Association of ions and molecules as observed by electrokinetic and diffusion NMR

István Furó

Department of Chemistry and Industrial NMR Centre, Royal Institute of Technology, Stockholm

Co-workers

Fredrik Hallberg

Peter Stilbs

Sergey Dvinskikh

Anton Frise

Göran Lindbergh

Takashi Kato

Financial support

Swedish Research Council (VR)

Knut and Alice Wallenberg Foundation

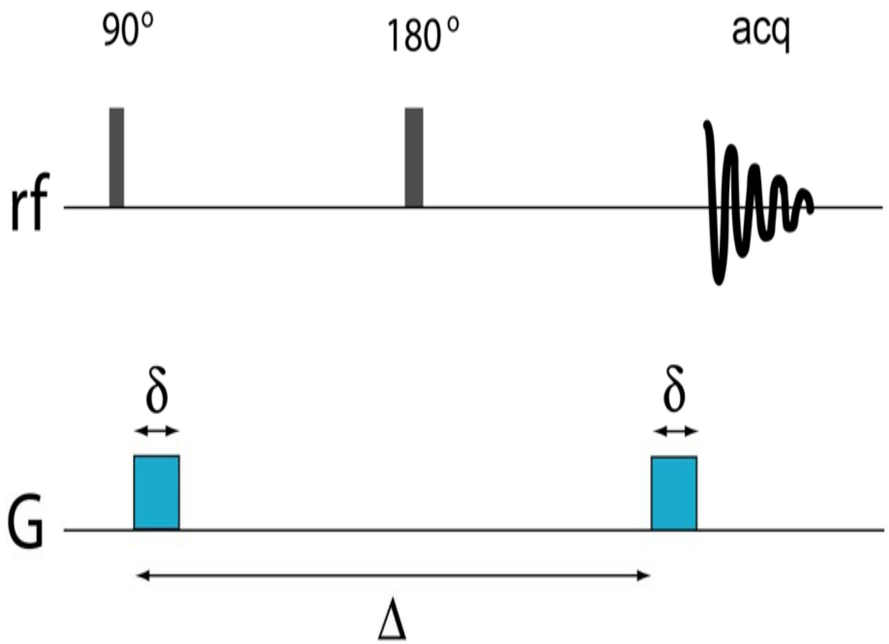
The state of association of charged objects (small ions, large biomolecules and polymers, particles) is of primary importance. Because of the long-range nature of interactions, modelling is often difficult.

Association changes the size, diffusion NMR can measure that. Association changes the charge, electrophoretic NMR can measure that.

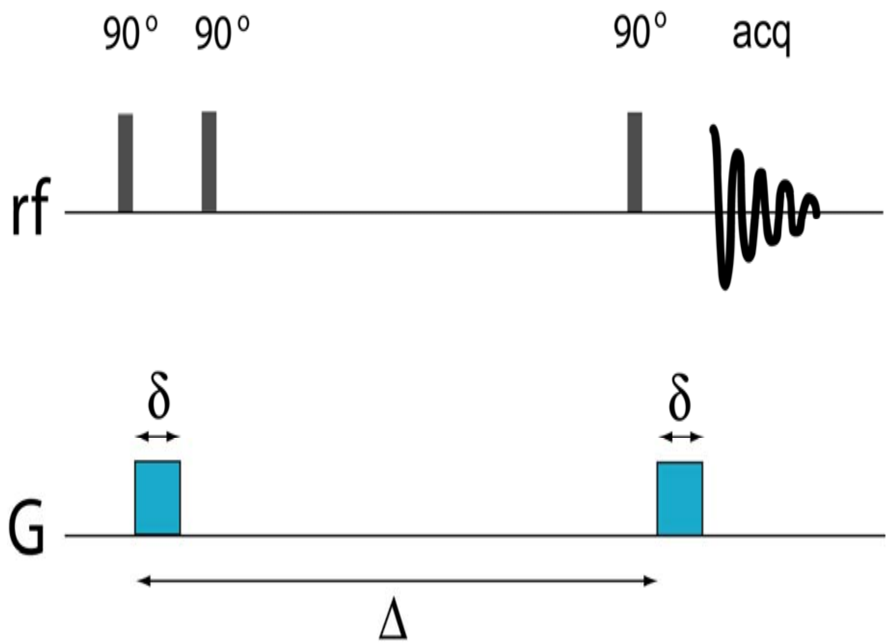
NMR has unparalleled chemical selectivity that comes free of charge.

The state of association of charged objects is difficult to assess experimentally. In particular, there is a lack of quantitative and stoichiometric data. Observations are often difficult in multicomponent systems.

An old acquaintance: the Diffusion NMR experiment



Spin echo

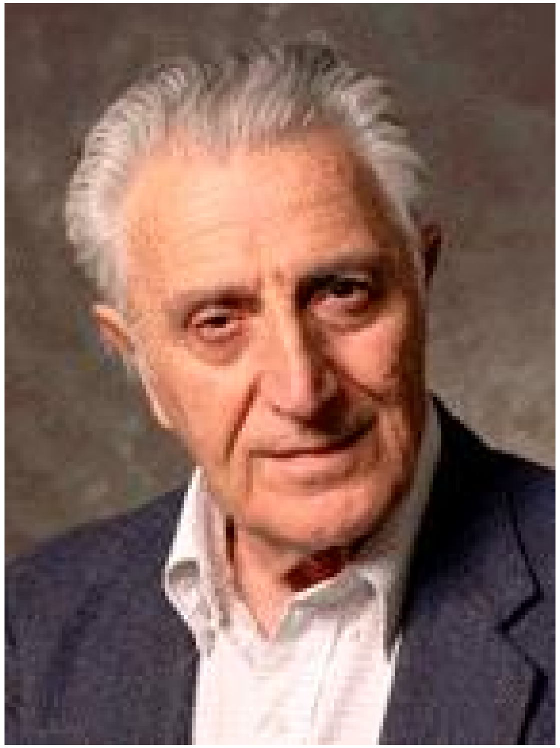


Stimulated echo

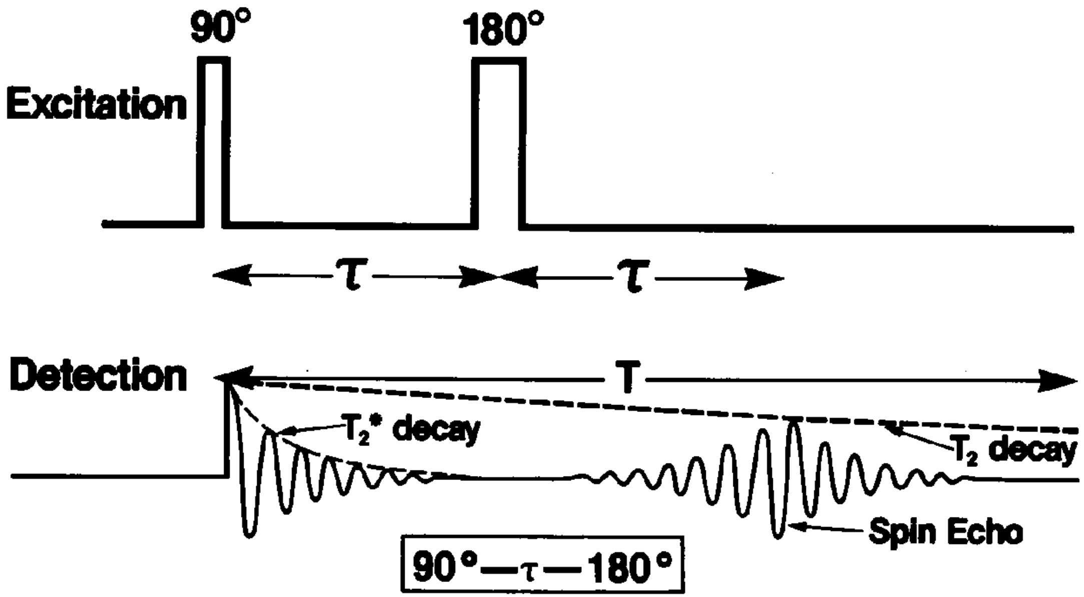
$$\text{Signal} \propto \exp[-D(\gamma G\delta)^2(\Delta - \delta/3)]$$

Flow: signal phase modulation instead of decay.

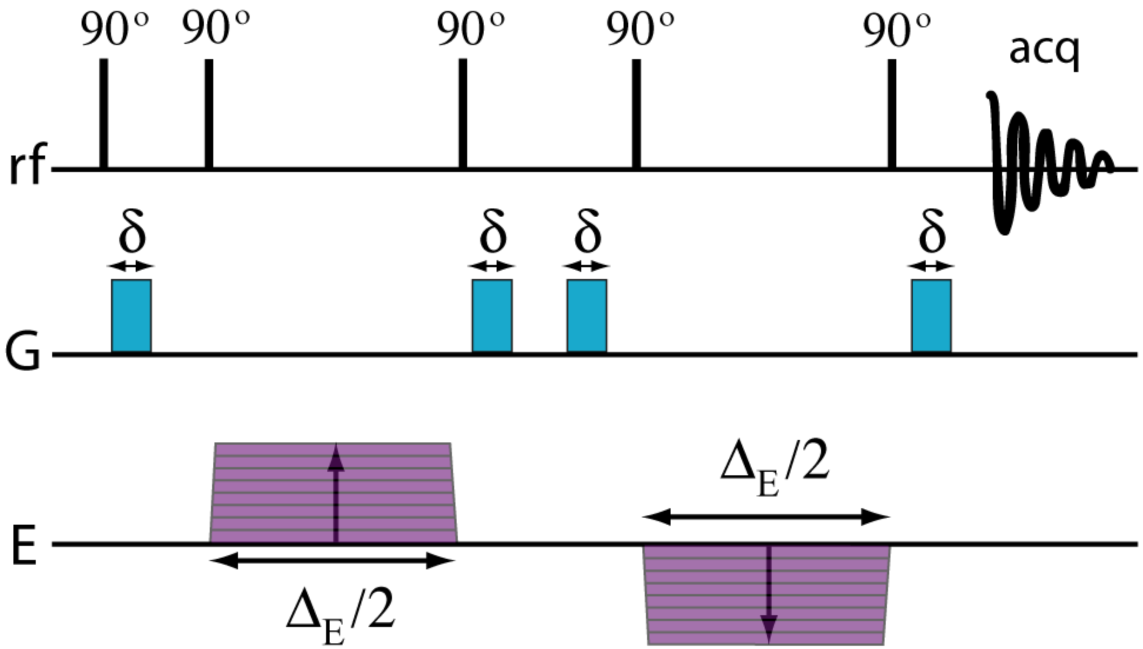
THE "HAHN SPIN ECHO" EXPERIMENT (1949) IS NOW 60 YEARS OLD



Hahn also described the basic NMR diffuson experiment and related things (Phys. Rev., 80 (1950) 580-594)



