Ionic association: harmful and useful manifestations

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Early development: Arrhenius-Ostwald dissociation concept, ion pairs vs. ionic atmosphere

Spectroscopic evidence of ion pairs; conductivity and ion pairs; redox potentials and ion pairs

Bjerrum and Fouss Equations, limitations

Ion pairs as the intermediate species in redox reactions

Ionic association at the interfaces in respect to electrochemical reactions

Possible manifestations in electrocatalysis

Arrhenius concept of ionic dissociation assumed that ion pairs (non-dissociated electrolyte) are 'inactive'

Arrhenius,
Z. phys. Chem.
1 (1887) 631

<1900 translation>

In a former communication "On the Electrical Conductivity of Electrolytes," I have designated those molecules whose ions are independent of one another in their movements, as active; the remaining molecules, whose ions are firmly combined with one another, as inactive. I have also maintained it as probable, that in extreme dilution all the inactive molecules of an electrolyte are transformed into active.† This assumption I will make the basis of the calculations now to be carried out. I have designated the relation between the number of active molecules and the sum of the active and inactive molecules, as the activity coefficient.‡ The activity coefficient of an electrolyte at infinite dilution is therefore taken as *unity*. For smaller dilution it is less than *one*, and from the principles

Ostwald's 'law of dilution'

$$K = \frac{[M^+][A^-]}{[MA]} = \frac{\alpha^2 c}{1-\alpha} \quad \Rightarrow \quad \alpha = \frac{\sqrt{K^2 + 4Kc} - K}{2c}$$

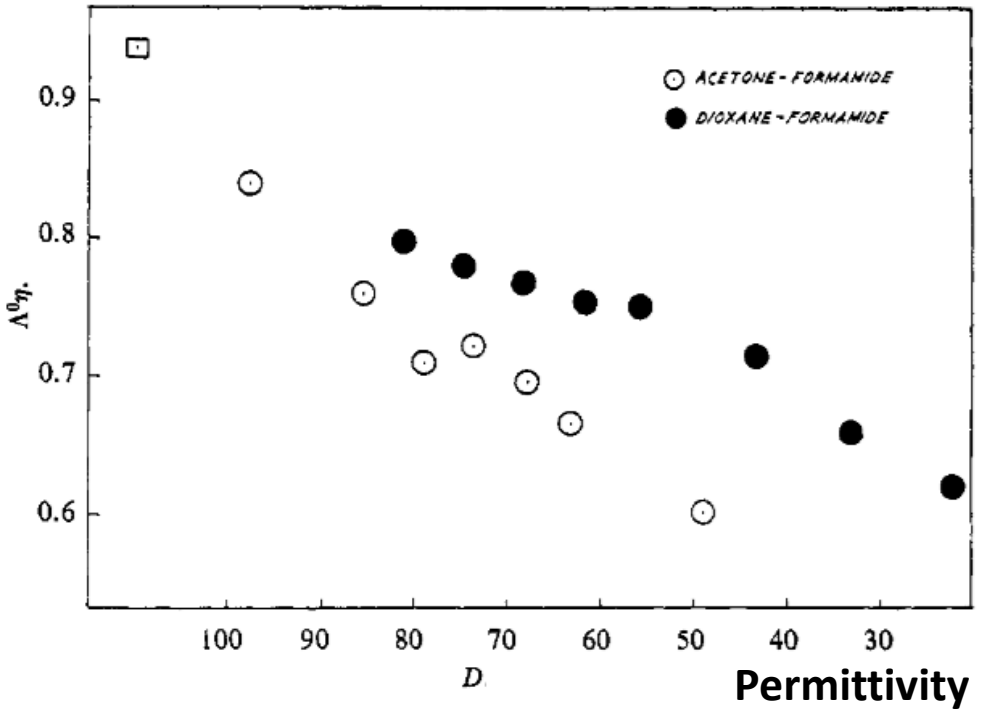
Later development (Debye-Hückel): ionic atmosphere effects, which include ion pairs formation

m/mol kg^{-1}	Li_2SO_4	Na_2SO_4	K_2SO_4	Rb_2SO_4	Cs_2SO_4	H_2SO_4
0.001	0.887	0.886	0.885	0.886	0.885	0.804
0.002	0.847	0.846	0.844	0.845	0.845	0.740
0.005	0.780	0.777	0.772	0.776	0.775	0.634
0.010	0.716	0.712	0.704	0.710	0.709	0.542
0.020	0.645	0.637	0.625	0.635	0.634	0.445
0.050	0.544	0.529	0.511	0.526	0.526	0.325
0.100	0.469	0.446	0.424	0.443	0.444	0.251
0.2	0.400	0.366	0.343	0.365	0.369	0.195
0.5	0.325	0.296	0.251	0.274	0.285	0.146
1.0	0.284	0.237	-	0.217	0.233	0.125

CRC Handbook of Chemistry and Physics

Qualitatively, one can judge about ion pairs formation from concentration dependence of activity coefficients

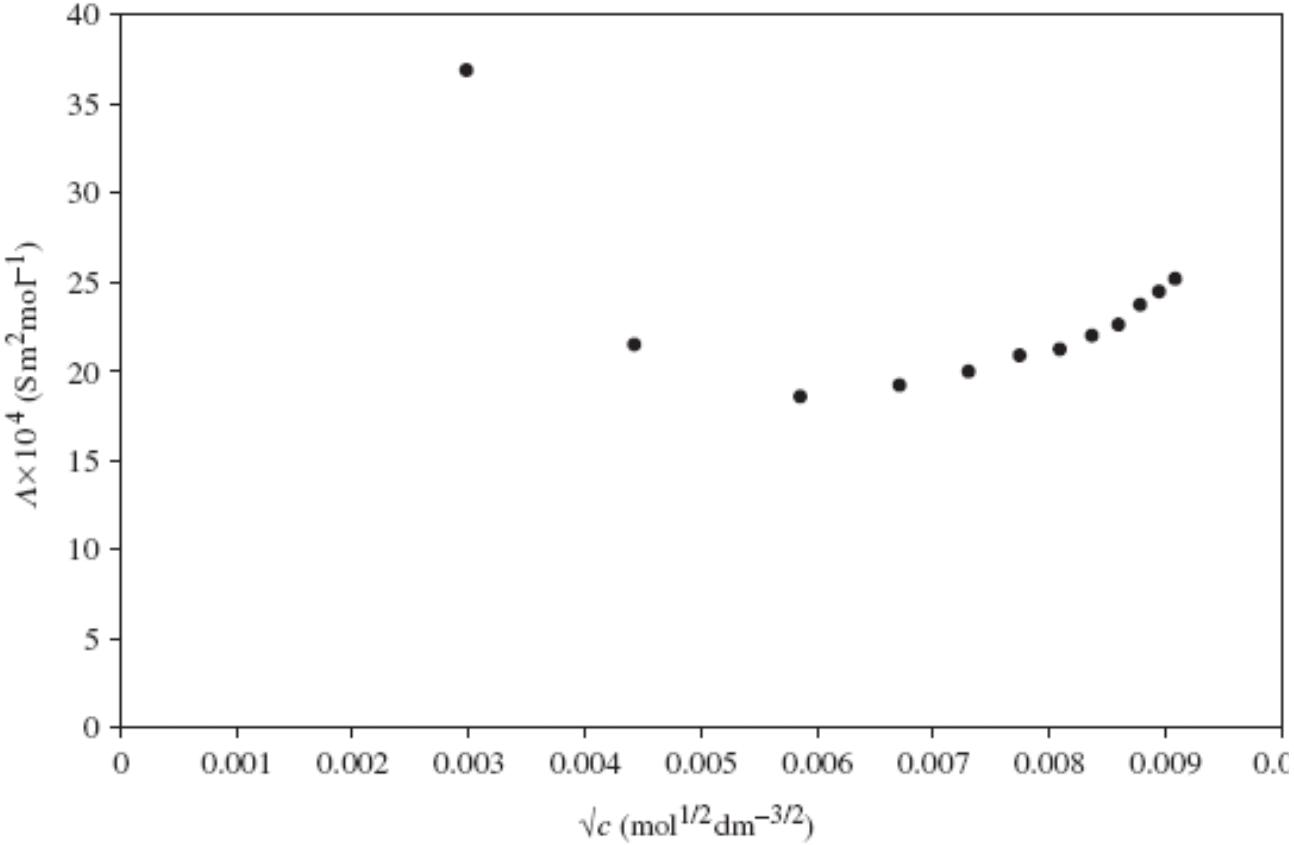
Conductivity·Viscosity



J. Amer. Chem. Soc. 87 (1965) 5691

Qualitatively, one can also judge from Walden product

Observation of the second association step in conductivity vs concentration dependence



