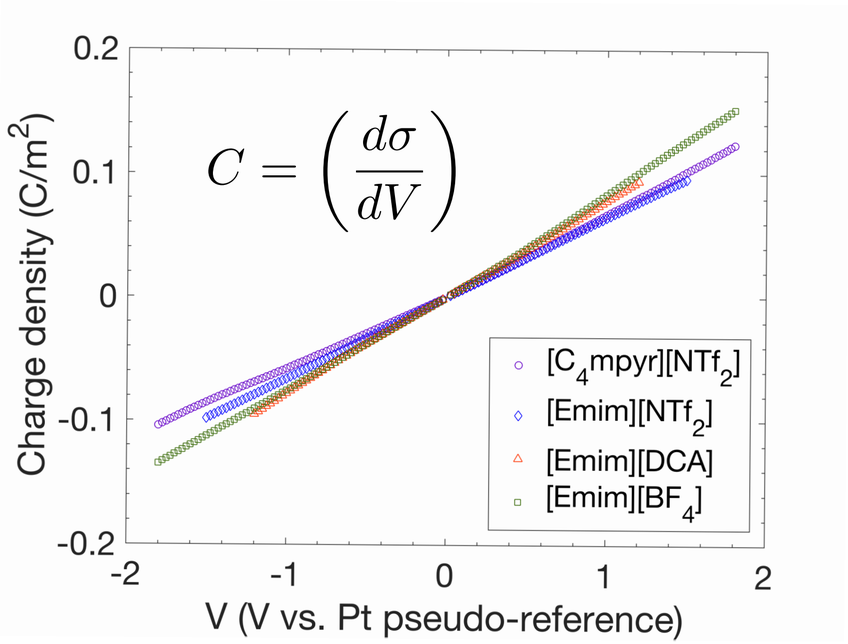
  [Emim][NTf_2]

  [Emim][DCA]

  [Emim][BF_4]