A more recent friend: the eNMR experiment



K. J. Packer 1969

M. Holz 1984

C. S. Johnson 1988-

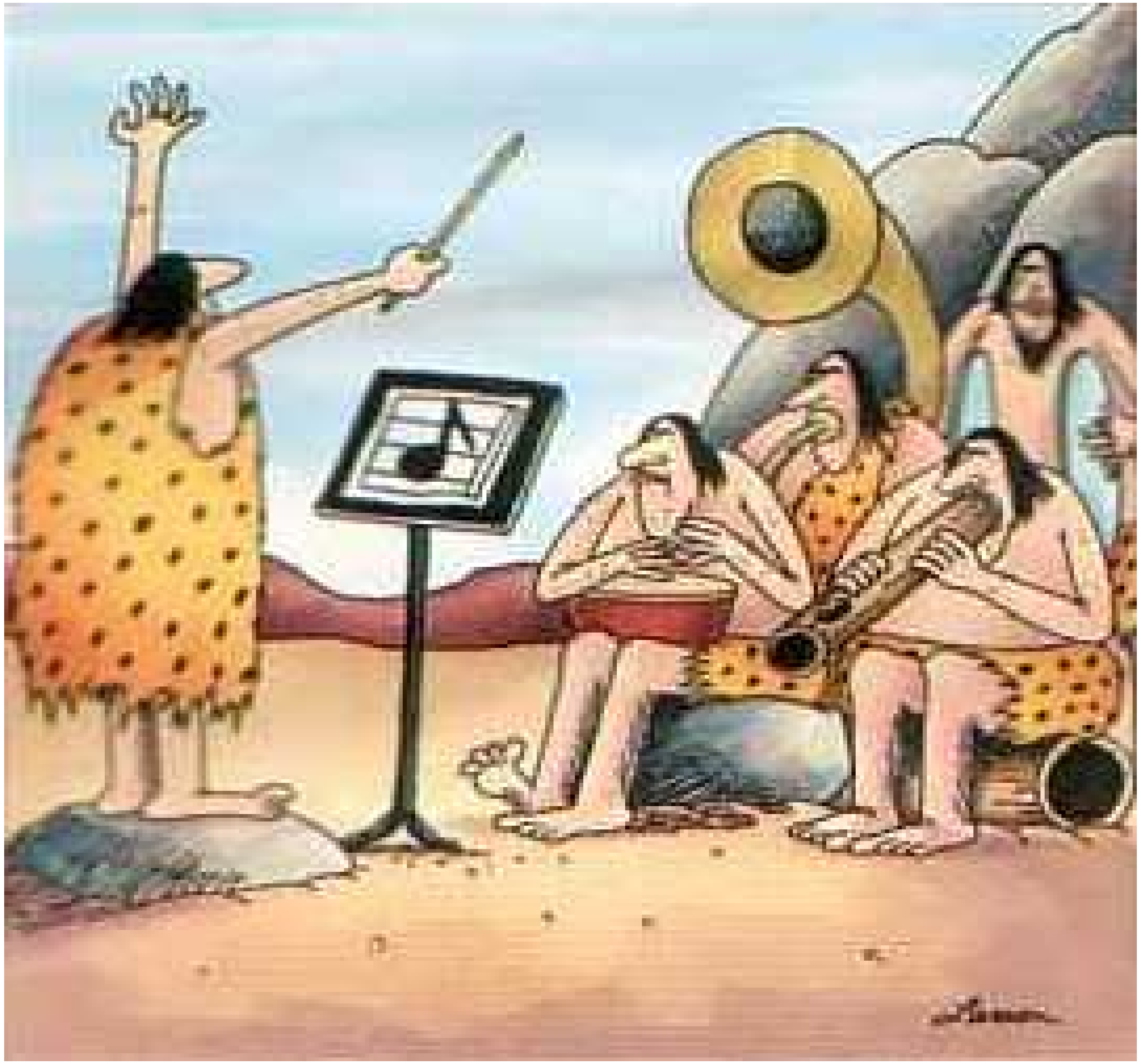
U. Scheler 200x

Electrophoretic mobility, proportional to charge

The electric field induces displacement, detected as NMR signal phase shift.

$$\phi = \gamma \delta g \Delta_E E \mu$$

$$\text{Signal} \propto \exp[-D(\gamma G \delta)^2 (\Delta - \delta / 3)] \cdot \exp[i\phi]$$



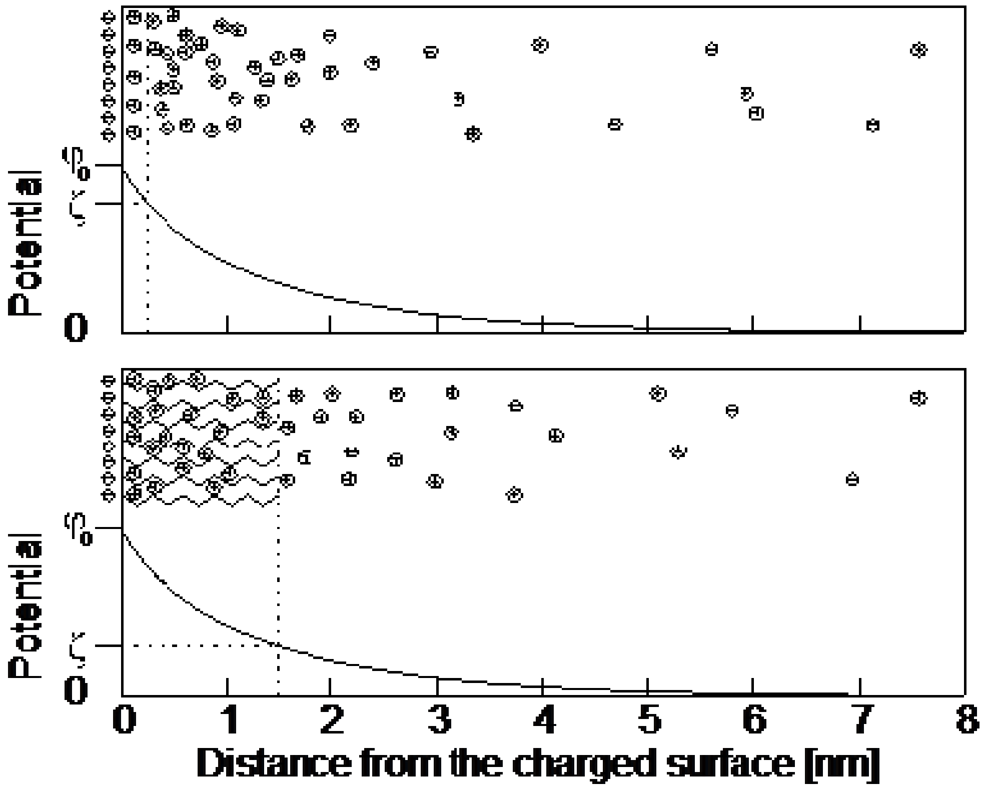
Charge is a measure of association that is often more sensitive than the hydrodynamic radius obtained by diffusion NMR.

Electrophoresis, electroosmosis,…

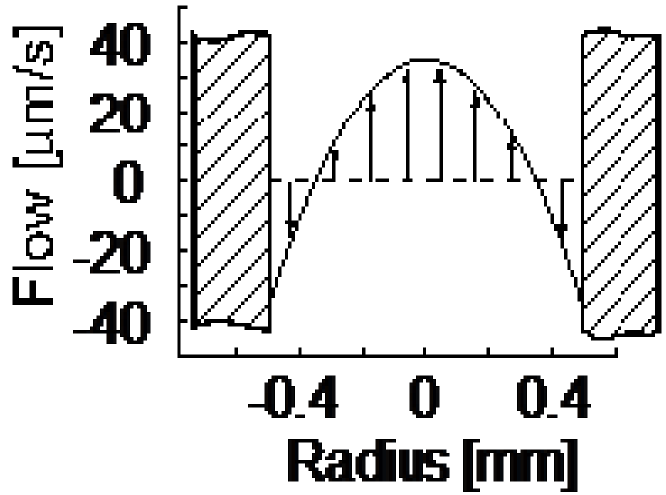
$$\mu_{EP} = \frac{zeD}{k_B T}$$

Electrophoresis: individual molecules.

Electroosmosis: viscous drag on the solvent.

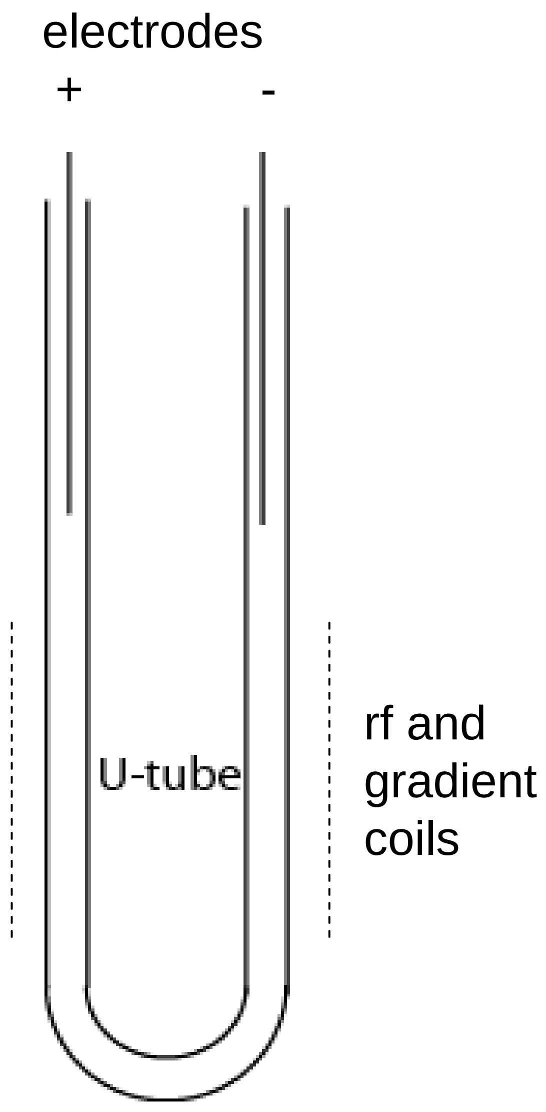


$$\mu_{EO} = \frac{\varepsilon_r \varepsilon_0 \zeta}{\eta}$$



Electroosmosis can lead to bulk convectional flow.

eNMR: making the charged particles FLOW



”Conventional” arrangement: U-tube!