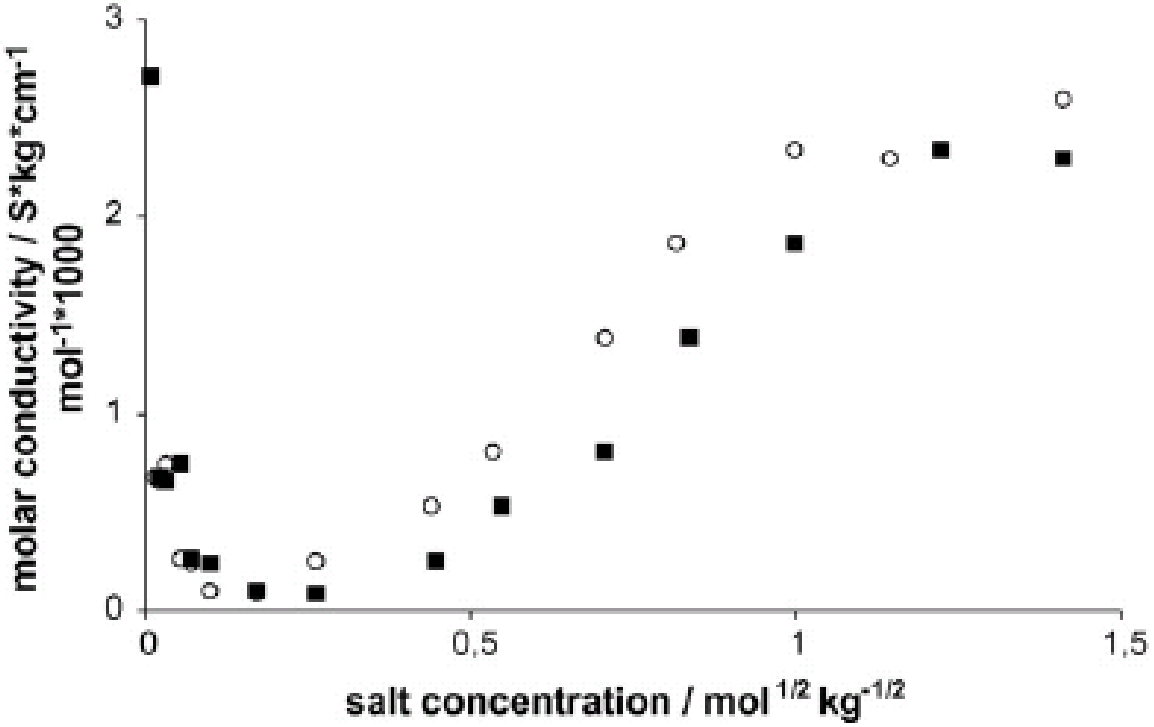
NaI in tetrahydrofuran

Phys. Chem. Liquids 45 (2007) 67

$$M^+ + A^- \leftrightarrow M^+ \cdots A^- \leftrightarrow MA$$

$$MA + M^+ \leftrightarrow MA\,M^+$$

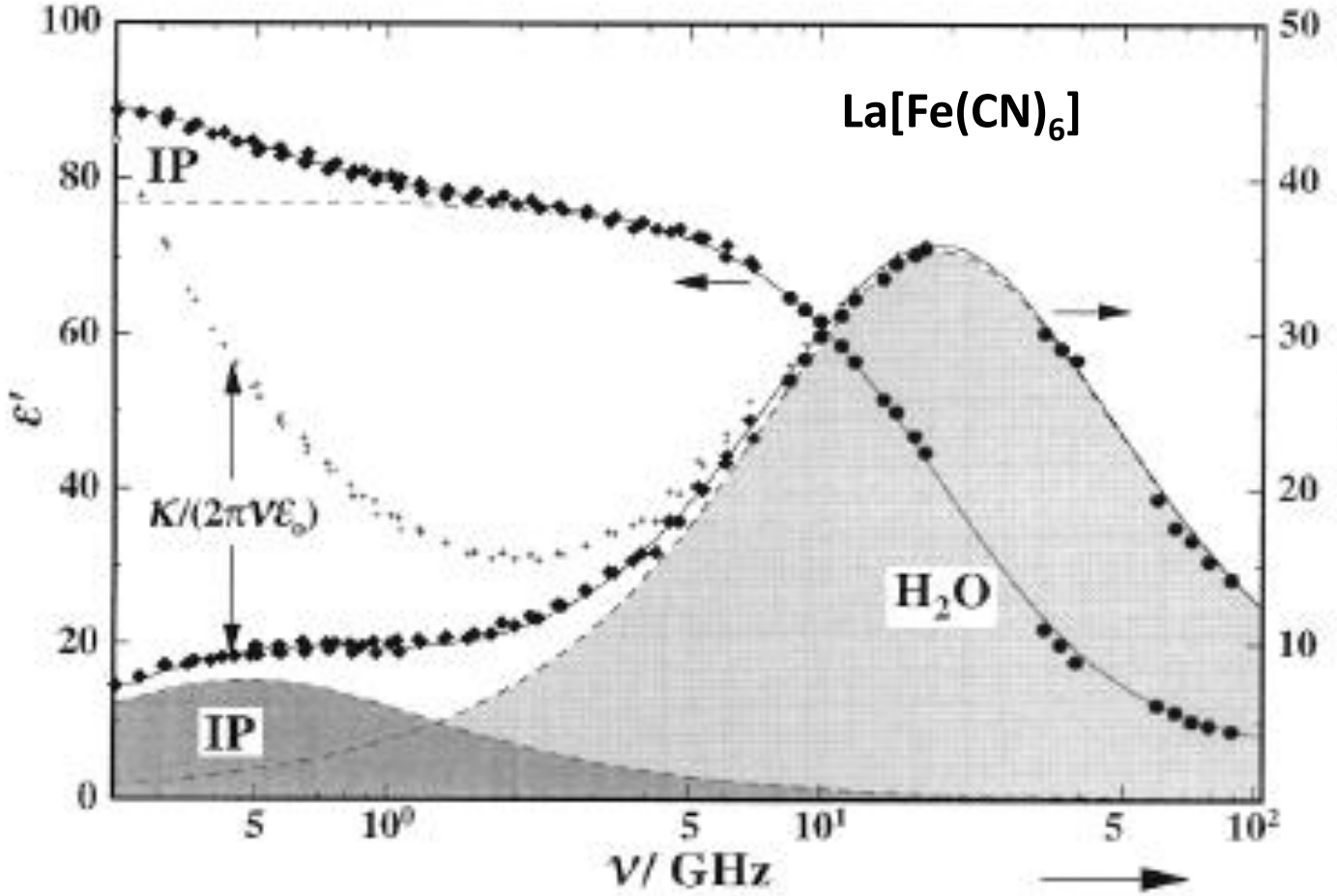
$$MA + A^- \leftrightarrow MA\,A^-.$$

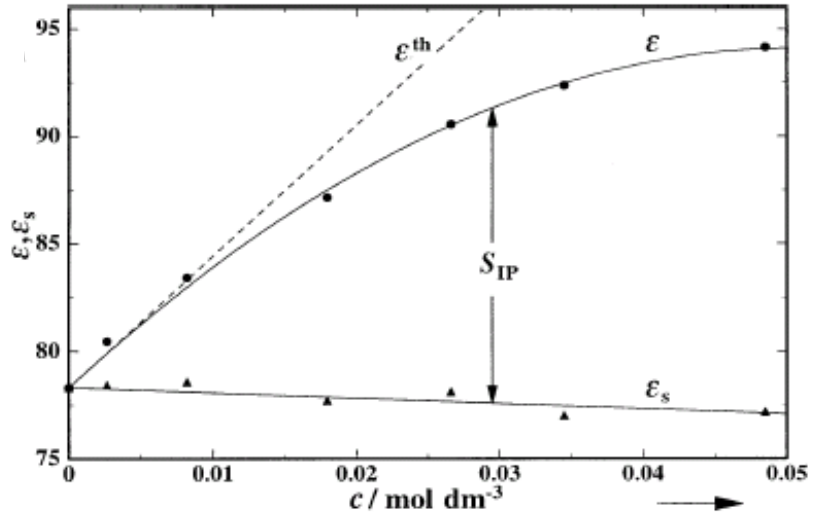


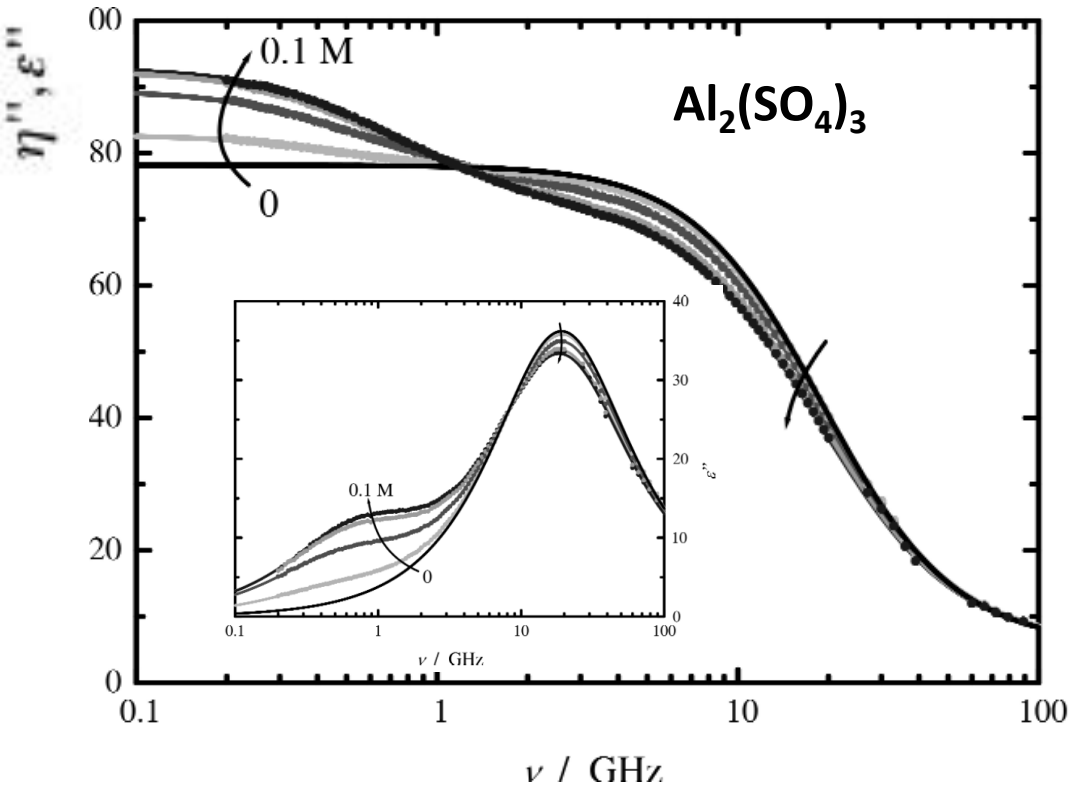
$LiBF_4$ in imethoxyethane + dioxane mixture