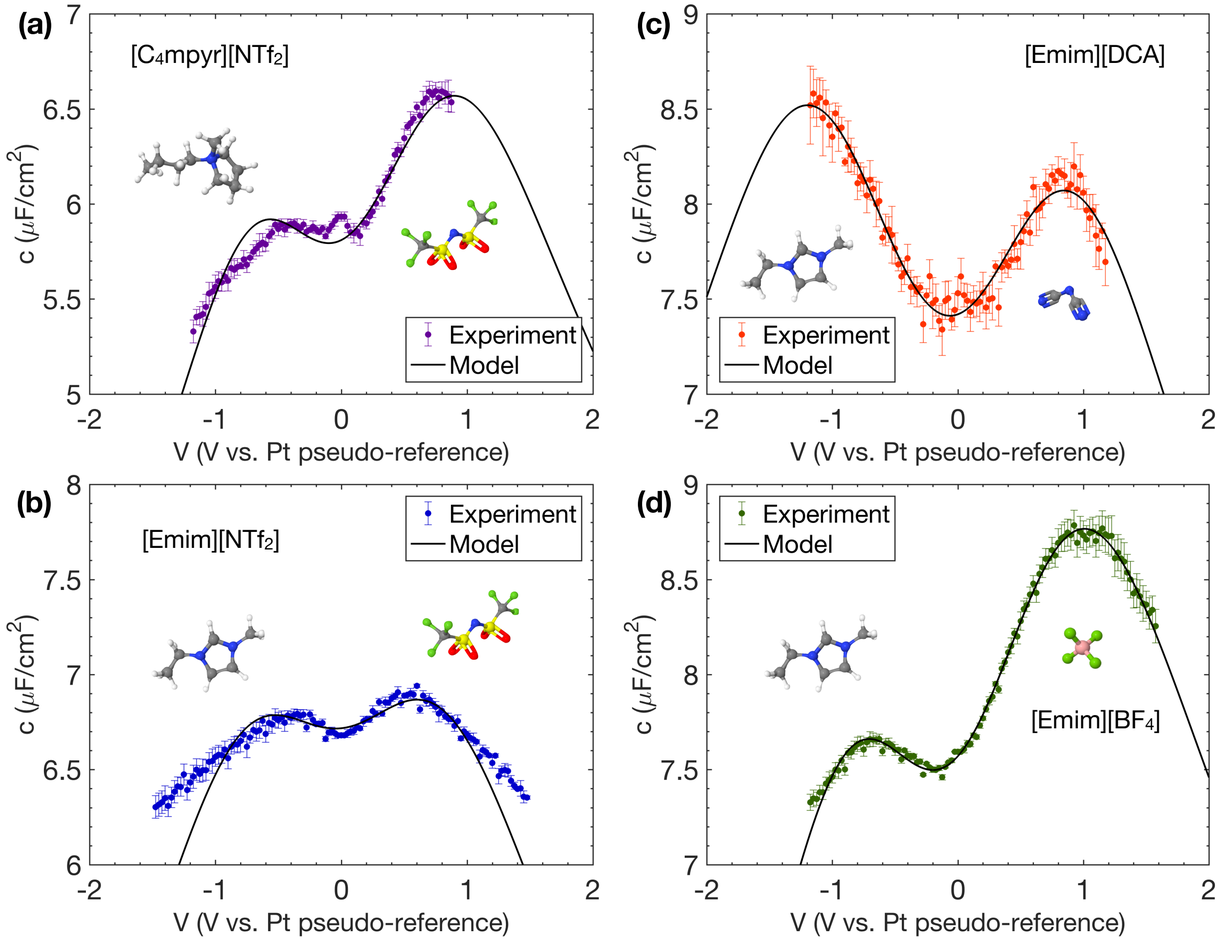






Ionic liquids: Differential capacitance

- Reproducible *C*(*V*) compared with the Goodwin–Kornyshev model

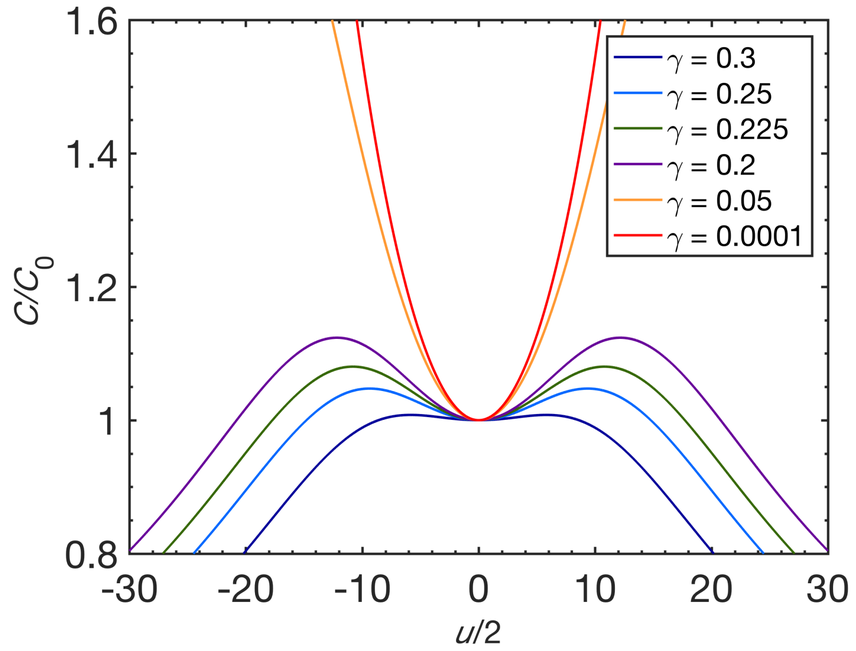


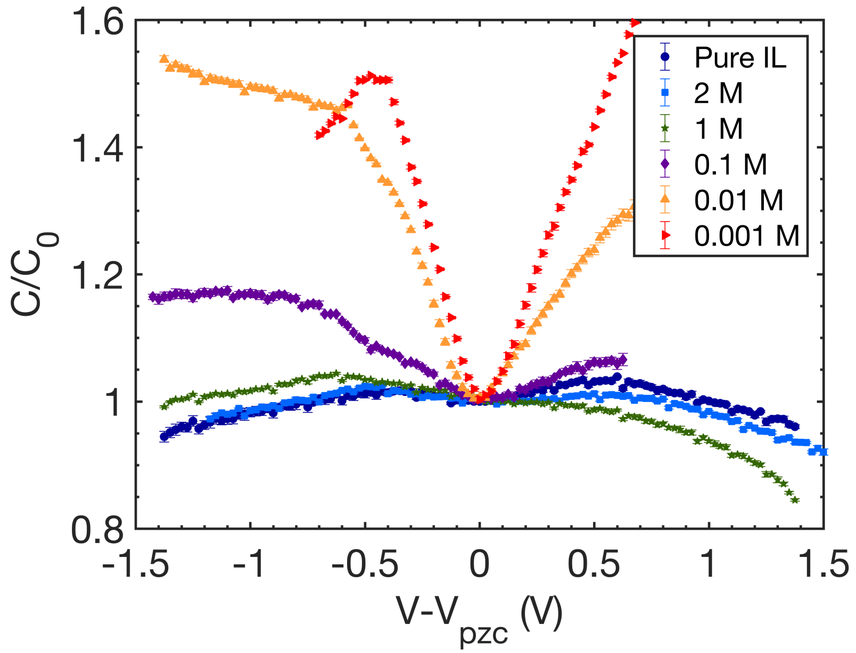
M. Jitvisate & J. R. T. Seddon, *J. Phys. Chem. Lett.*, **2018**