Advantages: no external wire into the NMR sample coil volume, no noise pickup, any bubbles exit upward.

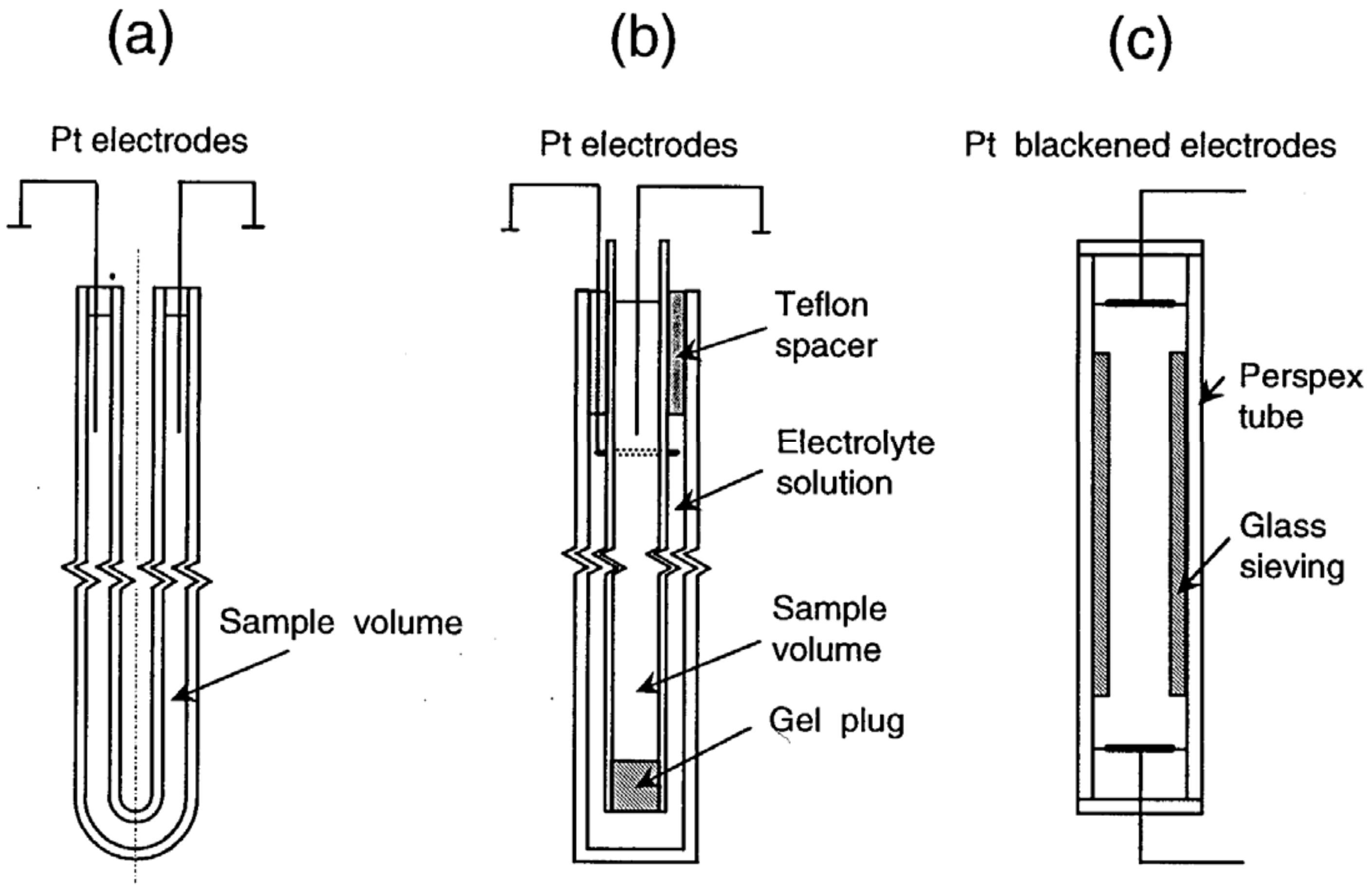
Disadvantages of the U-tube design:

- the sign of μ is not obtained, cosine modulation of the signal!

- low filling factor and thereby very weak NMR signal

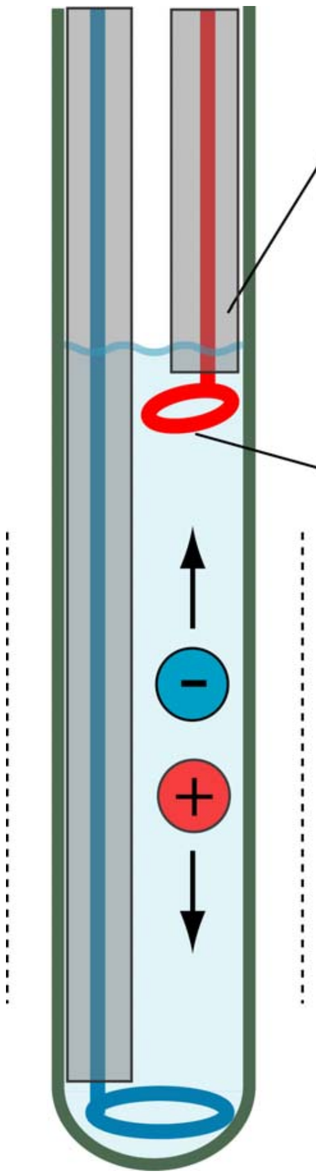
- results strongly depend on the quality of the anti-electroosmotic coating

POSSIBLE SAMPLE GEOMETRIES FOR eNMR



(From C.S. Johnson, Jr., Encyclopedia of NMR)

NOVEL SAMPLE CELLS FOR eNMR



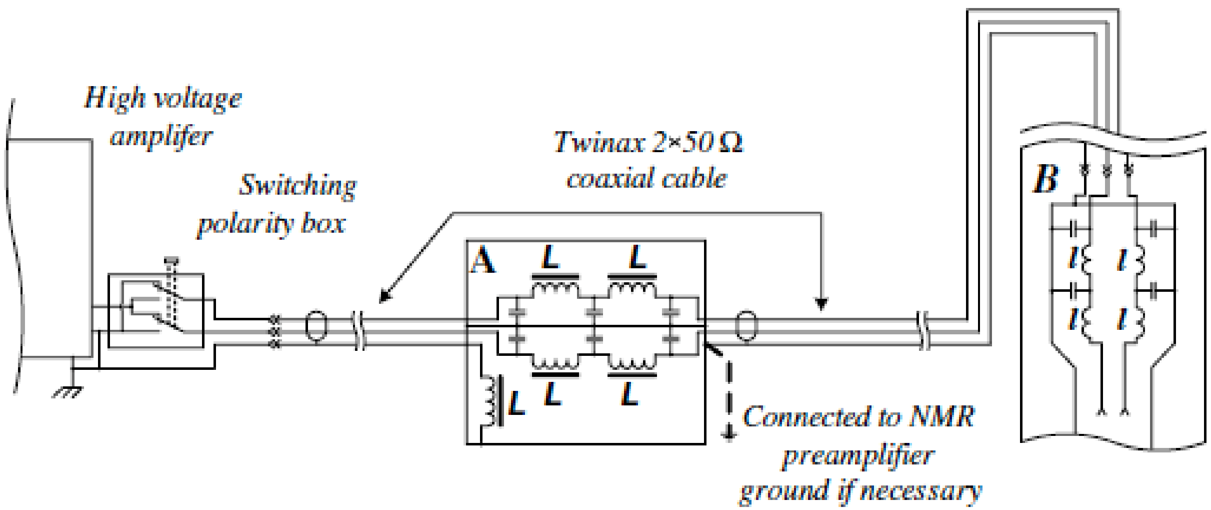
The sign of μ is preserved!

It fits to routine probes!

The filling factor is large!

Requires novel RF filters!

J. Magn. Reson. **192** 69-77 (2008).



One filter stage is inside this brass ”spinner”

