Charged interface and its effects on heterogeneous electron transfer: experimental information creating challenges and verification tools for theory.

# 2. Electron transfer at Hg-like electrodes

- Frumkin correction and attempts of its refinement, as aimed to explain qualitatively striking effects (*mostly known for reactions with electrode-reactant repulsion*)
- Consequences: potential-dependent contributions to electron transfer beyond overpotential and work terms
- Corrected Tafel vs. corrected Marcus plots, activationless electron transfer
- Solvent effects, adiabaticity
- Closer to electrocatalysis: comments on cations effects and distant-dependent solvent reorganization

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Based on a series of joint works with **Renat R. Nazmutdinov** (Kazan) and his team, with participation of **Michael Probst** (Innsbruck), **Ron W. Fawcett** (Davis), and with a great help from Frumkin Inst theoreticians (**Alexander Kuznetsov, Yuri Kharkats**).

#### **General approach**

When dealing with multifactor problem, make a choice of effect which (at least intuitively) is determined by **a single predominating factor**.

Do not fight for quantitative agreement with certain experiment. Instead, look for

- reliable explanation of various experiments (at least qualitative, but better semi-quantitative),
- absence of qualitative contradictions with any available experiment.

Use all discovered **deviations** from experiment as a hint, to involve new model ideas.

#### Methodology

The treatment is always based on **analytical** theory.

Computational work only aims to estimate the **parameters**, or their ratios, or upper/lower limits. This usually results in appearance of numerous scenarios.

Try to reject as many scenarios as possible by comparing with experiment. Continue with a limited number of scenarios.

#### Frumkin correction (1933), example for cathodic reaction O + e $\rightarrow$ R



*Various forms of these Eqs:* G.A. Tsirlina, J. Solid State Electrochem. 21 (**2017**) 1833 – 1845; 28 (**2024**) 981-993

Data treatment for outer-sphere reactions (two steps) for a series with various supporting electrolyte concentrations c

$$i = nFc_{0} kexp\left(\frac{zF\psi_{x}}{RT}\right) exp\left(\frac{\alpha F(|\eta| + \psi_{x})}{RT}\right)$$
Bare reactant  
or ion pairs? What is the location of  
effective point charge?

#### 2. Construct corrected Tafel plots

$$\ln i + \frac{zF\psi_x}{RT} = const + \frac{\alpha F(|\eta| + \psi_x)}{RT}$$

Make a choice if x resulting in coinciding curves for all c.

#### Compare for various electrode metals.

(If the resulting curve is non-linear, consider possible origin of non-linearity.)

#### A.N.Frumkin, O.A. Petry, N.V. Nikolaeva-Fedorovich, Electrochim. Acta 8 (1963) 177-192

This *z* was initially considered as the "mean reactant charge in solution bulk". More precisely, it is the bulk charge of the reactant which reduction is predominating.

**Determine z** 

At constant negative electrode charge  $\sigma$ , if  $|\sigma|$  is not too low (> 7-10  $\mu$ C/cm<sup>2</sup>), and the reactant is anion,

$$\psi_x = const + \frac{RT}{F} \ln c$$

$$\left(\frac{\partial \log i}{\partial \log c}\right)_{\sigma} = -z$$

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A.N.Frumkin, O.A. Petry, N.V. Nikolaeva-Fedorovich, Electrochim. Acta 8 (**1963**) 177-192

#### Reaction O + e ← R with reactant-electrode repulsion (cation oxidation at positively charged electrode)



+ Pit disappears after correction

- + Values for two *c* become closer, coincide at low overpotentials
- **Non-linearity**,  $\alpha$  decreases with overpotential (like for [Fe(CN)<sub>6</sub>]<sup>3-</sup> reduction) - **Anions** 'catalytic' effects are evident

L. Gierst, P. Cornelissen P, Coll. Czech. Chem. Commun. 25 (**1960**) 3004 - 3015



#### **Attempts to refine Frumkin correction**



1. Consider geometry and charge distribution in reactant and product, quantum chemistry.

For each i th atom, determine the local charge  $q_i$  and distance from the electrode  $z_i$ . Using Gouy-Chapman Eq, calculate  $\psi_i(z_i).$ 

- non-local electrostatic reactant/electrode interaction
- rate constant and transfer coefficient are potential-independent

More realistic estimate of work terms for multiatomic reactants of non-spherical shape and/or with complex charge distribution

> 2. Use either effective charges, or effective  $\psi_x$  for corrected Tafel plots.

**Oversimplification:** no account for dielectric cavity, or very approximate. However, the goal is not to quantify for certain reactant, but to compare reactants with essentially different charge distribution, and to estimate possible effects of reactant orientation.

R.R. Nazmutdinov, G.A. Tsirlina, Yu.I. Kharkats, O.A. Petrii, M. Probst, J. Phys. Chem. B 102 (1998) 677-686; R.R. Nazmutdinov, G.A. Tsirlina, O.A. Petrii, Yu.I. Kharkats, A.M. Kuznetsov, Electrochim. Acta 45 (2000) 3521-3536

**Basic problem has no simple solution:** the distance of closest approach  $x_{min}$  remains unknown. To address it, only self-consistent consideration of transmission coefficient, reorganization energy, and work terms can help.