Ionic liquids: Dilute ILs

- By adding molecular solvent (DMSO) → the ion concentration can be varied → "packing parameter (γ)"
- Transition from high to low packing parameter can be demonstrated.
- Electrostatic response of ILs at interface is intuitively understood (support a crowding-controlled picture).

$$C = \tilde{C}_0 \frac{\cosh(\alpha u/2)}{1 + 2\gamma \sinh^2(\alpha u/2)} \sqrt{\frac{2\gamma \sinh^2(\alpha u/2)}{\ln[1 + 2\gamma \sinh^2(\alpha u/2)]}}$$





M. Jitvisate & J. R. T. Seddon, *J. Phys. Chem. Lett.*, **2018**

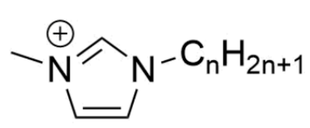
Ionic liquids: Chain length effect

- How does the ion chain length affect the EDL structure?
- Would it be explainable within the scope of the existing mean-field model?

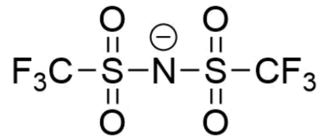
  → C_d increases at high $|V|$, deviating from model prediction.

  → Increase of charging time constant, τ.

  → Suggests slow ion reorganisation.