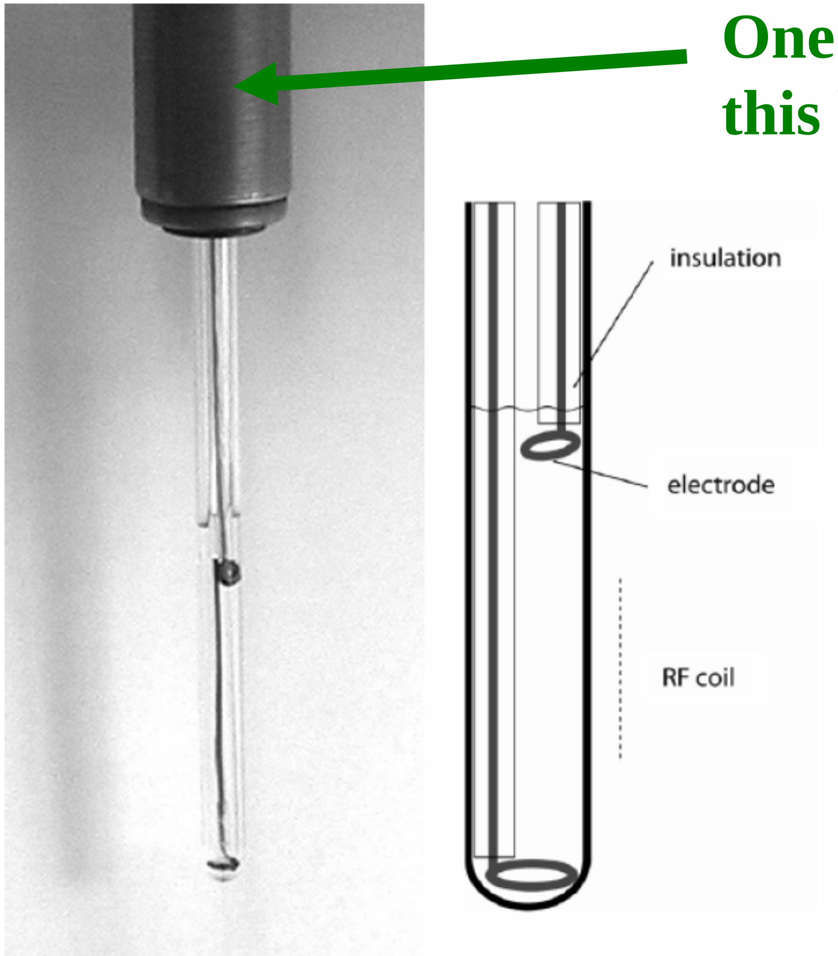
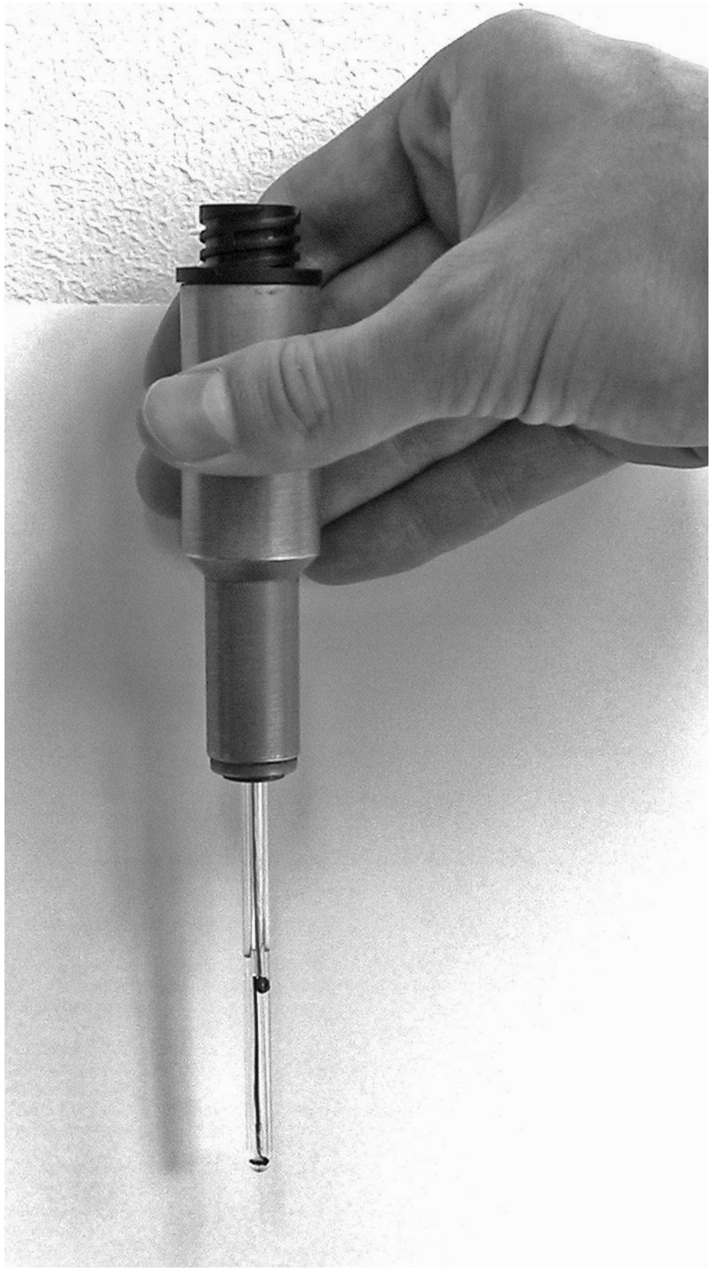
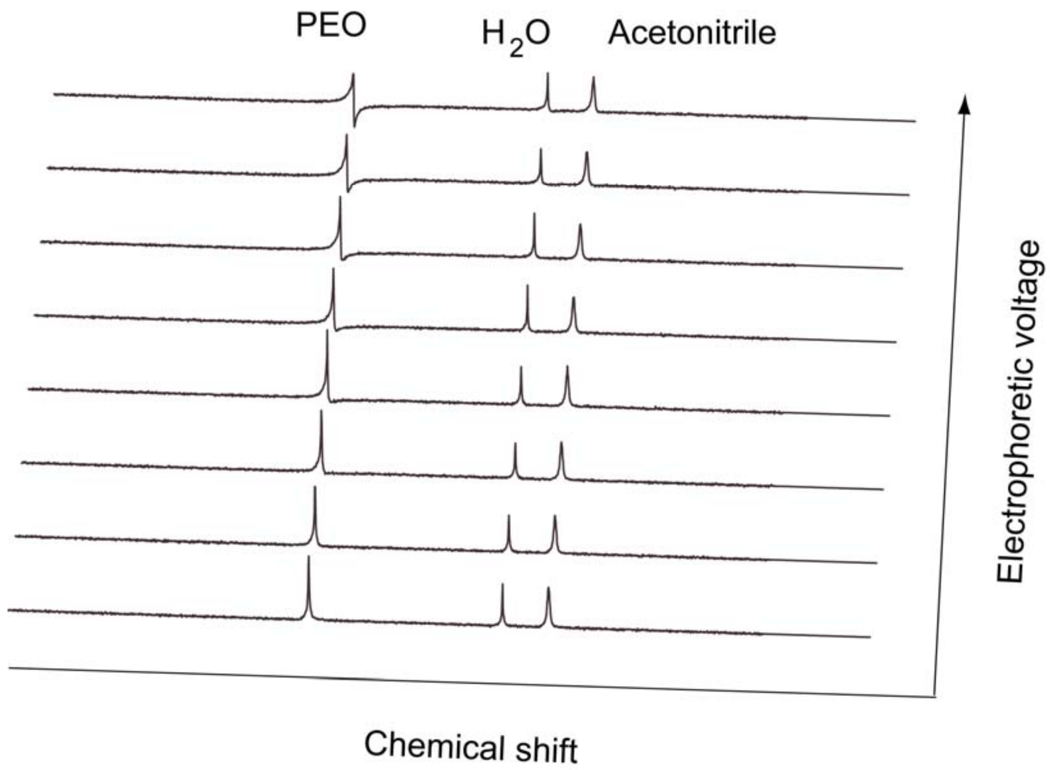


Figure 4; Photograph and schematic of the electrophoretic cell developed by Hallberg *et al* [1]. Photograph copyright F. Hallberg. The electrophoretic sample cell is based on a conventional 5 mm NMR tube. The distance between the electrodes is roughly 3 cm.



"Bunsen, I must tell you how excellent your study of chemical spectroscopy is, as is your pioneer work in photochemistry — but what really impresses me is that cute little burner you've come up with."

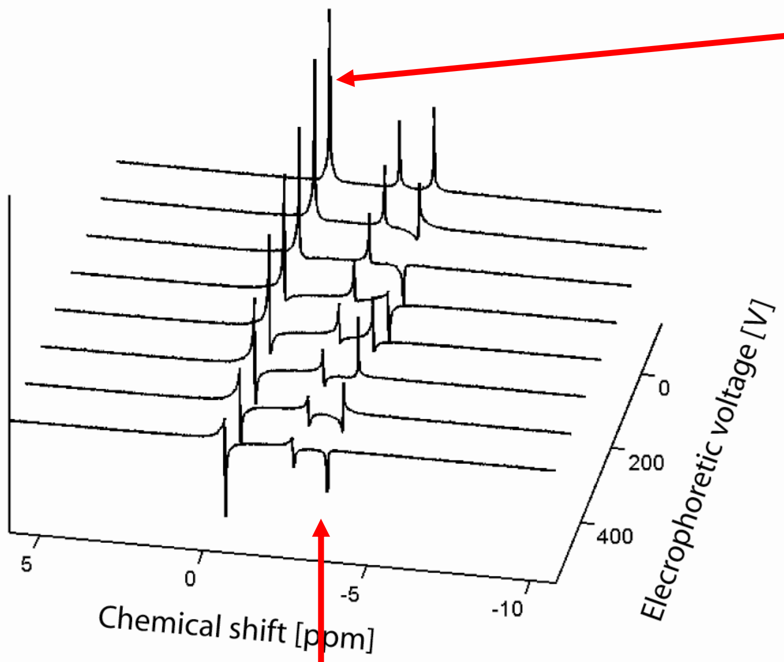
Phase shift ∝ displacement for charged entities, irrespective how they obtain their charge…



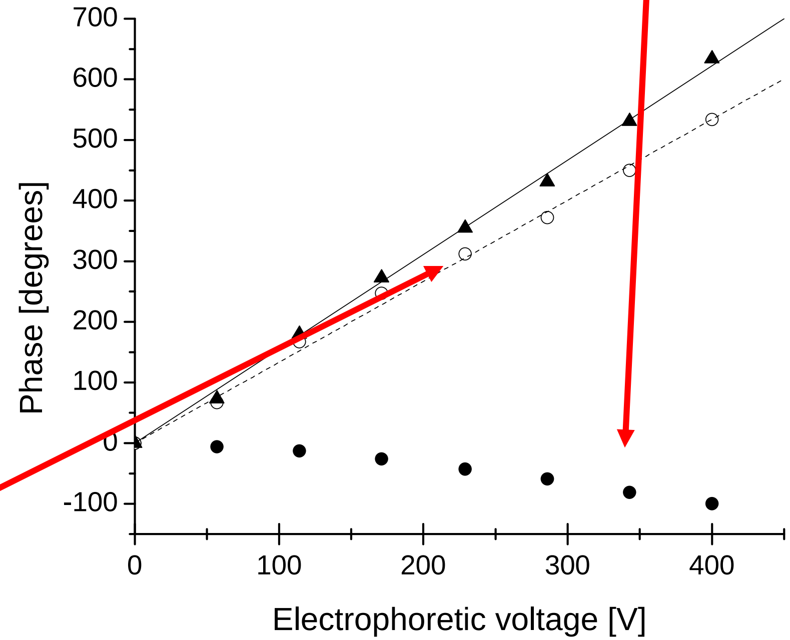
10 mM $LiClO_4$ and 10 mM EO units in M_w = 22000 low polydispersity PEO dissolved in d_3-acetonitrile.

Li^+ binds to PEO…

Phase shift ∝ displacement



Uncharged molecules incl water: should not move!



Charged molecule (TMA^+): should move!

Because of the preserved sign of displacement, electroosmotic effects can be corrected for – the accuracy improves by more than an order of magnitude! Will eNMR become a routine method?

Will eNMR become a routine method?

- moderate electroosmosis is not a problem any more.

- sample holder fits to routine probes.

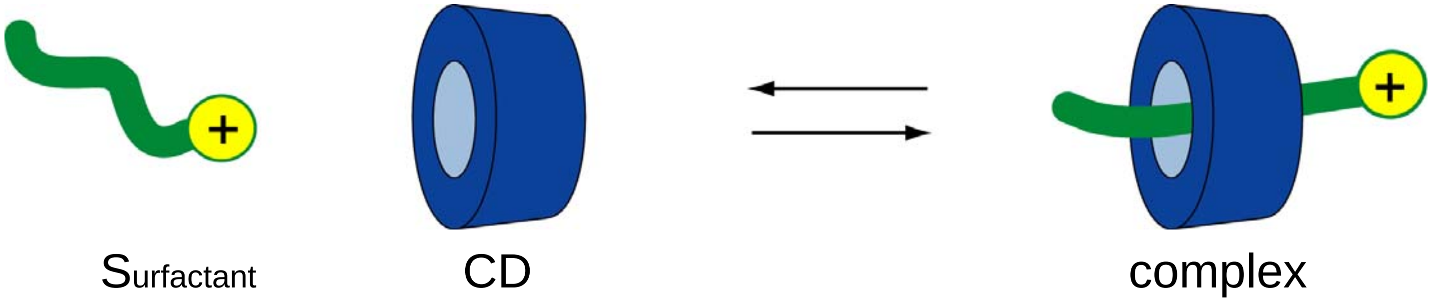
- voltages/currents sufficient for many applications are relatively easy to generate, so are suitable external triggers.