Electrochim. Acta 53 (2007) 1527

Direct observation of ion pairs in dielectric spectra



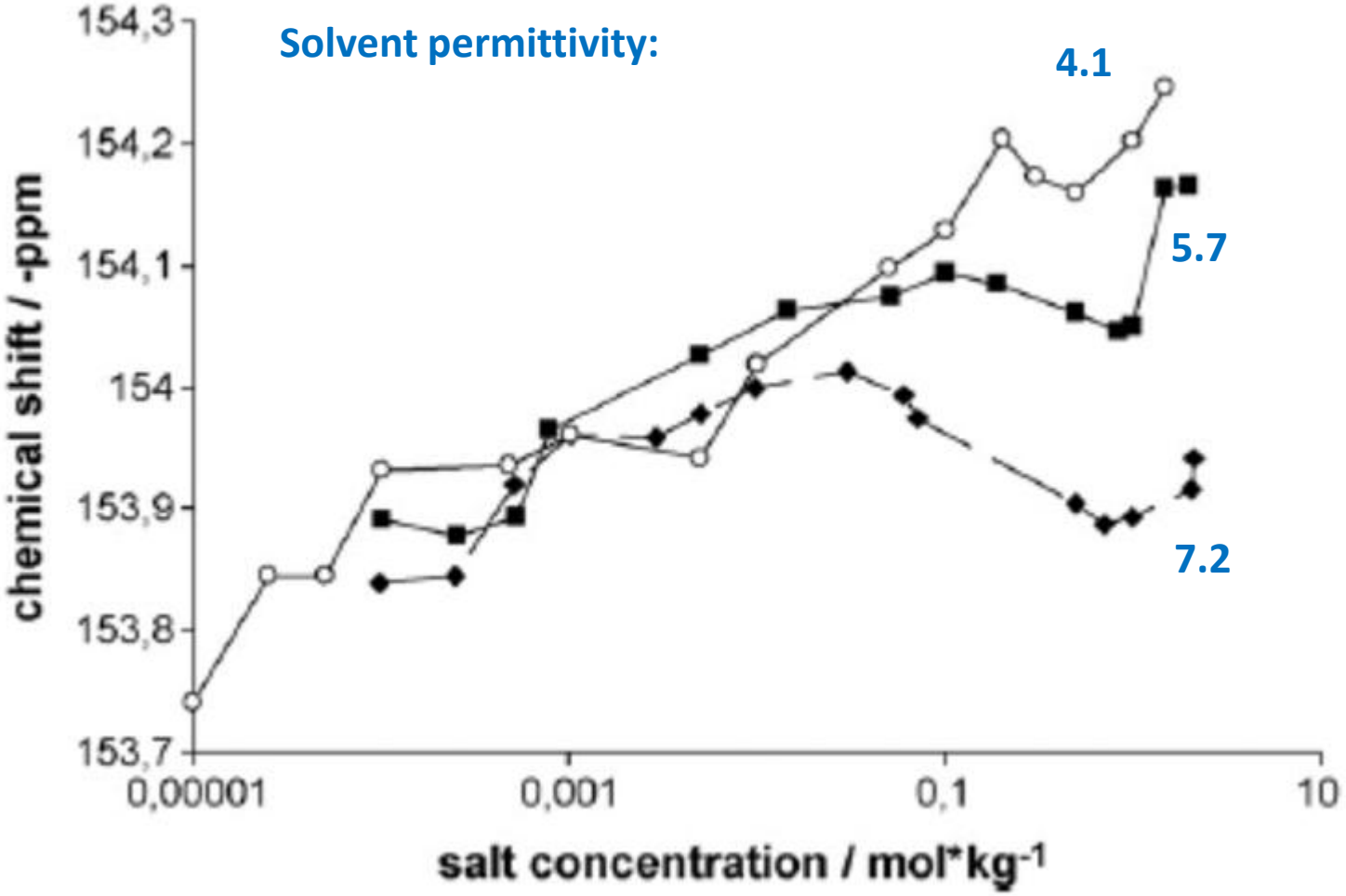


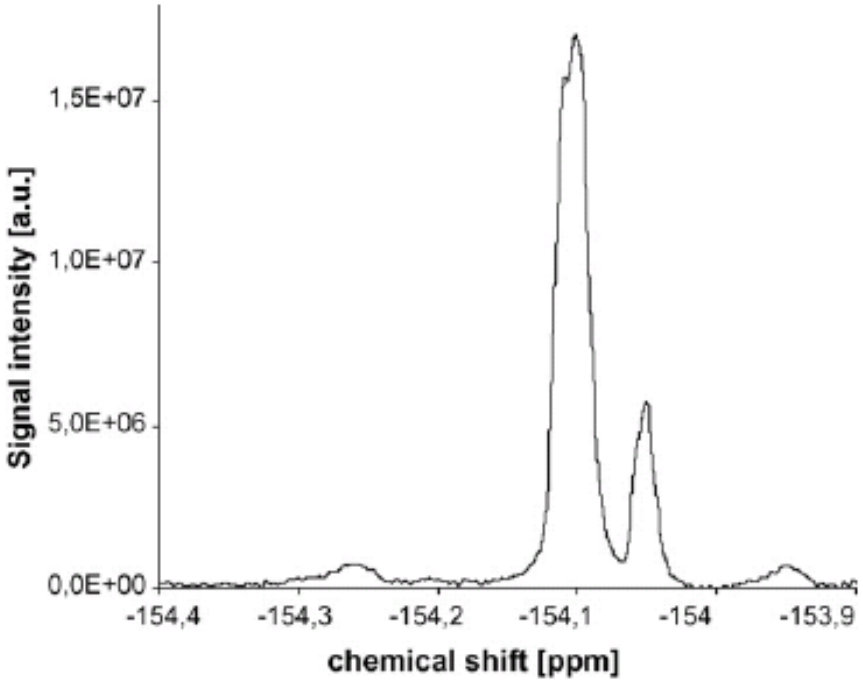


Pure Appl. Chem. 80 (2008) 1239

Observation of ion pairs in NMR spectra

^{19}F NMR in $LiBF_4$ solutions





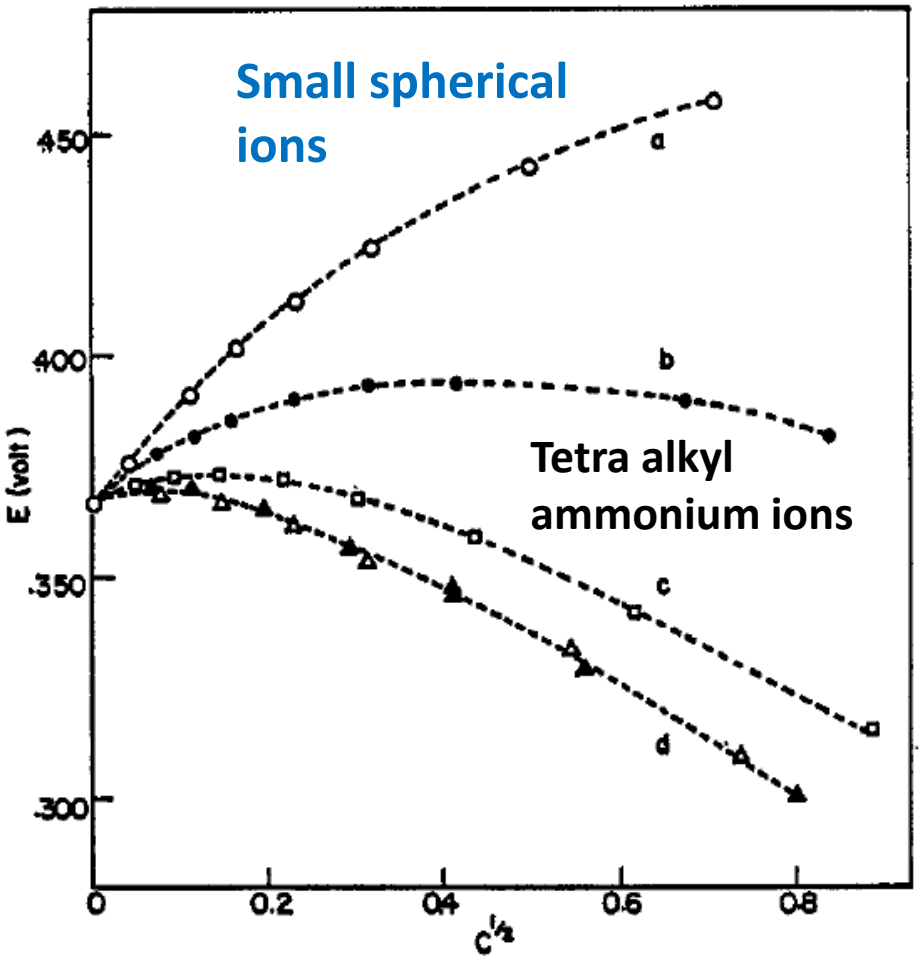
Electrochim. Acta 53 (2007) 1527

Dimethoxyethane + dioxane mixtures

Redox potentials determined by association constants

$$K^+ + Fe(CN)_6^{4-} \rightleftharpoons KFe(CN)_6^{3-}$$

$$K^+ + Fe(CN)_6^{3-} \rightleftharpoons KFe(CN)_6^{2-}$$



Temperature, °C	9.9	15.0	25.0	35.0	40.0	45.0
Equilibrium 1						
(1.00×10^{-3} *M* $K_4Fe(CN)_6$)	88.9	94.0	101	...	102	103
Equilibrium 2						
(1.25×10^{-3} *M* $K_3Fe(CN)_6$)	16.1	18.2	17.6	18.6	...	18.9

$[K_3Fe(CN)_6] \times 10^{-3}$	[Free K^+] $\times 10^{-3}$	*K*	Ionic strength $\times 10^{-3}$	Log *K*° (eq 4)
1.00	2.95	19.4	5.84	1.50
1.25	3.67	17.6	7.27	1.48
2.00	5.84	14.6	11.5	1.45
2.50	7.27	14.3	14.3	1.46
5.00	14.3	10.8	28.0	1.44
			Mean	1.46 ± 0.02

J. Phys. Chem. 71 (1967) 2016; 2022

Attempts of quantitative description of association constants $K_A = \frac{a_{IP}}{a_{M^+} a_{X^-}}$

Niels J. Bjerrum (1879-1958)

Raymond M. Fuoss (1905-1987)

Z. phys. Chem. 119 (1926) 145

J. Amer. Chem. Soc. 80 (1958)

$$K_A = \frac{4\pi N_A r_{min}^3 \exp\left[-\frac{U(r_{min})}{kT}\right]}{3000}$$

$$U(r_{min}) = \frac{z_1 z_2 e_0^2}{\varepsilon r_{min}(1 + B\sqrt{J} \cdot r_{min})}$$

$$K_A = \frac{4\pi N_A}{1000}\left(\frac{z_+ z_- e^2}{\varepsilon kT}\right)^3 \int_2^b e^y y^{-4}\, dy,$$

$$b = \frac{\lambda_B}{a} = \frac{z_+ z_- e^2}{\varepsilon a kT} = \frac{2q}{a},$$

Bjerrum length

- **purely electrostatic models (no specific bonding)**
- **homogeneously charged spherical ions**
- **continuum model of solvent**

Anion-anion association → cationic catalysis

The Oxidation of Iodide Ion by Persulfate Ion.

$$\log k = \log k_0 + z_A z_B \sqrt{\mu}$$

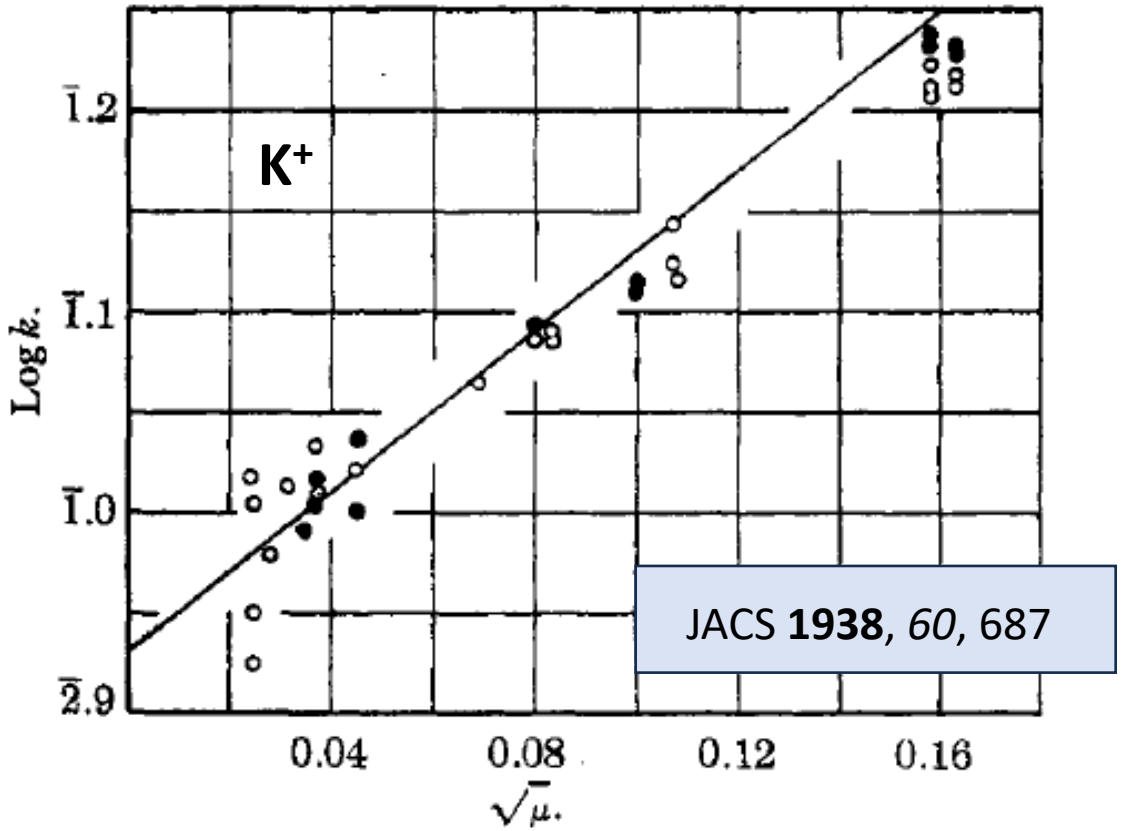
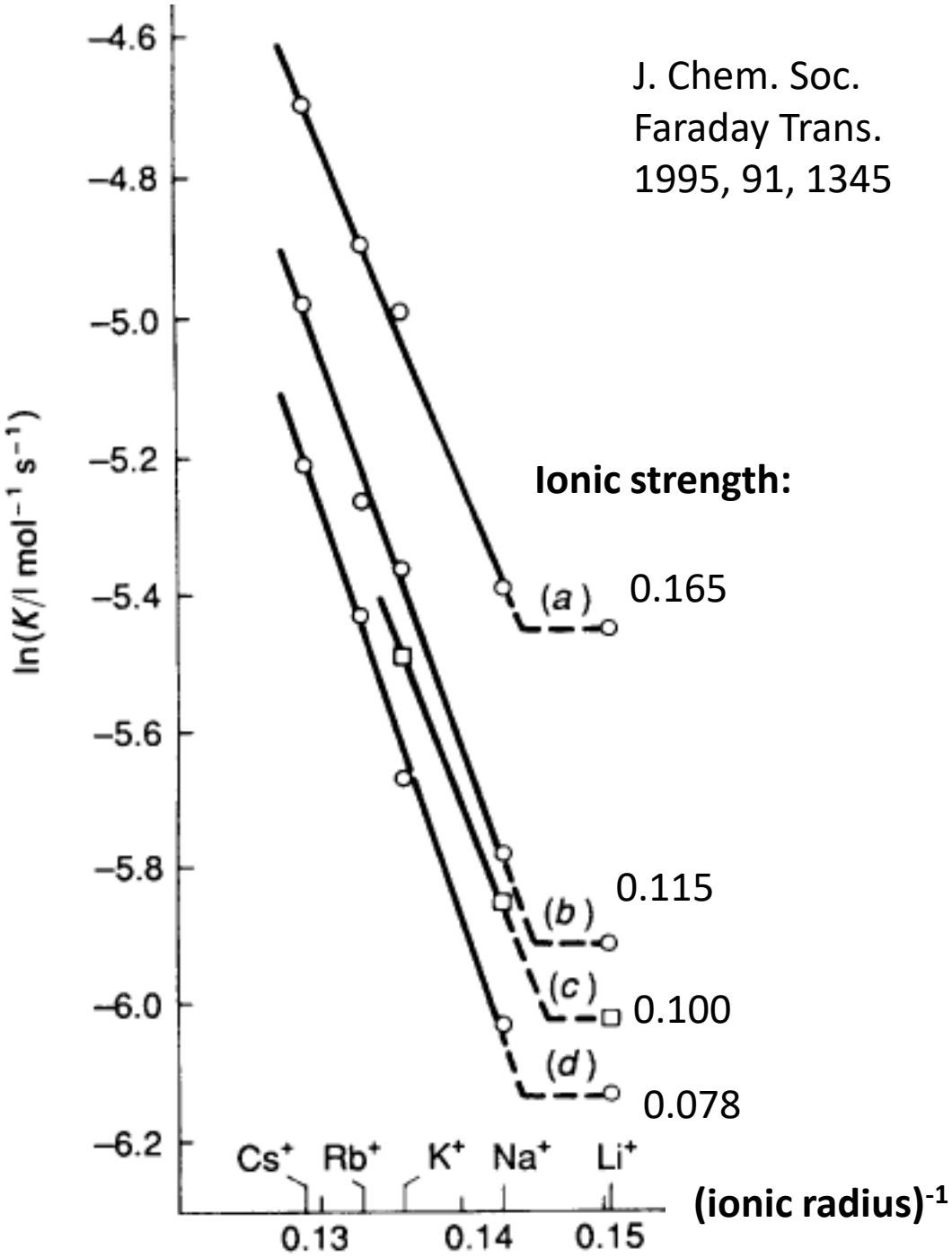


Fig. 3.—The plot of log k *vs.* $\sqrt{\mu}$: black circles, potassium nitrate present.