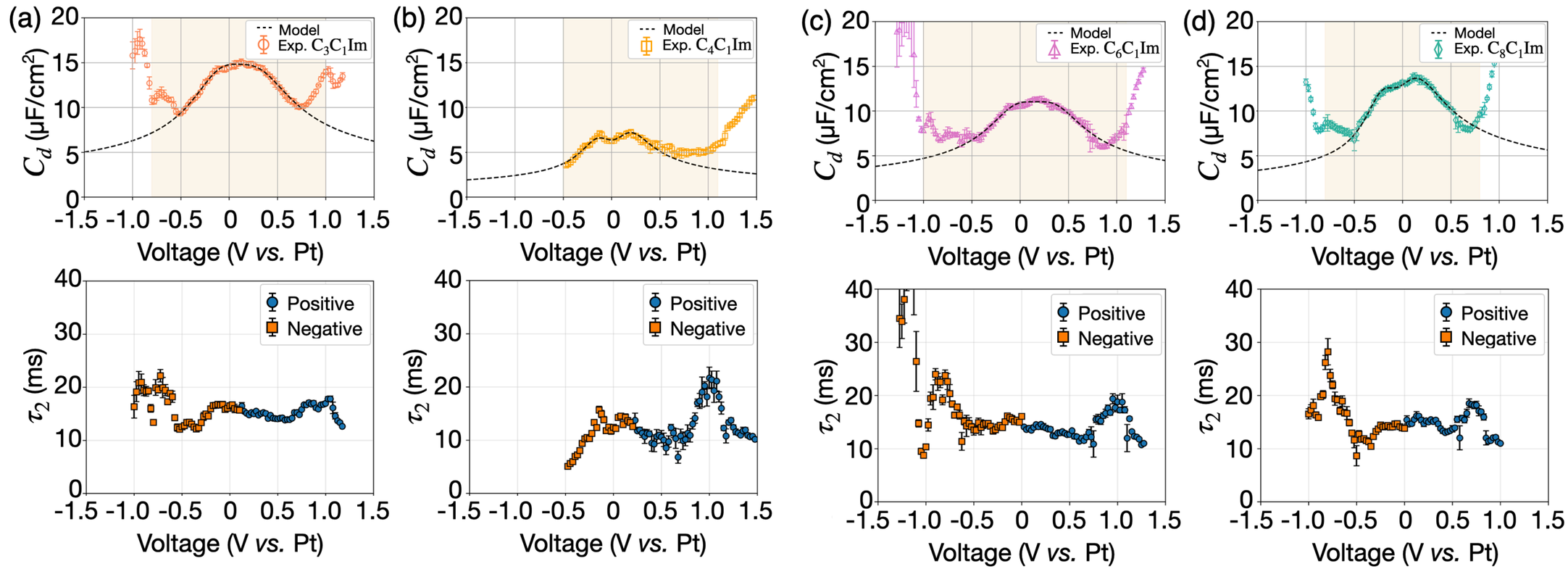


$[C_nC_1Im]^+$



$[NTf_2]^-$

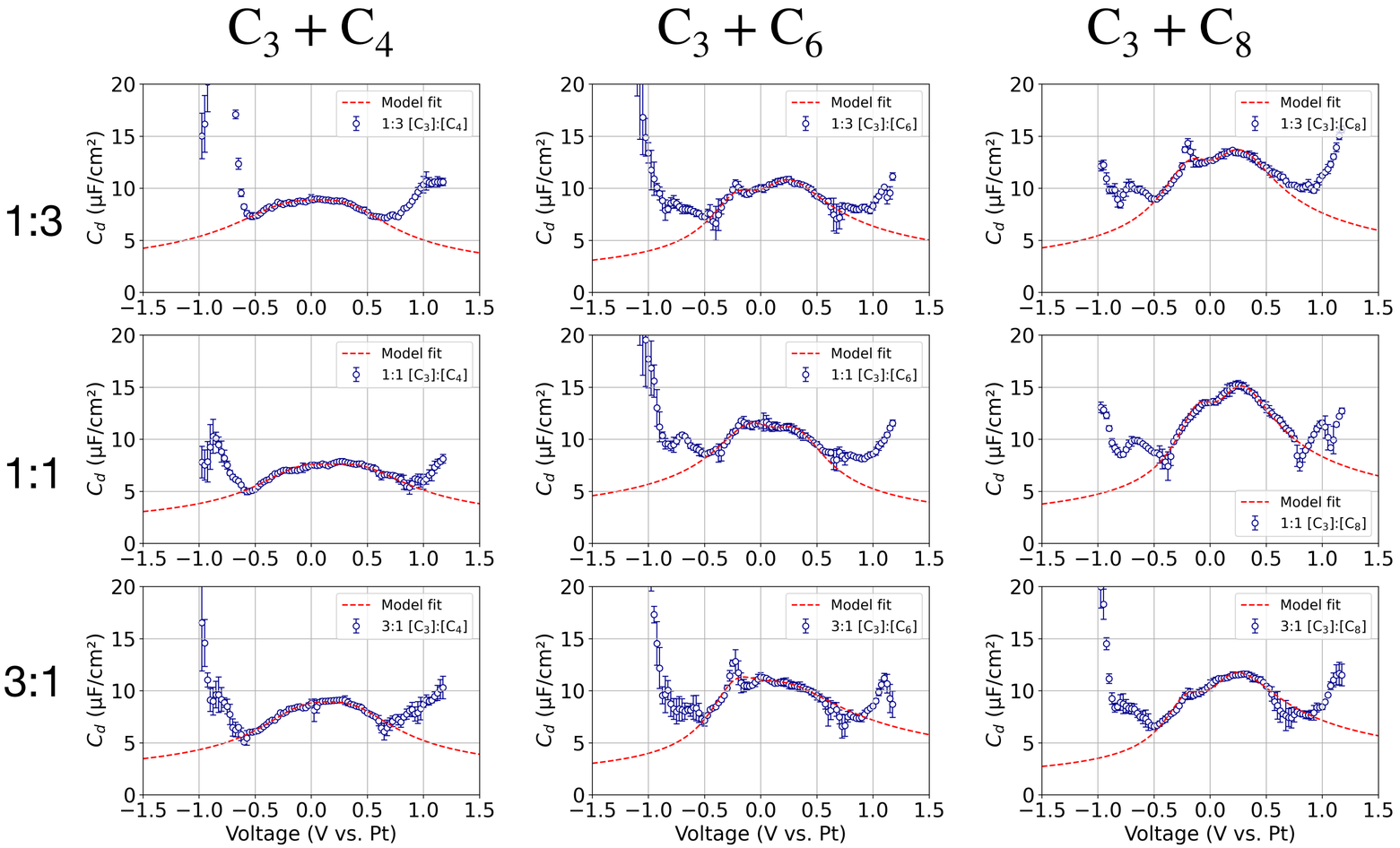
For $n = 3, 4, 6, 8$



M. Jitvisate et al., *J. Phys. Chem. Lett.*, **2026**.

Ionic liquids: Ion-size mismatch

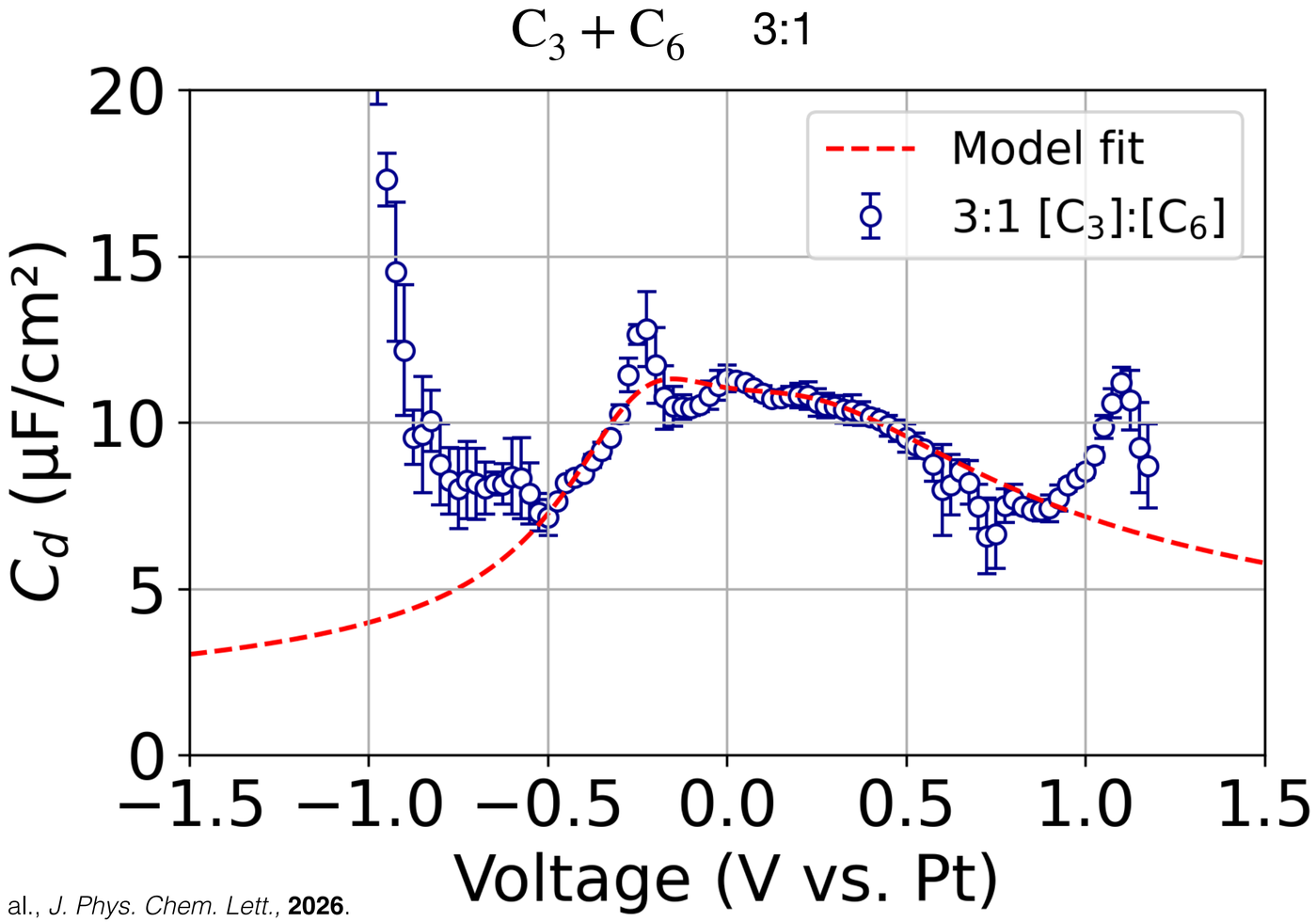
- How would mixing ILs affect the EDL structure?
- Binary mixtures of $C_3 + C_4$, $C_3 + C_6$, and $C_3 + C_8$ (degree of size mismatch)
- Each with molar ratios 1:3, 1:1, and 3:1 (ion population)