- conductivity must be in a suitable range.

- Joule heating is a limiting factor.

- electrode reactions may happen.

APPLICATION: ASSOCIATION OF A CHARGED SURFACTANT (DeTAB OR CsPFO) WITH NON-CHARGED CYCLODEXTRINS



$$\left.\begin{aligned} \mu_{CD,obs} &= p\mu_{complex} \\ \mu_{S,obs} &= p\mu_{complex} + (1-p)\mu_{S,free} \end{aligned}\right\} p = 1 - \frac{\mu_{S,obs} - \mu_{CD,obs}}{\mu_{S,free}}$$

Similarly from diffusion coefficients:

$$p = 1 - \frac{D_{CD,obs} - D_{S,obs}}{D_{CD,free} - D_{S,free}}$$

J. Am. Chem. Soc. **130** 7550-7551 (2008).

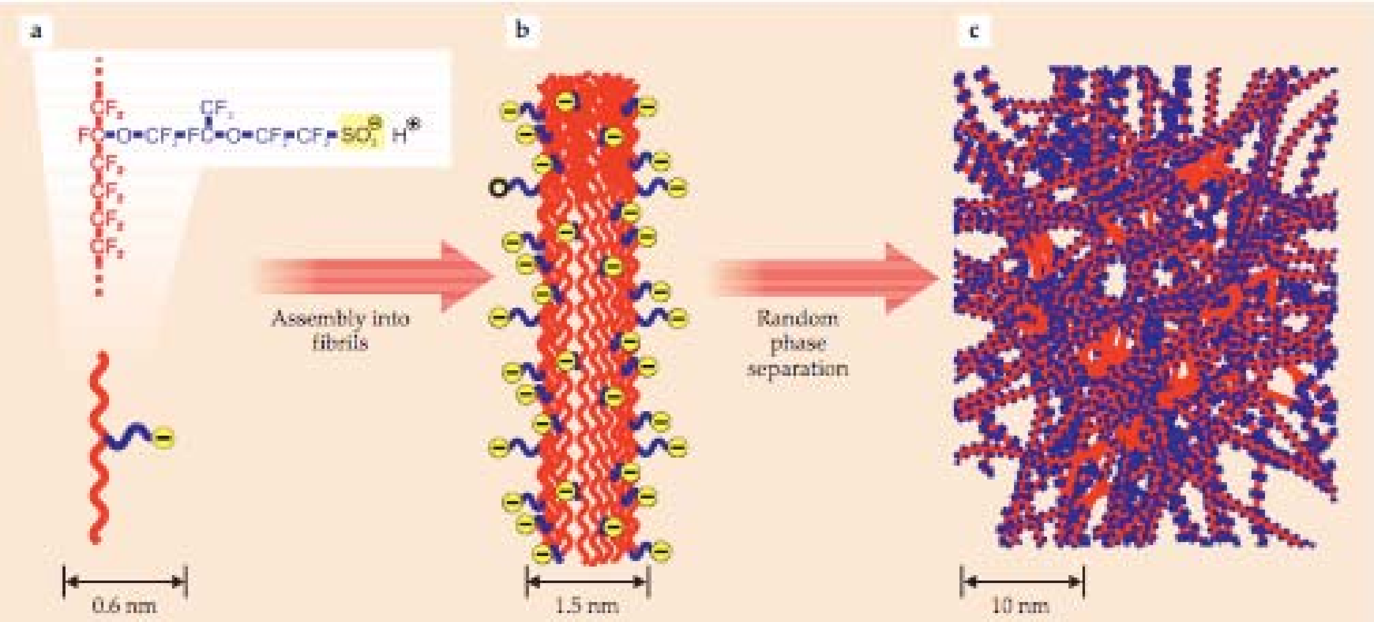
Fraction bound molecules obtained from diffusion coefficients (a) and electrophoretic mobilities (b).

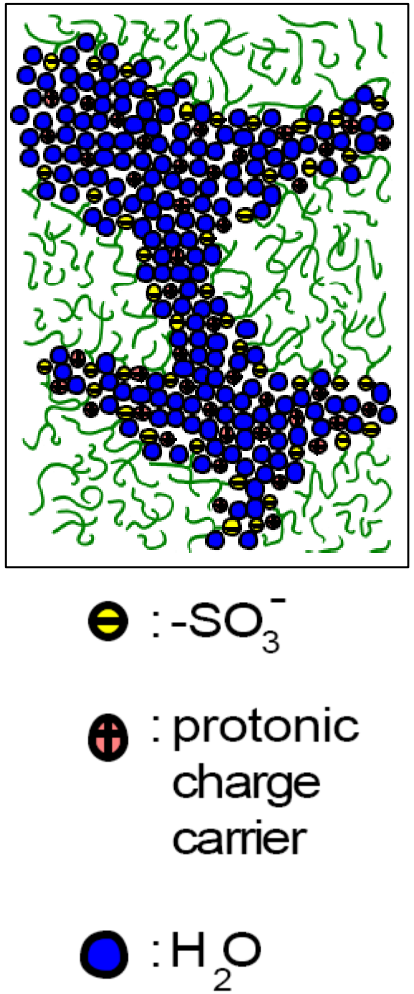
(c) Nominal charges (z) obtained from

$$z = \frac{\mu k_B T}{eD}$$

	D (10^{-10} m^2/s)	μ (10^{-9} m^2/Vs)	z	p	p
$DeTA^+$	5.51	19.9	0.93		
PFO^-	4.96				
α-CD	2.75	0			
β-CD	2.56	0			
$DeTA^+$/α-CD	3.04/2.61	10.7/8.1	0.80	0.84	0.87
$DeTA^+$/β-CD	2.87/2.42	11.0/7.8	0.82	0.85	0.84
PFO^-/α-CD	4.48/2.63	/-1.6	-0.17	0.15	
PFO^-/β-CD	2.71/2.38	/-8.3	-0.97	0.87	

APPLICATION: ELECTROOSMOTIC DRAG IN FUEL CELL MEMBRANE MATERIALS

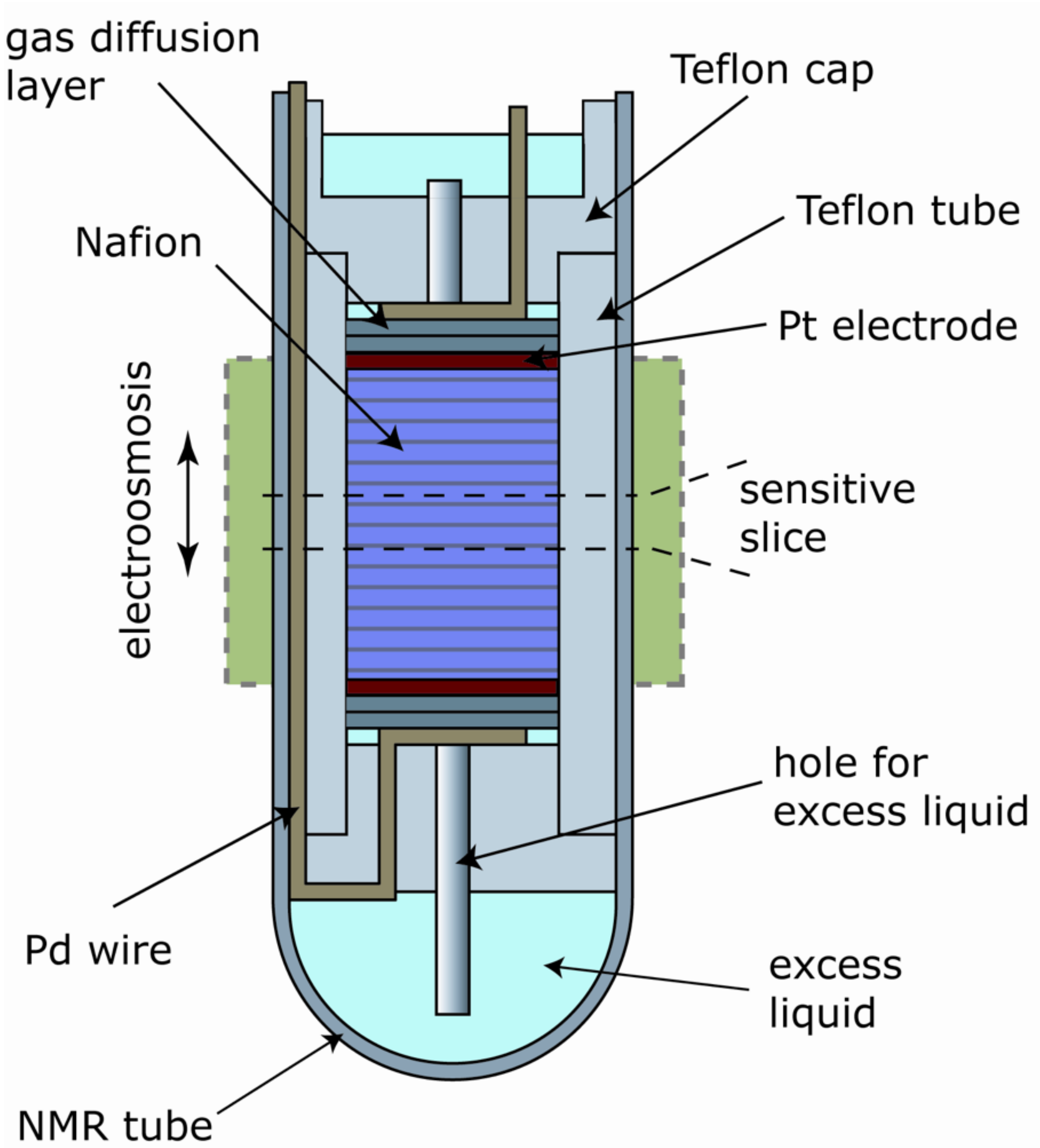




Nafion 117

Fuel cell performance depends on transport coefficients.

Experiments with Direct Methanol Fuel Cells (DMFC) – Nafion saturated with methanol/water mixtures.