JACS **1938**, *60*, 687

Review: Chem. Rev. **1962**,*62*, 185

J. Chem. Soc. Faraday Trans. 1995, 91, 1345



Cationic catalysis, formal “geometric” consideration

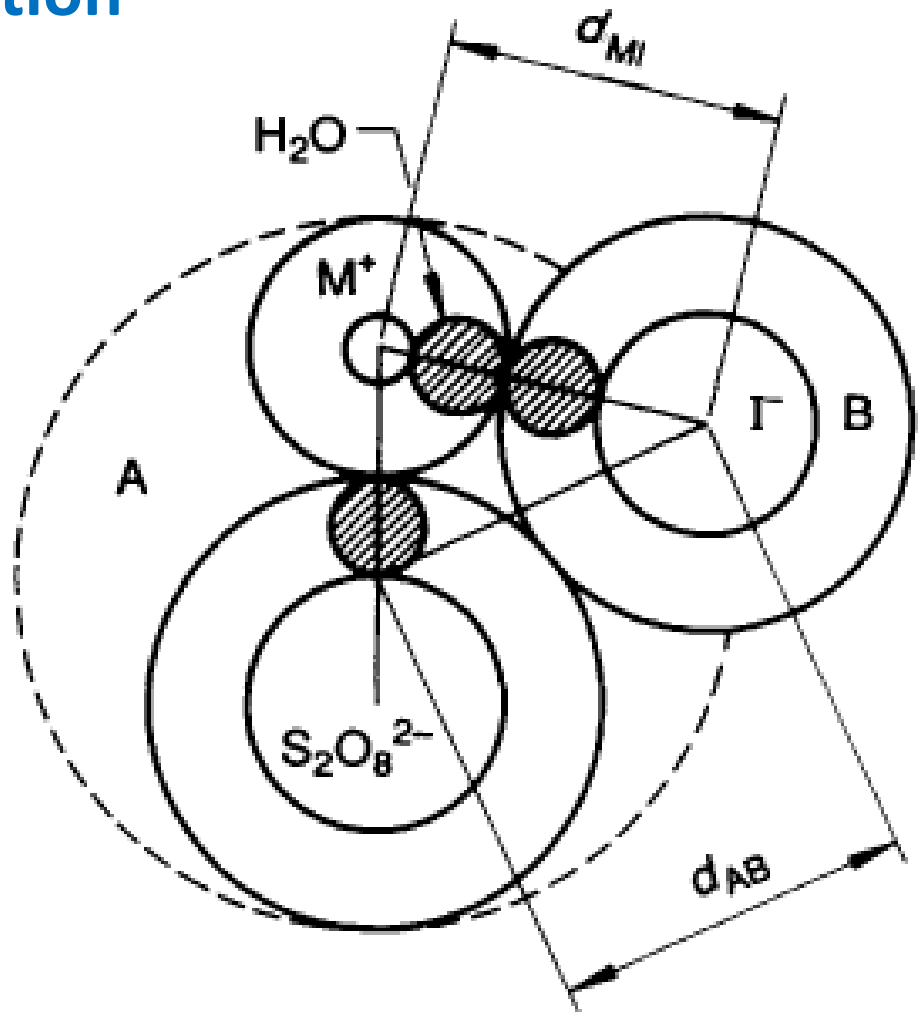
$$\ln K = \ln K_0 - \frac{Z_A Z_B N_A e^2}{\varepsilon_r R T d_{AB}}$$

$$\ln K = a - b\,\frac{1}{d_{MI}}$$

J. Chem. Soc. Faraday Trans. 1995, 91, 1345

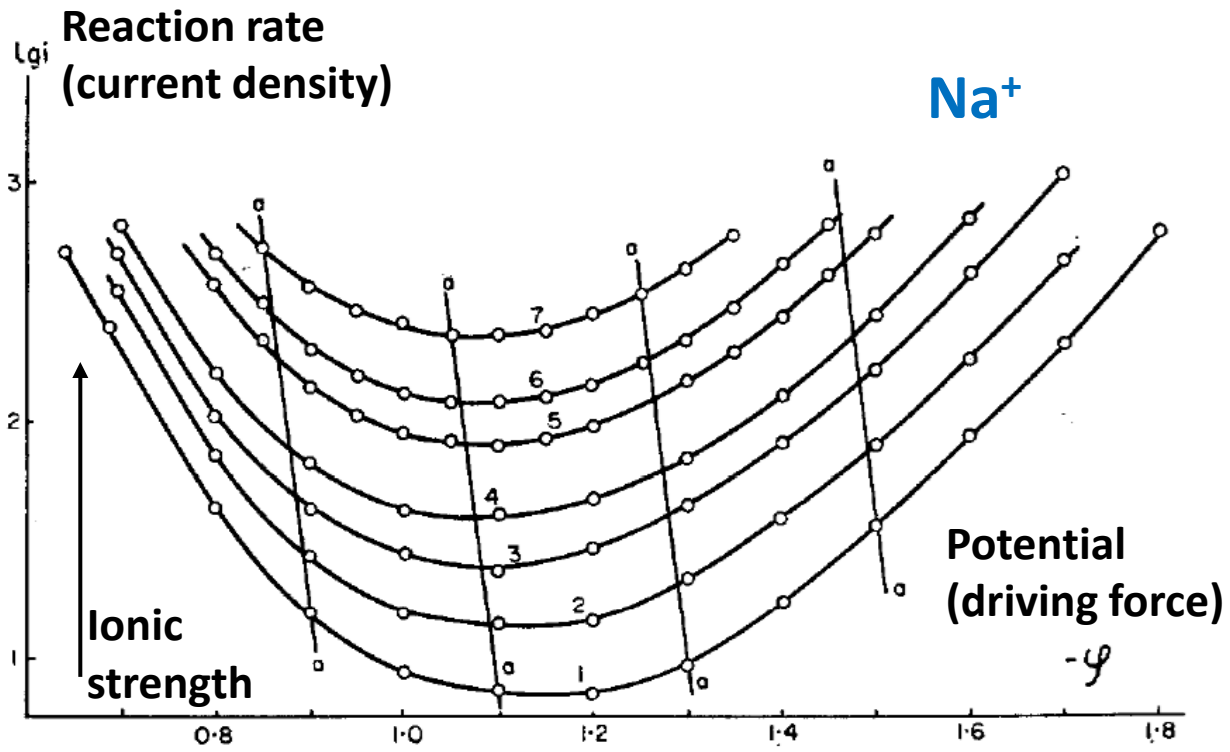
Table 1 Second-order rate constants ($K/10^{-3}$ l mol^{-1} s^{-1}) for the reaction of $S_2O_8^{2-}$ with I^- at 25 °C

	I/mol l^{-1}			
alkali-metal iodide	0.165	0.115	0.075	0.1[a]
LiI	4.30	2.71	2.17	2.43
NaI	4.55	3.07	2.41	2.84
KI	6.85	4.70	3.45	4.12
RbI	7.75	5.52	4.38	—
CsI	9.15	6.87	5.45	—



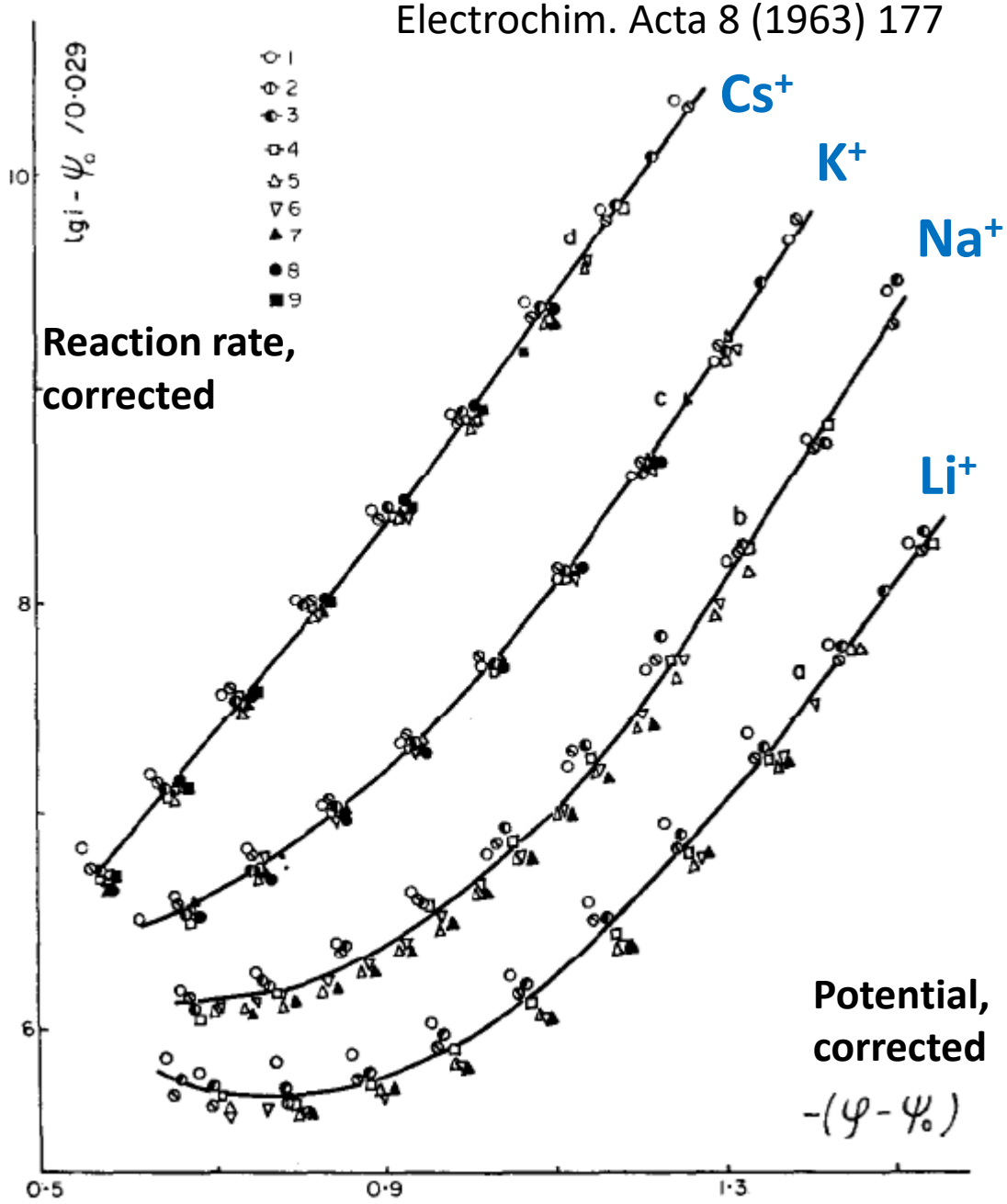
For more realistic consideration, non-spherical shape and inhomogeneous charge distribution should be addressed.