- Camel-shape profile of C_4 is suppressed in similar cation size mixture ($C_3 + C_4$).
- Sharp peak appears at negative surface polarisation in mixtures with higher degree of size and ratio mismatches.
- This anomalous feature is not predicted by the mean-field model.

M. Jitvisate et al., *J. Phys. Chem. Lett.*, **2026**.

Ionic liquids: Ion-size mismatch



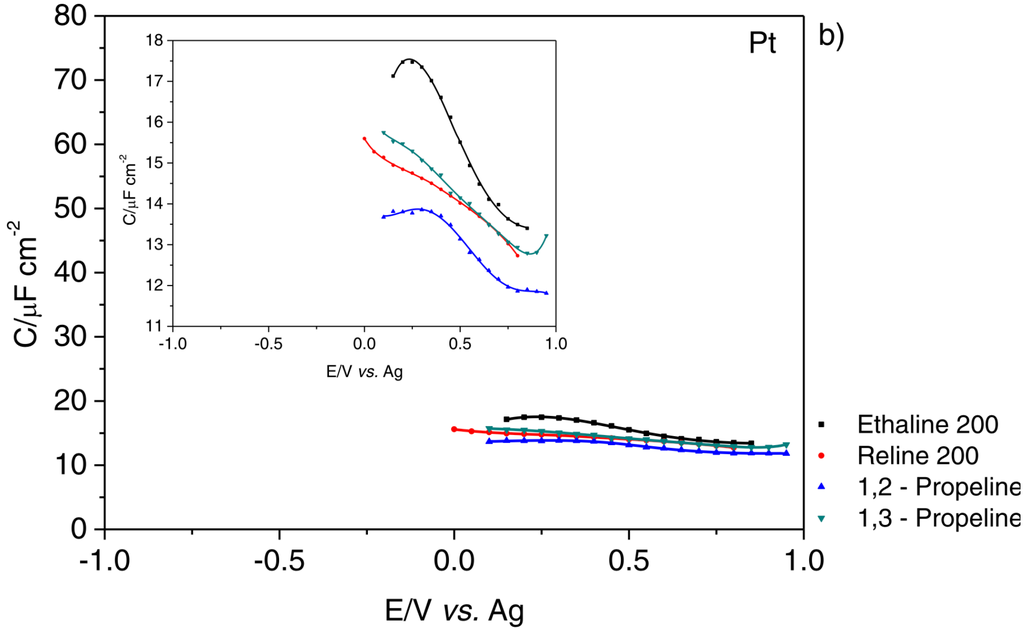
M. Jitvisate et al., *J. Phys. Chem. Lett.*, **2026**.