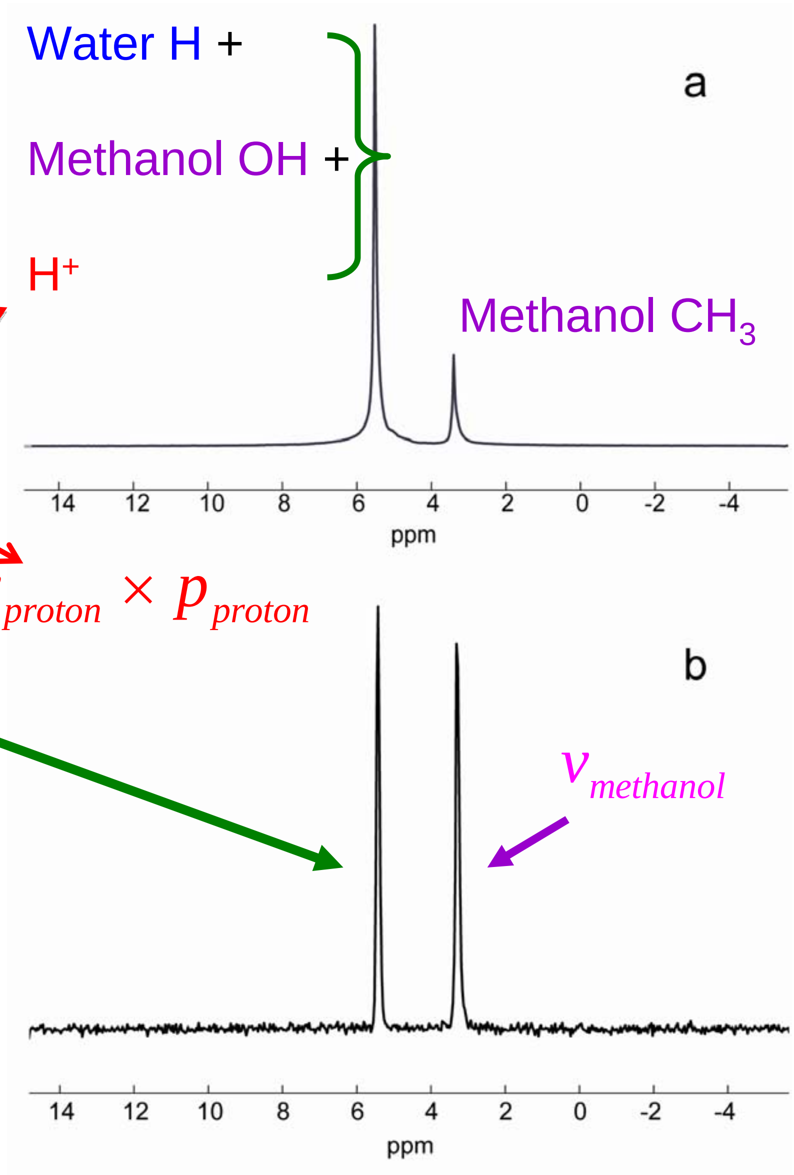
Electrochim. Acta, **accepted** (2010).

Phase connects to drift velocity:

$$v_i = \frac{\pi}{180^o} \frac{\phi_i}{\gamma g \delta \Delta_E}$$

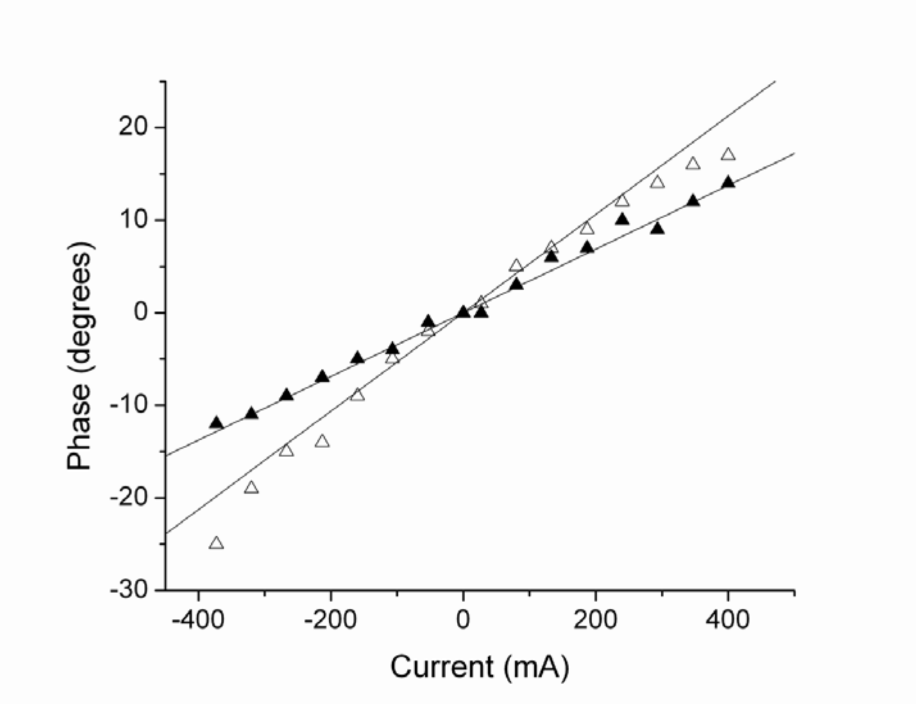
Provides the current

$$v = v_{water} \times p_{water} + v_{methanol} \times p_{methanol} + v_{proton} \times p_{proton}$$



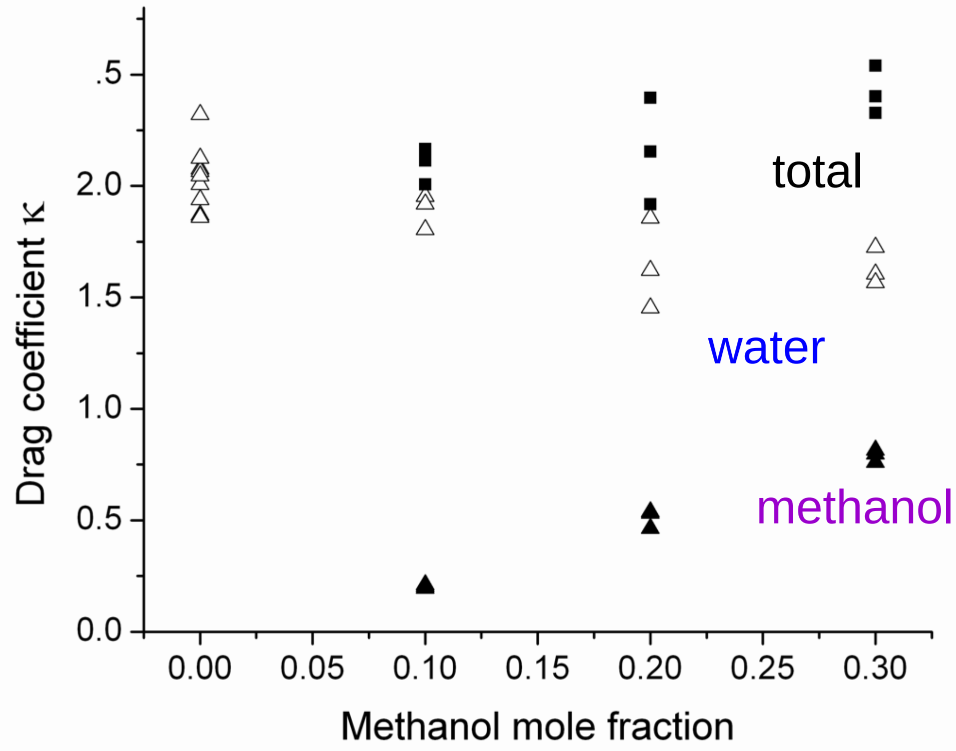
Definition of the drag coefficient:

$$\kappa_i = \frac{j_i}{j_{proton}}$$



Experimental phase shifts.

Molecularly selective experimental drag coefficients:



APPLICATION: ION PAIRING BETWEEN ANIONS IN THE HOFMEISTER SERIES AND THE TETRAMETHYLAMMONIUM CATION (TMA^+)

Ions are ordered according to their relative influence on the physical behavior of aqueous processes such as

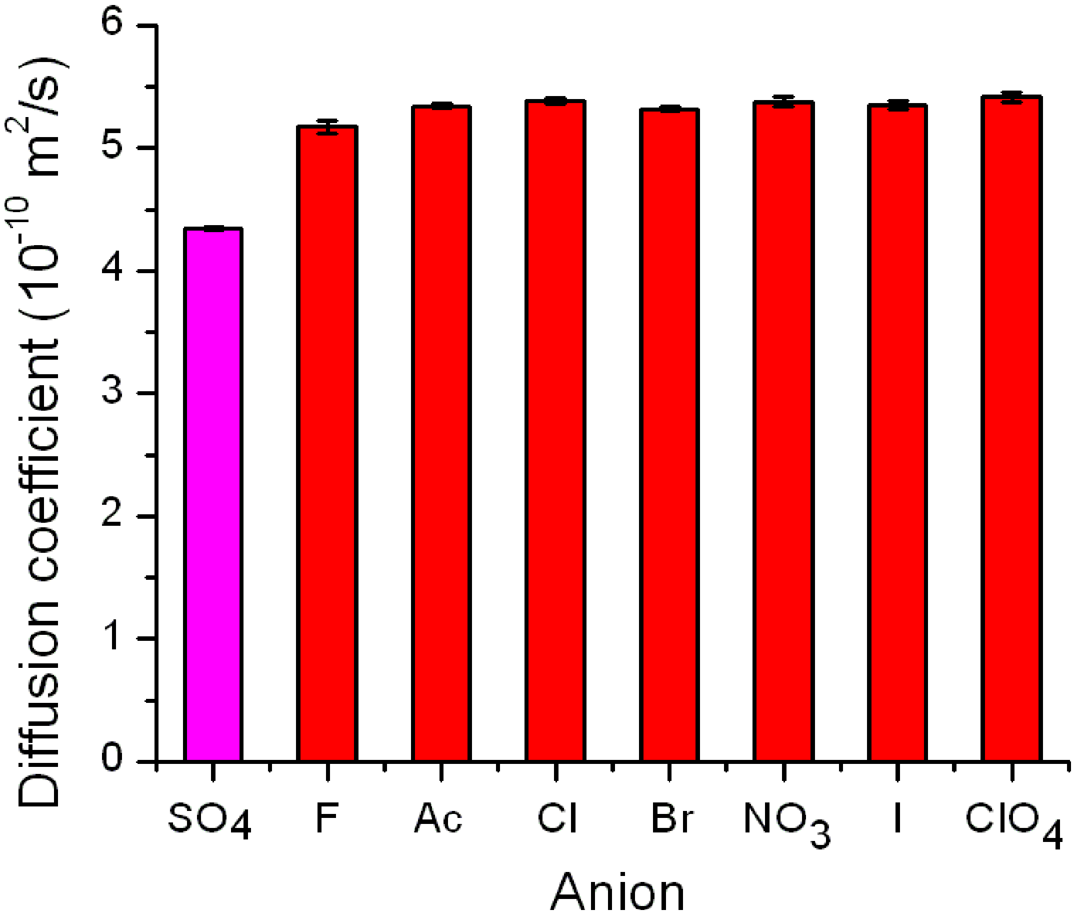
- **protein solubility and stability**
- **surface tension**
- **micelle formation**