Cationic catalysis of electrochemical reactions: anions reduction at the negatively charged surface



Account for non-local repulsion resolves the problem of non-monotonic shape, but it is helpless in respect to cations effects

Electrochim. Acta 8 (1963) 177



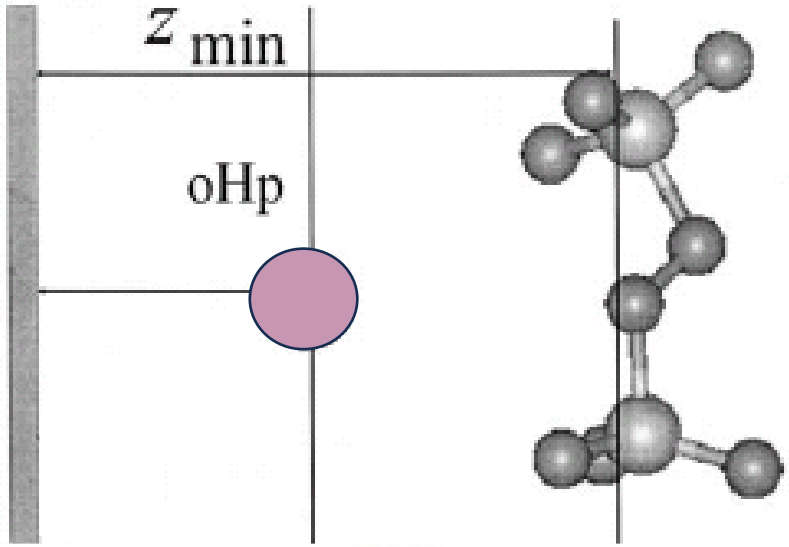
Cationic catalysis of electrochemical reactions

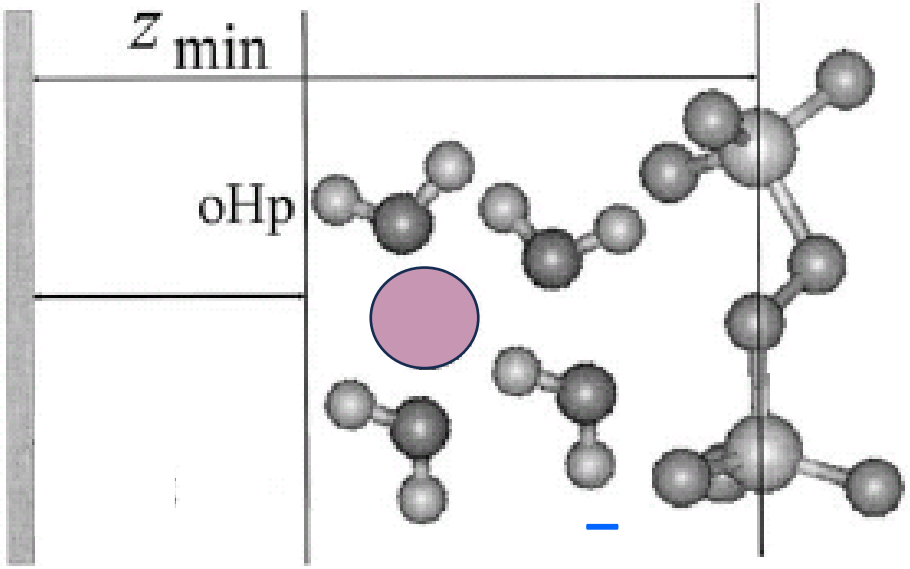
J. Electroanal. Chem. 552 (2003) 261;
582 (2005) 118

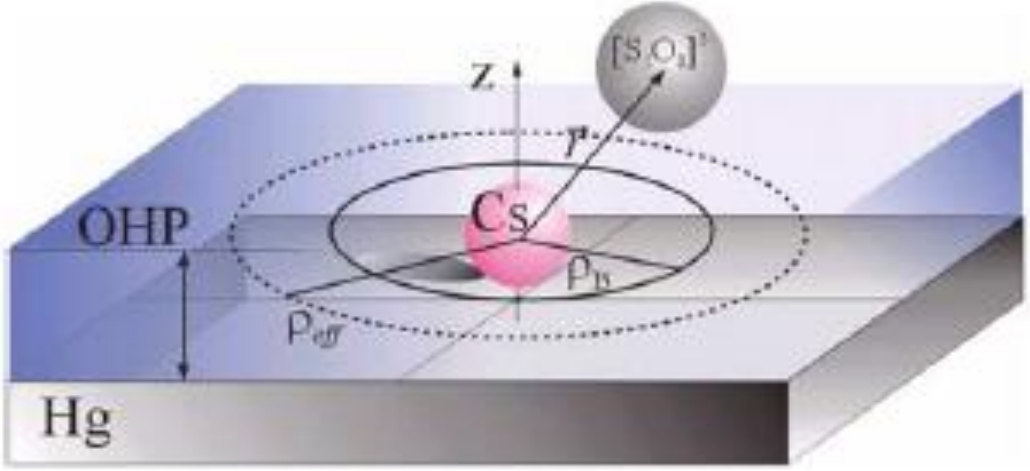
"local" ion pair

ion pair "from the bulk"

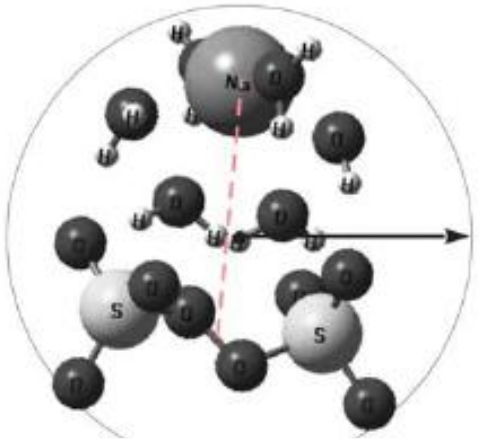
Hg electrode, negatively charged



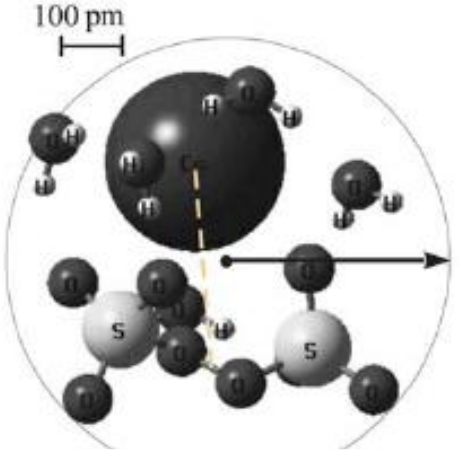




$$U_{\text{loc}}(\rho, z, x_1) = q_{\text{ads}} \cdot \Phi(\rho, z, x_1)$$



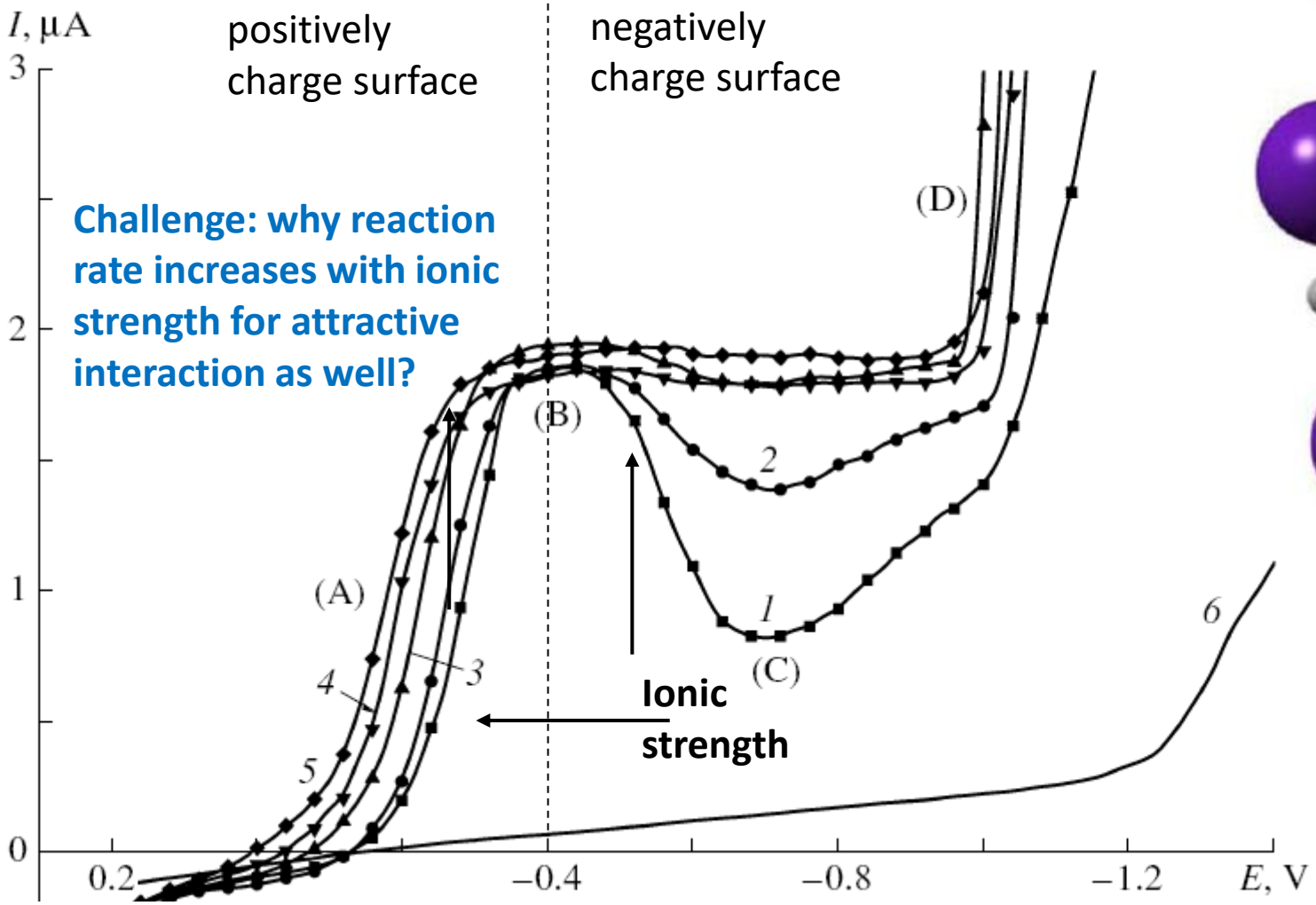
Ion pairs with **sodium**



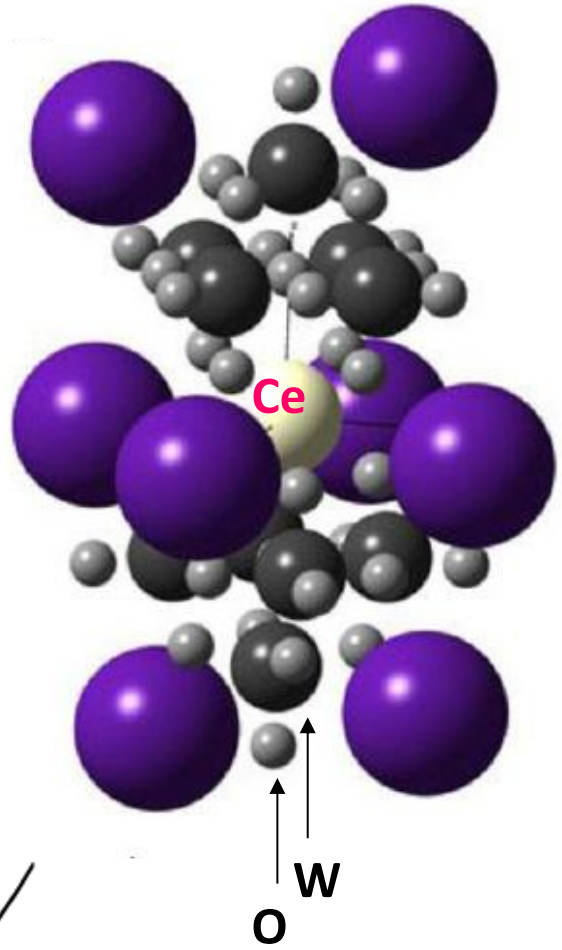
and with **cesium**

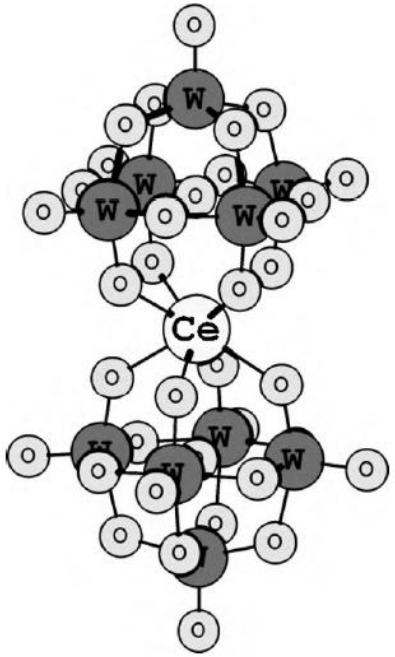
Cationic catalysis of electrochemical reactions, polyoxometalate challenge

$$[Ce^{IV}W_{10}O_{36}]^{8-} + e = [Ce^{III}W_{10}O_{36}]^{9-}$$



Challenge: why reaction rate increases with ionic strength for attractive interaction as well?