DES: Recent studies

- As mentioned in the few previous slides, measuring $C(V)$ can tell us about the EDL structure at interfaces (as explained by mathematical models).
- One significant question is….**Can we still use the existing model (for ILs) to describe DESs?**
- Only **few papers has reported** $C(V)$ in the past 5–6 years.
- Despite this fact, **is a new model needed?**.

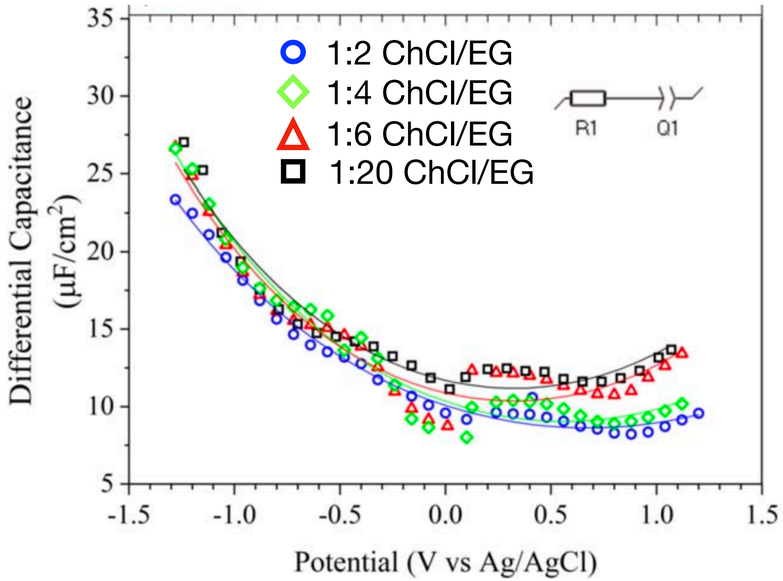
Proposed model for DESs

$C = C_D \cosh(\beta eV/2kT)$ → Stretched U-like capacitance curve



- Some DESs measured on Pt electrode.
- $C(V)$ do not seem to obey the existing theoretical model.

R. Costa *et al.*, *Electrochim. Acta*, **461**, 142653 (2023).

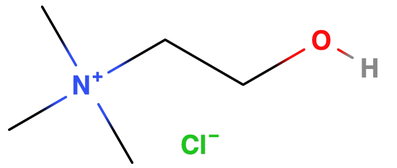


- ChCl/EG with various molar ratios measured on GC electrode.
- $C(V)$ exhibits U-like shape but hardly fit with GC model.

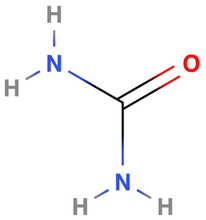
W. Dean *et al.*, *J. Electrochem. Soc.*, **168**, 026503 (2021).

DES: Differential capacitance

- Measurement on the same system was done to verify the validity of the technique.
- **1:2 ChCl/urea on Pt**
- Both $C(V)$ **curve feature** and **magnitude** are comparable as measured with different technique.