Hofmeister series of some anions:

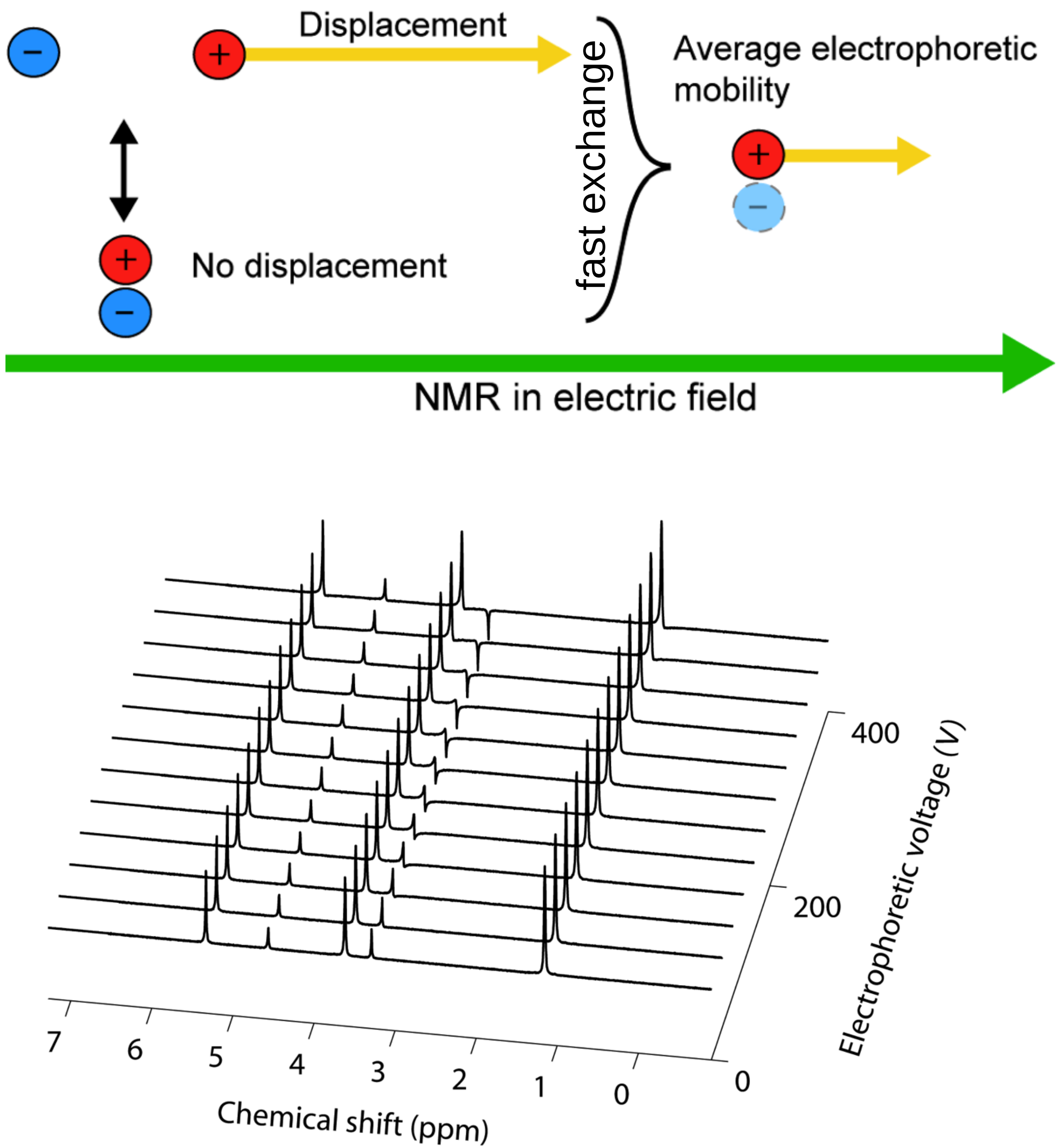
$$SO_4^{2-} > F^- > Ac^- > Cl^- > Br^- > NO_3^- > I^- > ClO_4^- > SCN^-$$

J. Am. Chem. Soc. **131** 13900-13901 (2009).

Conventional approach: measuring diffusion.



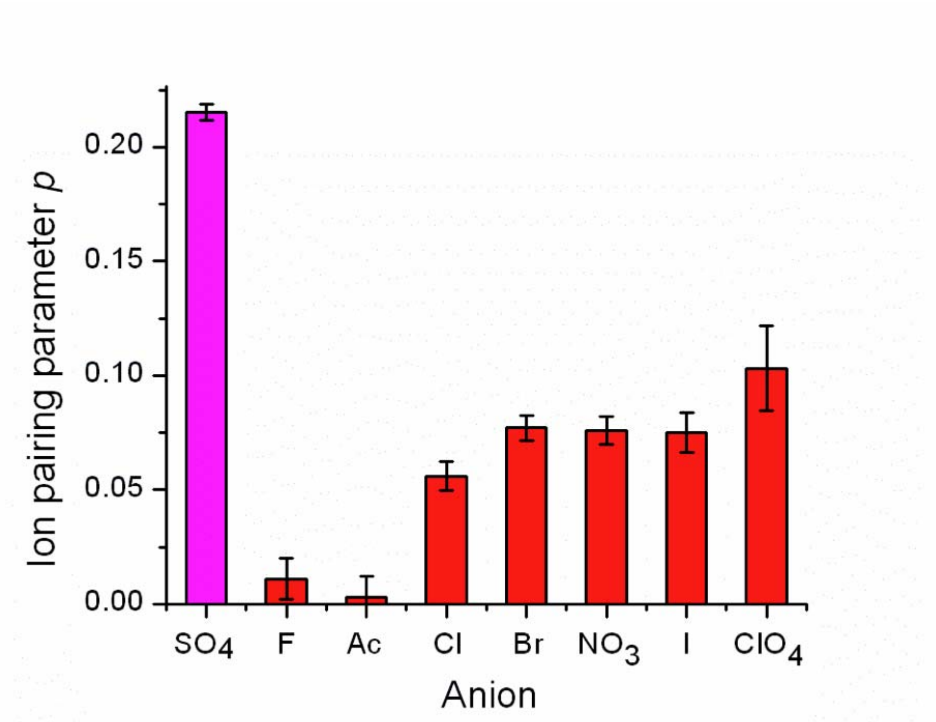
^{1}H diffusion experiments on the TMA^+ ion.

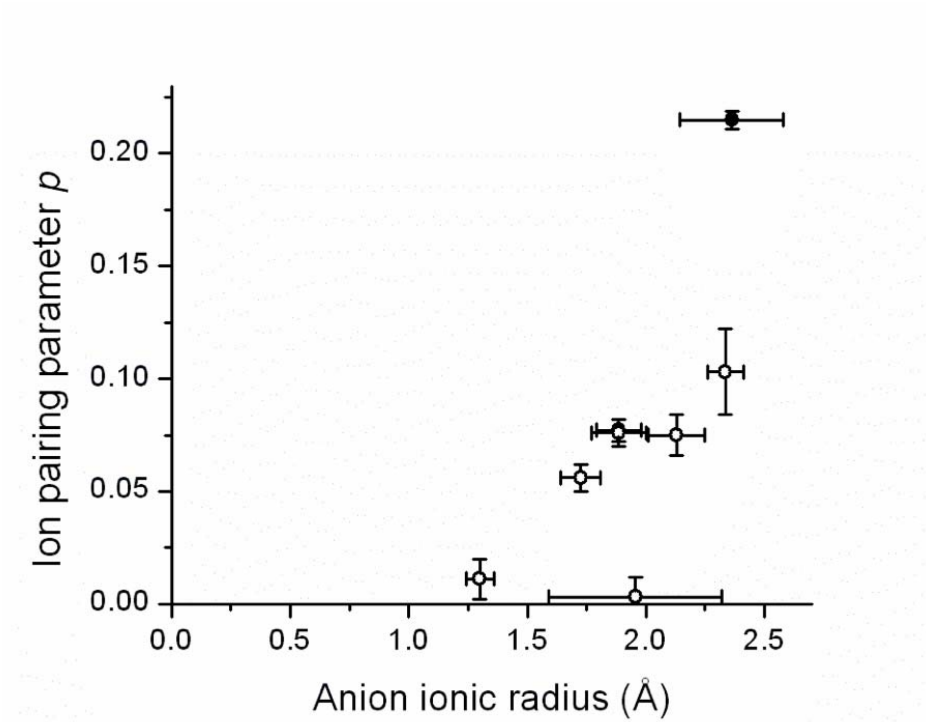

Displacement
fast exchange
Average electrophoretic mobility
No displacement
NMR in electric field
7
6
5
4
3
2
1
0
Chemical shift (ppm)
0
200
400
Electrophoretic voltage (V)

Ion pairing to TMA^+ correlated with...

the order of anions in the Hofmeister series

the ionic radii of anions





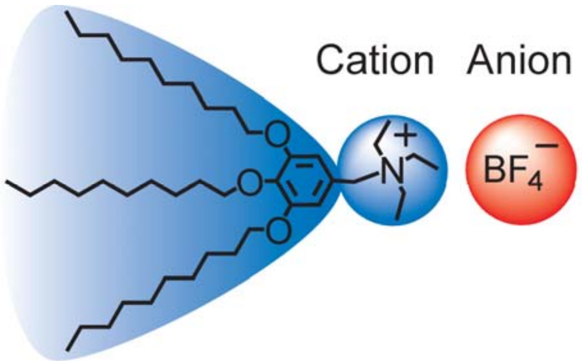
…in a 2 mM solution in deuterated ethanol/water mixture.