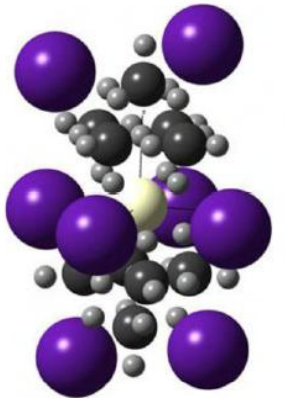


Rus. J. Electrohem. 40 (2004) 500
J. Solid State Electrochem. 10 (2006) 157
Electrochim. Acta 55 (2010) 6064

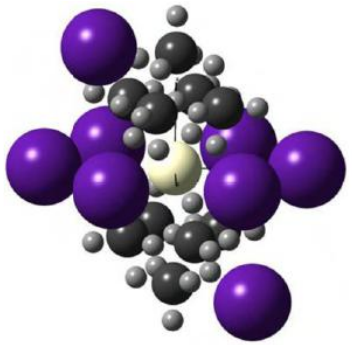
Polyoxometalate anions, multistep ionic association

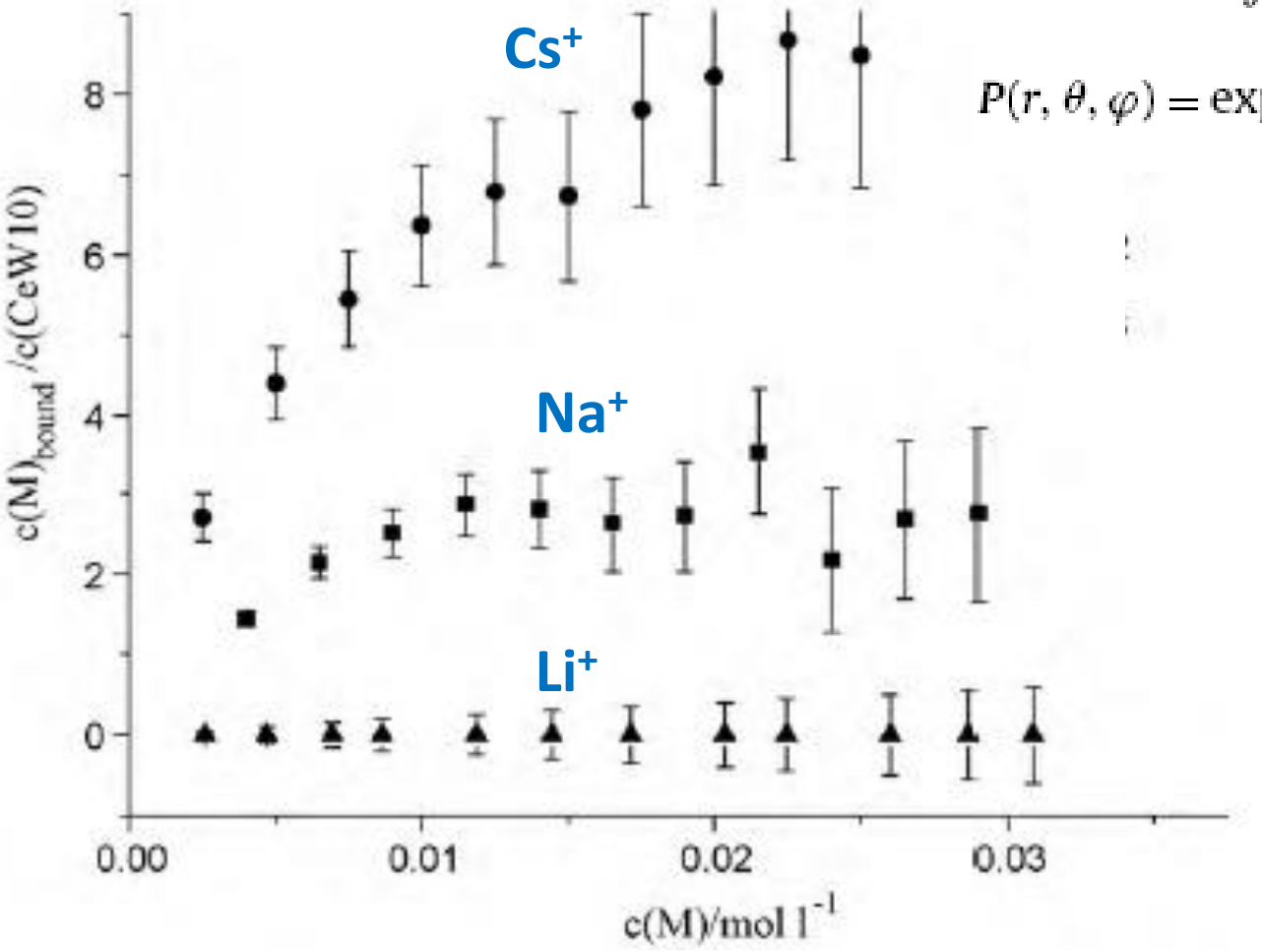
$$K_{ass} = N_A 10^{-3} \int_{V-V_0} P(r, \theta, \varphi)\, d\Omega,$$

$$P(r, \theta, \varphi) = \exp\left\{-\frac{U_{el}(r, \theta, \varphi)}{\varepsilon k_B T}\right\}$$



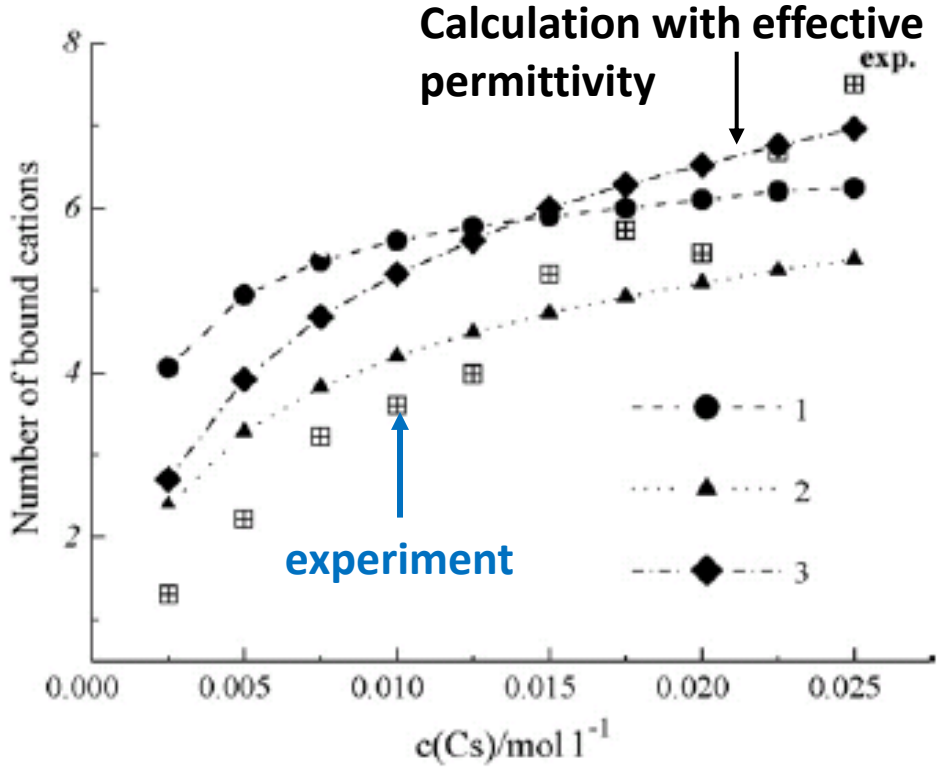
or





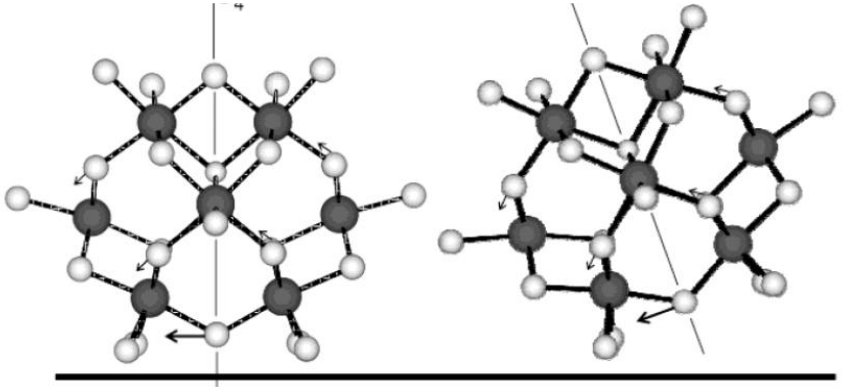
Measured by Ion-selective electrodes

Two former steps correspond to innersphere association; further steps follow Fuoss Eq



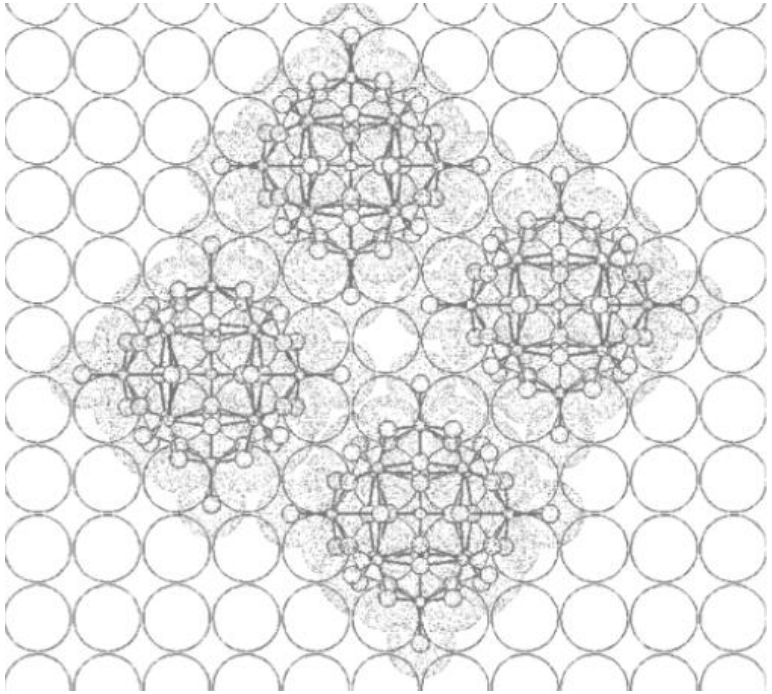
Electrochim. Acta 55 (2010) 6064

Polyoxometalate challenge: the answer is adsorption of ionic associates



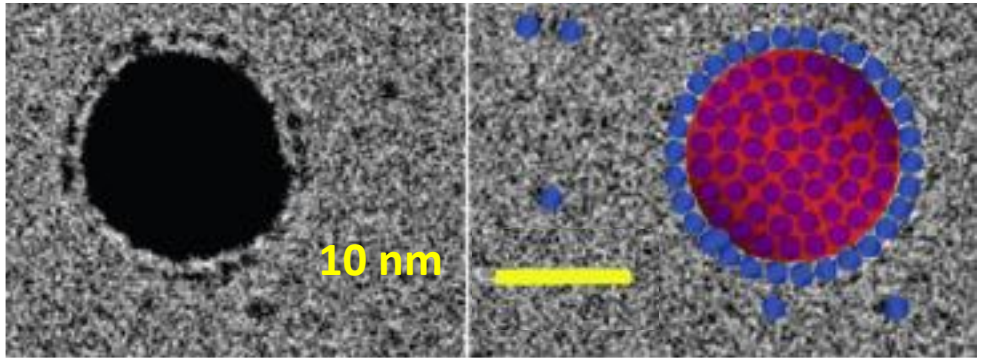
Answer from IR spectra of adsorbates: very strong polyoxometalate-surface bonding via external oxygens

J. Phys. Chem. B. 108 (2004) 1974



Answer from STM and XAS: very high surface coverage for polyoxometalates, only weakly affected by surface charge

J. Amer. Chem. Soc. 123 (2001) 8838



Answer from low-temperature TEM of gold colloid particles stabilized by polyoxometalate

J. Amer. Chem. Soc. 131 (2009) 17412

Enormous Coulomb repulsion of the multicharged anions is only possible if many cations are co-adsorbed.