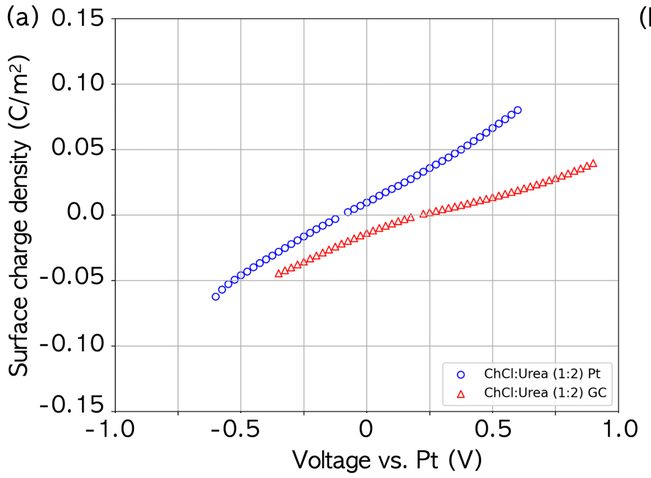


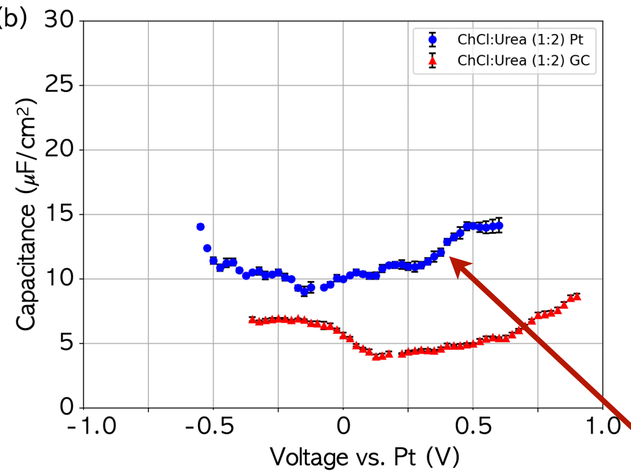
Choline chloride (ChCl)



Urea

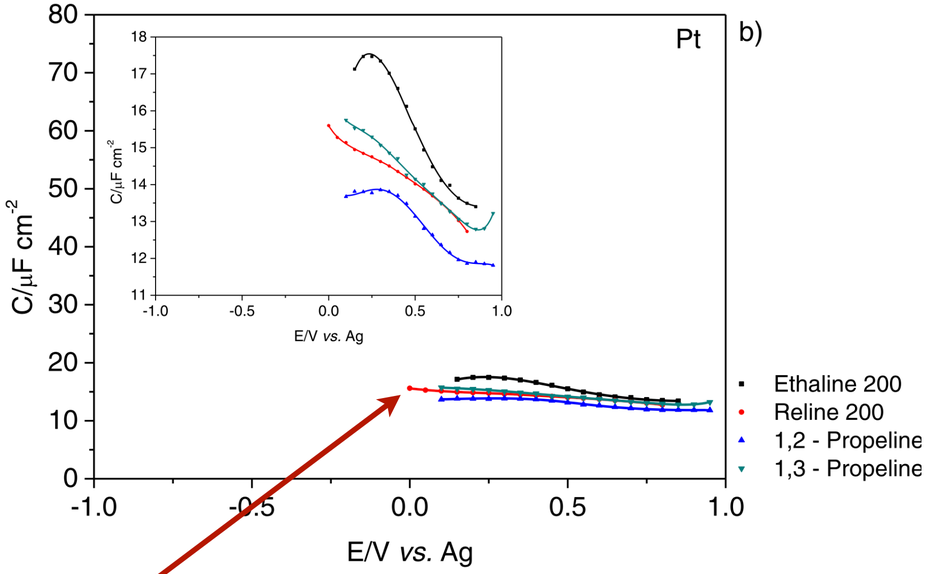
Our result (CA)





M. Jitvisate, *J. Phys. Chem. Lett.*, **15**, 9637–9643 (2024).

Literature (EIS)

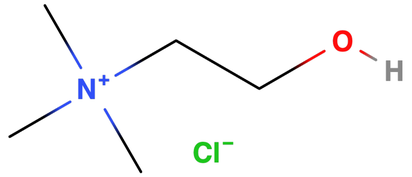


R. Costa *et al.*, *Electrochim. Acta*, **461**, 142653 (2023).

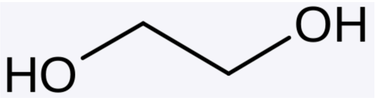
Almost flat capacitance curve over the entire electrochemical window.

DES: Electrode materials

- **1:2 ChCl/EG on Pt and GC at varied molar ratios**
- $C(V)$ **curve feature measured on Pt changes with molar ratios.**
- But it seems **unchanged on GC.**