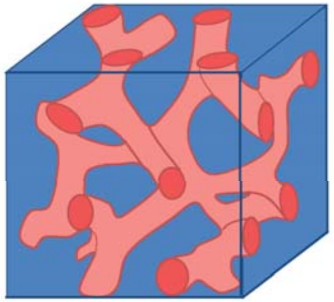
$$z = \frac{\mu_{obs} k_B T}{e D_{obs}}$$

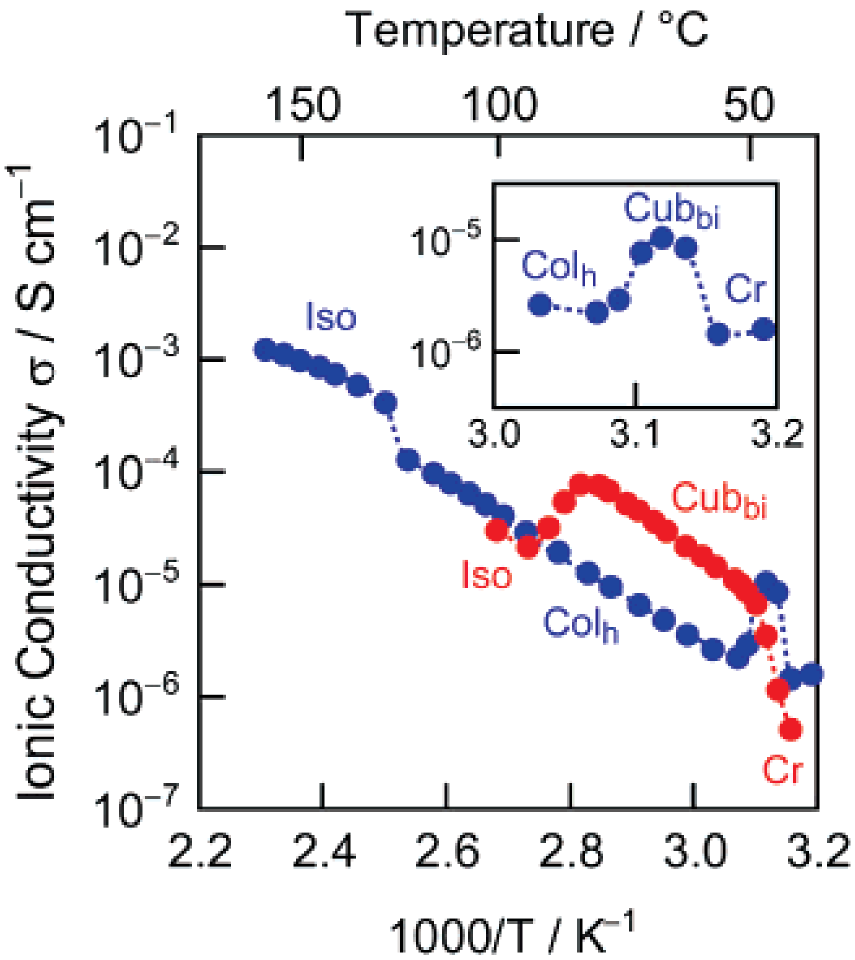
$$p = \left(1 - z\right) / z_{anion}^{formal}$$

…brought to you by NMR!

A SIMILAR DIFFUSION APPLICATION: ION PAIRING IN IONIC THERMOTROPICS





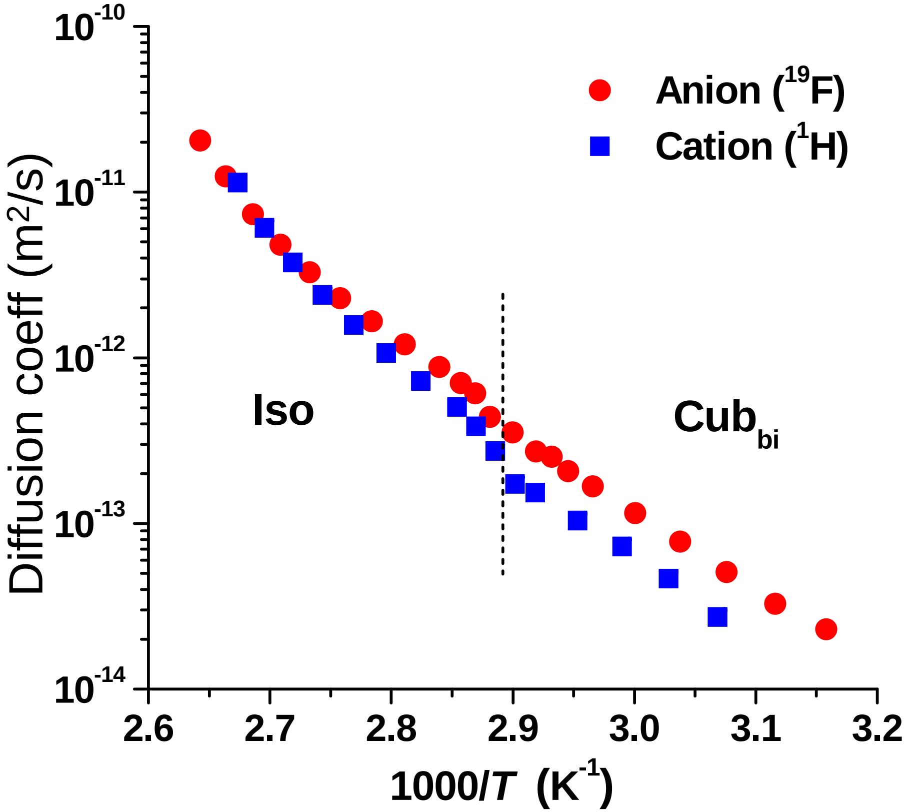


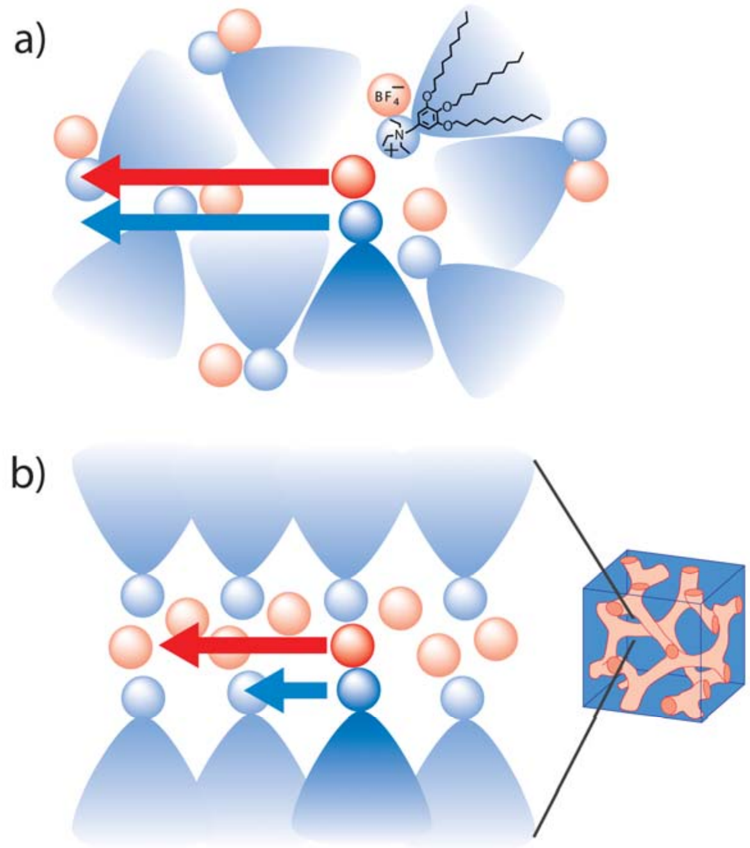
Why does the ionic conductivity decrease at the cubic/isotropic phase transition?

Chem. Comm. **46** 728-730 (2010).

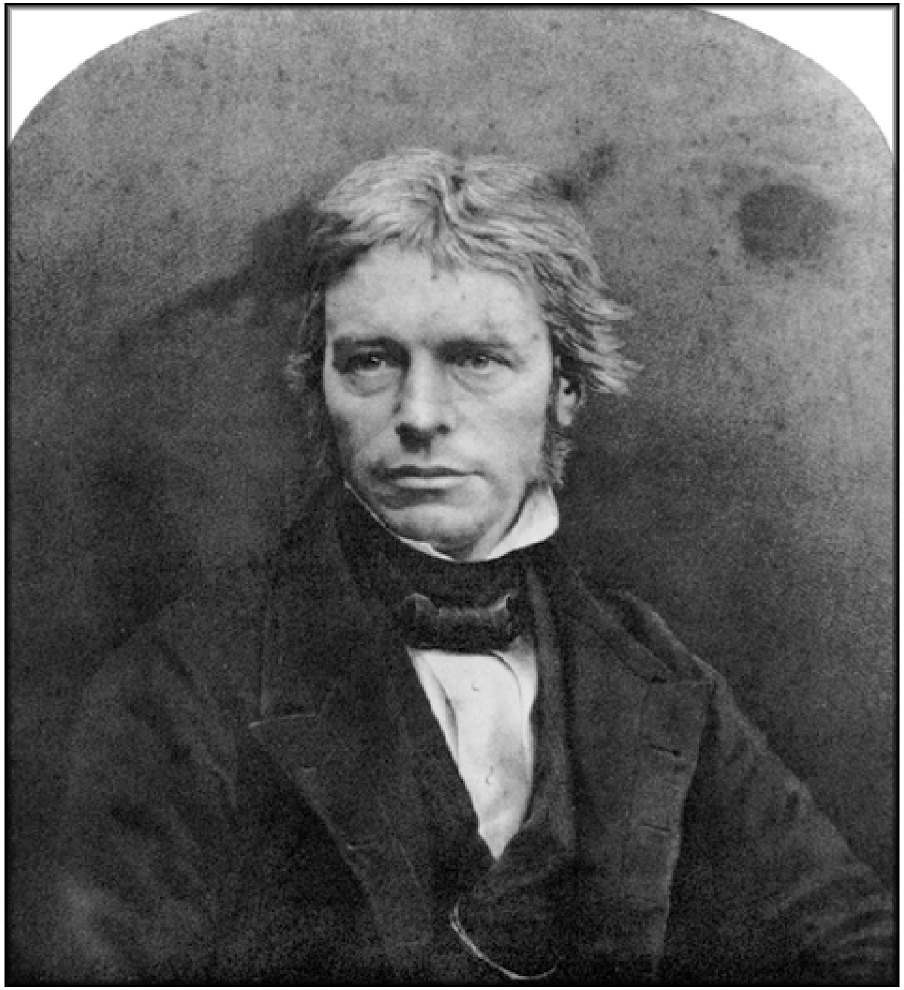
Diffusion of the different ions – exploring the chemical selectivity.

Broad lines (T_2 ~ ms) require large (up to 10 T/m) gradients.





The net charge transport (ion conductivity) is lowered in the isotropic phase by ion pairing.



Thank You!