The shift of redox potentials easily discovers ion pairs formation

$$\boxed{\text{A}:}\ \mathrm{Ox} + \mathrm{C} \leftrightarrow [\mathrm{Ox}\cdot\mathrm{C}]$$

$$[\mathrm{Ox}\cdot\mathrm{C}] + e^- \xrightarrow{E_N} [\mathrm{Red}\cdot\mathrm{C}]$$

From ΔEp analysis, Scheme A is concluded

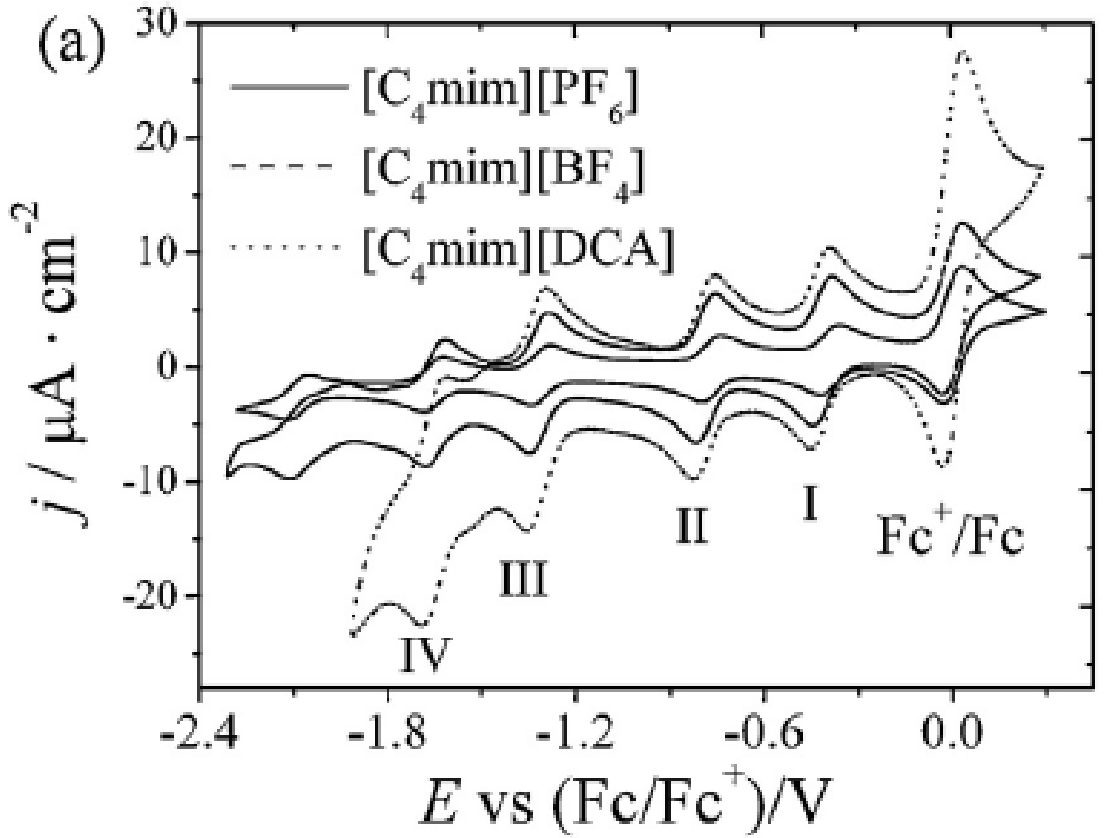
$$\boxed{\text{B}:}\ \mathrm{Ox} + e^- \rightarrow \mathrm{Red}$$