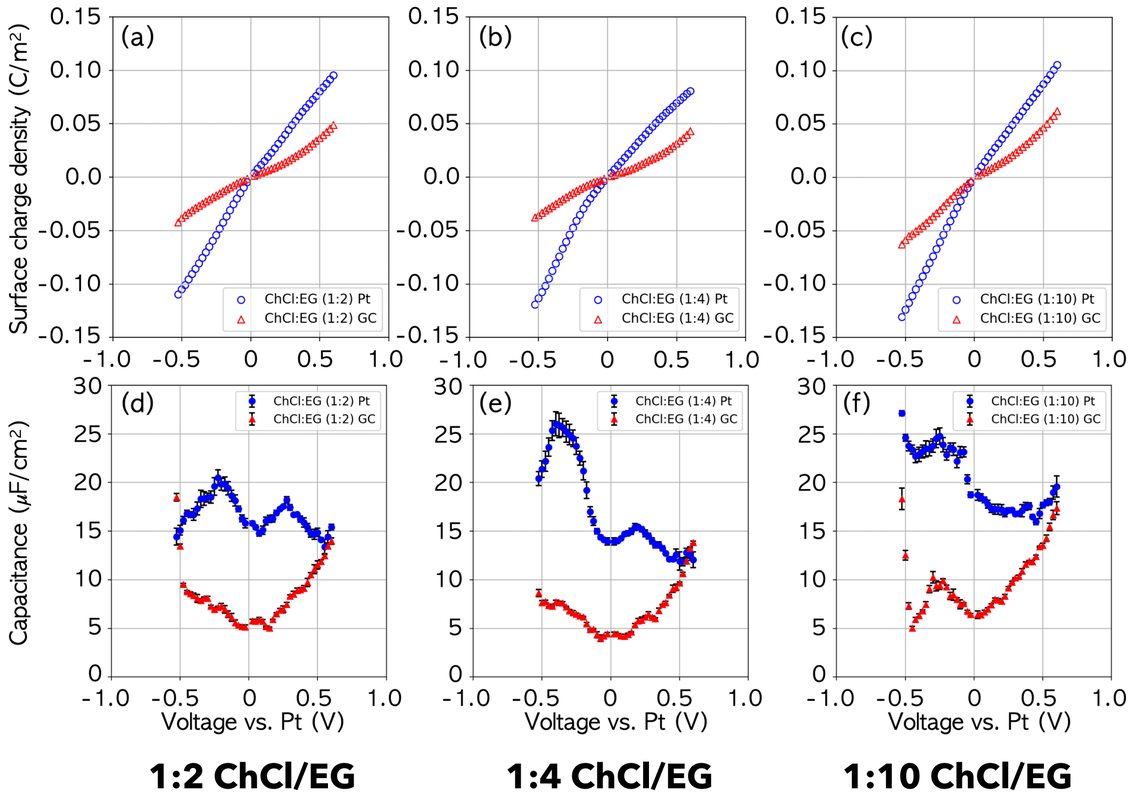


Choline chloride (ChCl)



Ethylene glycol (EG)

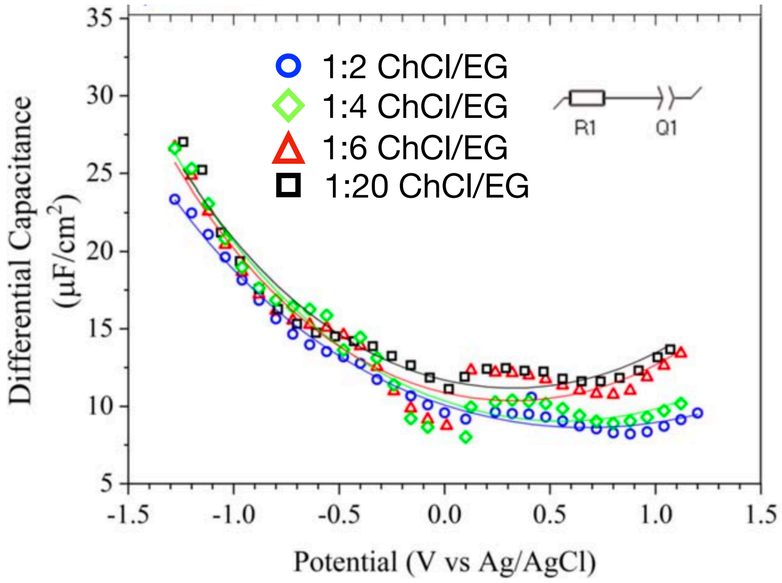
Our result (Pt vs. GC)



1:2 ChCl/EG **1:4 ChCl/EG** **1:10 ChCl/EG**

M. Jitvisate, *J. Phys. Chem. Lett.*, **15**, 9637–9643 (2024).

Literature (GC)



W. Dean *et al.*, *J. Electrochem. Soc.*, **168**, 026503 (2021).

Concluding remarks

- PB/Gouy–Chapman fails for dense ionic fluids, where λ_D is below the ion size.
- Chronoamperometry gives $\sigma(V)$ directly, so $C(V)$ probes EDL structure.
- A lattice-gas model with packing (γ) and correlation (α) parameters captures the main trends: camel → bell → U with dilution, and crowding at high $|V|$.
- Chain length and size-mismatched mixtures go beyond mean-field: C_d rises at high $|V|$, charging slows, and a sharp feature appears at negative potentials.
- For DESs, the same model fits ChCl/EG on Pt. Water content, electrode material and ion segregation remain open.

Thank you.