$$\mathrm{Red} + \mathrm{C} \rightarrow [\mathrm{Red}\cdot\mathrm{C}]$$

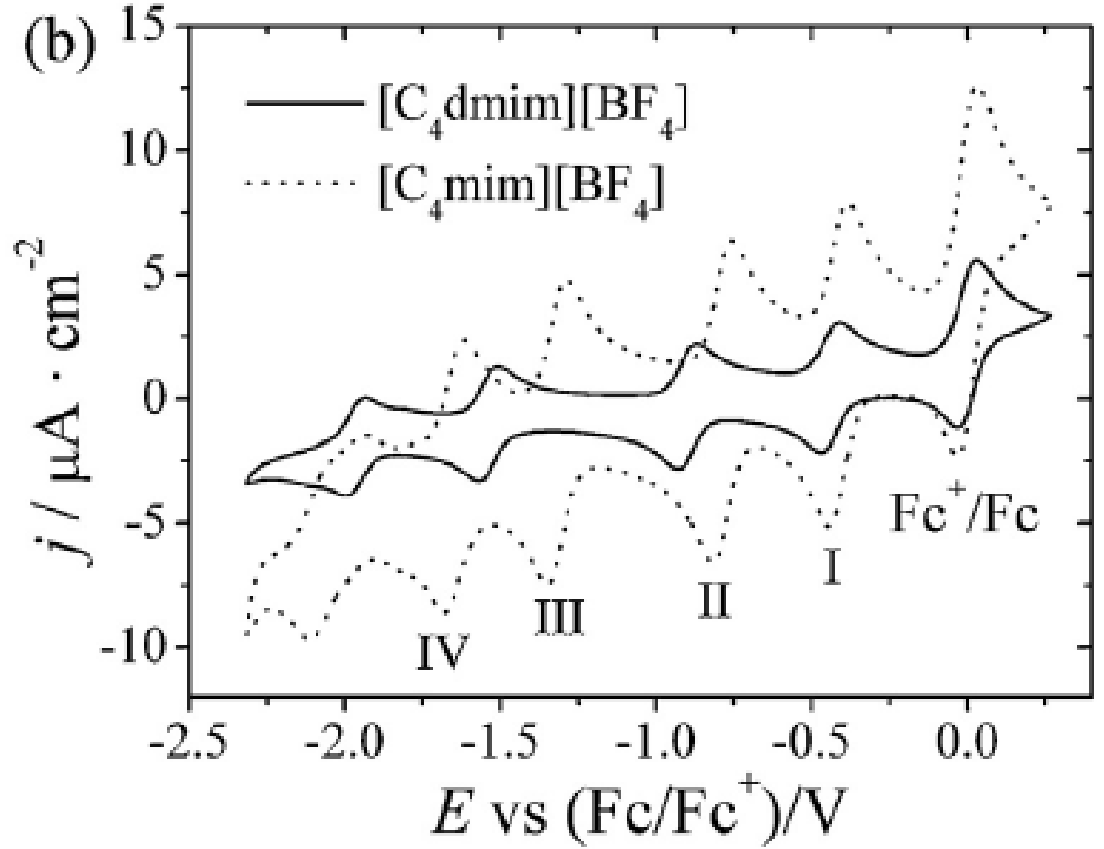
Electrochim. Acta 103 (2013) 243

$(Bu_4N)_3PW_{12}O_4$

in ILs with identical cation

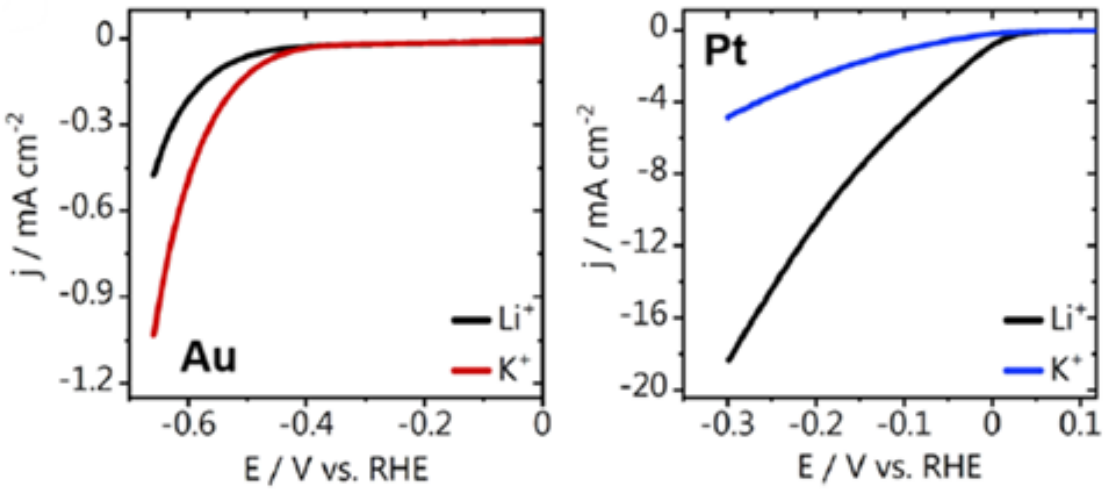


in ILs with identical anion

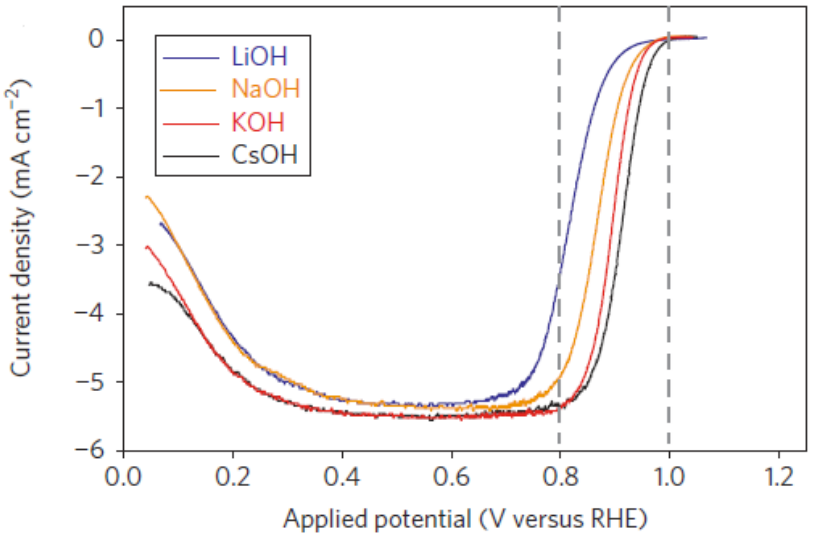


Currently going mainstream: cations effects in electrocatalysis

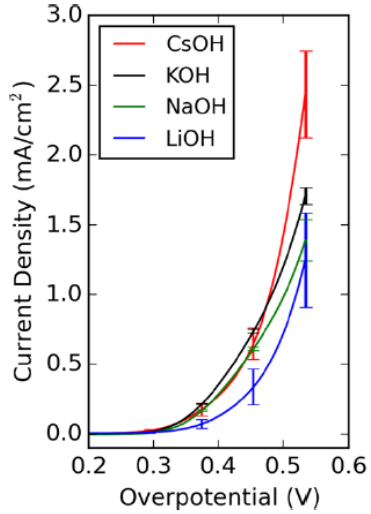
Hydrogen evolution



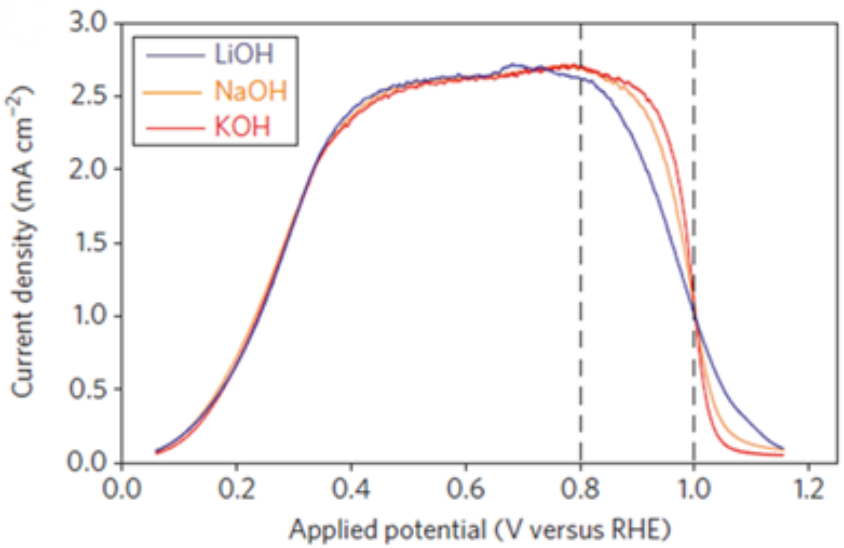
Oxygen reduction



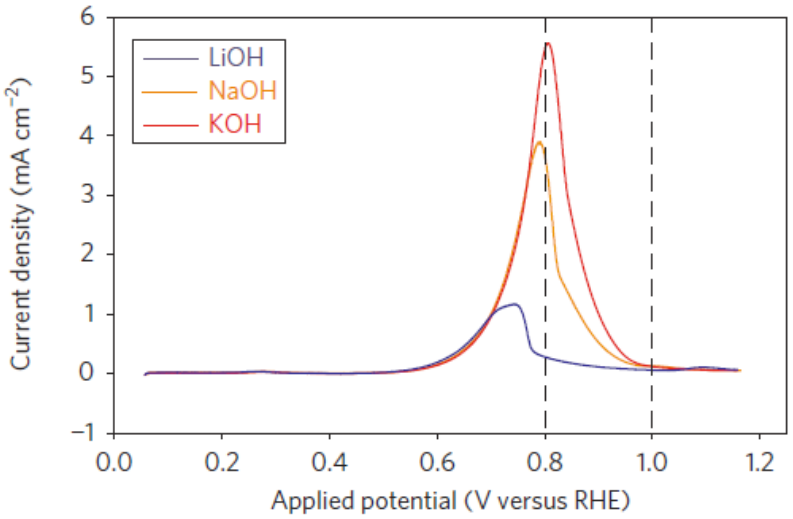
Oxygen evolution



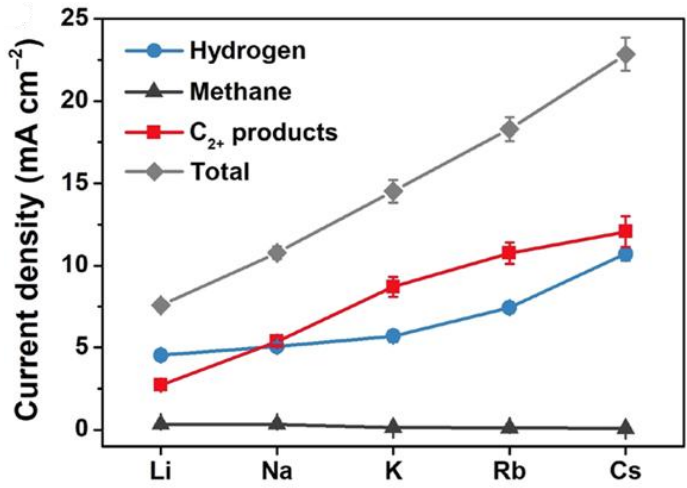
Hydrogen oxidation



Methanol oxidation



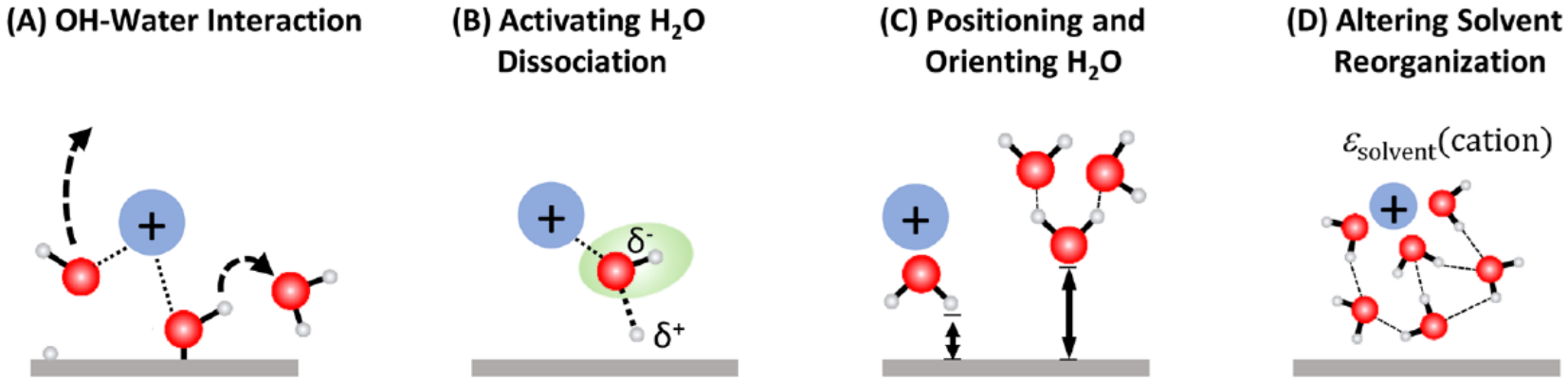
Carbon dioxide reduction



Hypotheses under discussion can be roughly separated into two groups

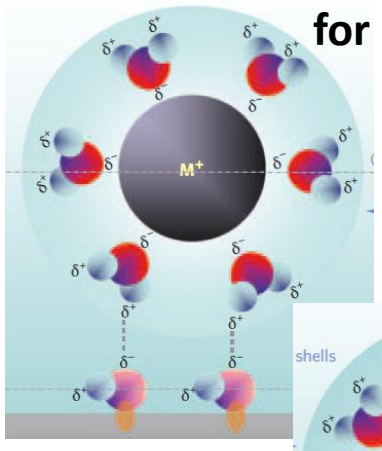
Group 1: effects on water (on its dissociative adsorption, stability, orientation at the surface, and mutual orientation)

J. Chem. Phys. 151 (2019) 160902

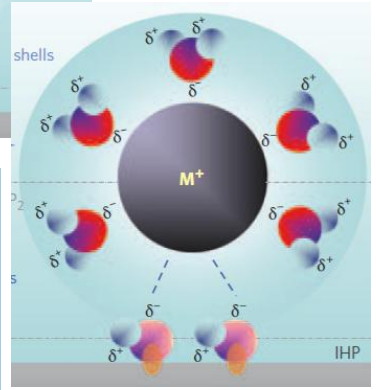


For both groups, and for the choice between them, cations localization is crucial:

Suspected for Cs^+, K^+

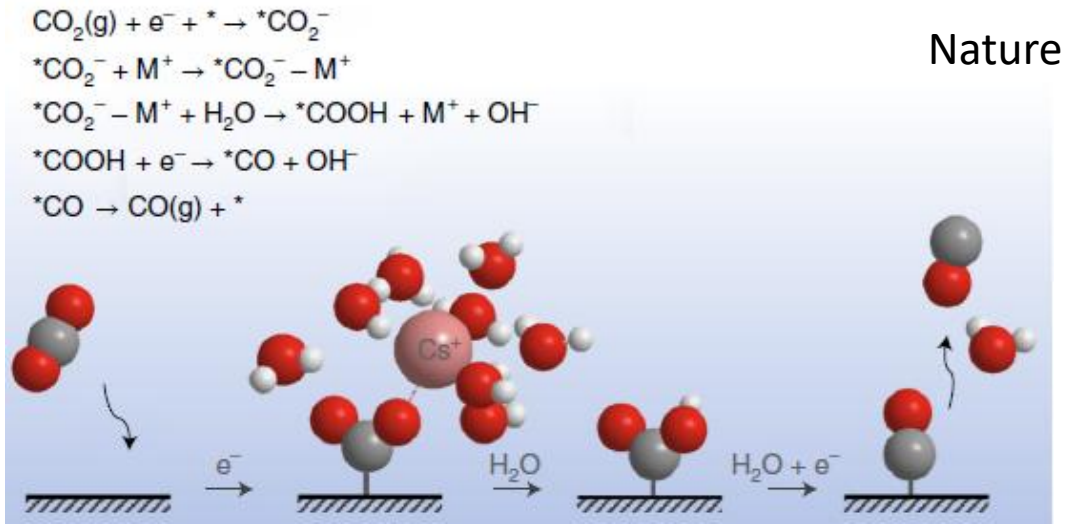


Suspected for Na^+, Li^+



Group 2: ionic association with reactants or intermediate species (e.g., $CO_2^{\bullet -}$, $O_2^{\bullet -}$)

Nature Catal. 4 (2021) 654-662



Contrary to reactions mentioned above, electrocatalytic reactions assume typical location of reaction layer directly at the surface. This allows application of the same molecular modeling techniques, but makes permittivity uncertainties even more essential.

Slovenian details, in brief

https://www.ijs.si/ijsw/V001/JSI

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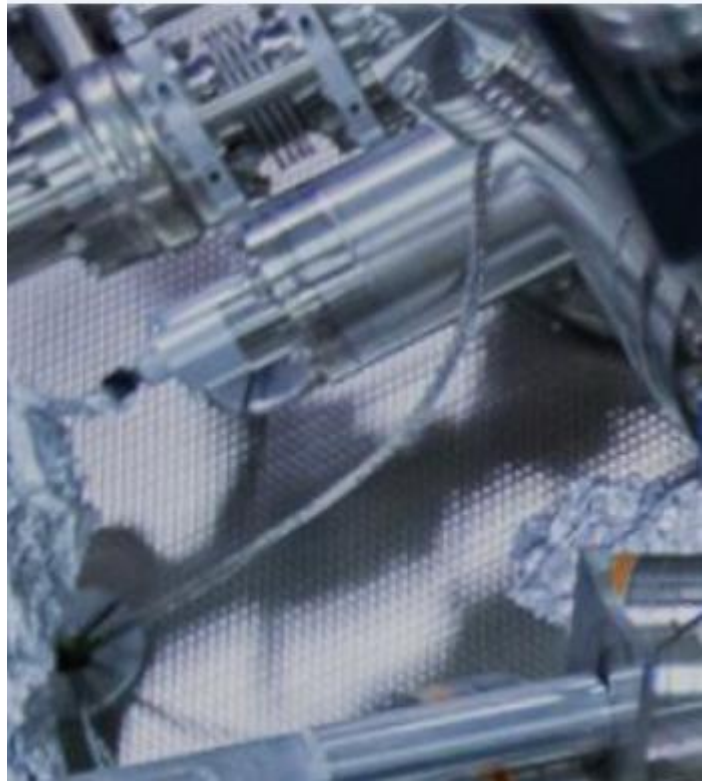
What can we do for you



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Electrifying **ideas**
that catalyze **progress**.

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Konstantin N. Mikhelson (StPetersburg): potentiometry with ion-selective electrodes

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