Attempts to refine Frumkin correction using effective values: narrow intervals of potential/electrode charge. Mercury



W.R. Fawcett, M. Hromadova, G.A. Tsirlina, R.R. Nazmutdinov, J. Electroanal. Chem. 498 (2001) 93-104;
M.Yu. Rusanova, G.A. Tsirlina, R.R. Nazmutdinov, W.R. Fawcett, J. Phys. Chem. A 109 (2005) 1348-1358;
R.R. Nazmutdinov, M.Yu. Rusanova, D. VanderPorten, G.A. Tsirlina, W.R. Fawcett, J. Phys. Chem. C 113 (2009) 2881-2890.

Note: effective reactant charge depends on the electrode charge in a wide range.

Orientational effects: square complex anions undergoing two-step hydrolysis



Mercury electrode, 0.5 mM K<sub>2</sub>PtCl<sub>4</sub>

Orientational effects and the increase of overlap with negative free electrode charge (?), [CrEDTA]<sup>-</sup>



R.R. Nazmutdinov, G.A. Tsirlina,Yu.I. Kharkats, O.A. Petrii, M. Probst, J. Phys. Chem. B 102 (**1998**) 677-686; *see also* Russ. J. Electrochem. 34 (**1998**) 325-333

*Theoretical prediction:* A.A. Kornyshev, A.M. Kuznetsov, J. Ulstrup, J. Phys. Chem. 98 (**1994**) 3832-3837

**The strongest repulsion** (oxygens close to the

surface), higher interfacial concentrations are

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#### Increase of transmission coefficient with negative free charge?



overpotential

**Sluyters' series** 

Coinciding plots for In(Hg) and Tl(Hg): L. Koene, M. Sluyters-Rehbach, J.H. Sluyters, J. Electroanal. Chem. 402 (1996) 57-72

Different plots for amalgams and gallames: T.G.J. van Venrooij, M. Sluyters-Rehbach, J.H. Sluyters, J. Electroanal. Chem. 419 (**1996**) 61-70; 472 (**1999**) 64-70

**Opposite trend for individual Ga and Hg**: T.G.J. van Venrooij, M. Sluyters-Rehbach, J.H. Sluyters, J. Electroanal. Chem. 472 (**1999**) 53-63

Effects are comparable for Zn<sup>2+</sup> and [CrEDTA]<sup>-</sup>, calling into question the statement

rate constant and transfer coefficient are potential independent, both can be affected by the electrode charge

#### **Attempts to refine Frumkin correction**



- **point reactant** approximation
- **non-local** electrostatic reactant/electrode interaction
- rate constant and transfer coefficient are potentialindependent





Local interaction can be modeled by analogy with Fuoss approach.



R.R. Nazmutdinov, D.V. Glukhov, O.A. Petrii, G.A. Tsirlina, G.N. Botukhova, J.Electroanal. Chem. 552 (2003) 261-278;

R.R. Nazmutdinov, D.V. Glukhov, G.A. Tsirlina, O.A. Petrii, J.Electroanal. Chem. 582 (2005) 118-129.

and bare anion + account for local electrostatics  $\rightarrow$  different Cs/Na ratios of current; a number of scenario can be excluded

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The choice of possible configurations crucially depends on transmission coefficient



rate constant and transfer coefficient are potential-independent, can be affected by the electrode charge, both the quantity and the slope of its distance dependence

R.R. Nazmutdinov, D.V. Glukhov, O.A. Petrii, G.A. Tsirlina, G.N. Botukhova, J.Electroanal. Chem. 552 (**2003**) 261-278

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#### **Consequences of charge-dependent transmission coefficient: reaction volume**



R.R. Nazmutdinov, D.V. Glukhov, O.A. Petrii, G.A. Isirlina, G.N. Botukhova, J.Electroanal. Chem. 552 (**2003**) 261-278

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 $\delta x / pm$ 

hexacyanoferrate

Where we are?

- (1) If k depends on the electrode charge, experimental  $\alpha$  does not present the real transfer coefficient.
- (2) We are dealing with anions reactions at high overpotentials, and cannot see the region of low and mid overpotentials G.A. Tsirlina, N.V. Titova, R.R. Nazmutdinov, O.A.



Calculated for reorganization energies 70 and 90 kJ/mol

Experiment for 0.33 mM  $[Fe(CN)_{6}]^{3-}+1 \text{ mM KCl},$ with various versions of Frumkin correction and of ion pairs participation

Are we already in the activationless region?



Still too many unknowns, **BUT linearity criteria can be formulated.** To see how it works, we need the reaction to be observable **in mid overpotentials intervals**.

It must be reaction with repulsion, to avoid diffusion limitations in a wide potential interval.

P.A. Zagrebin, G.A. Tsirlina, R.R. Nazmutdinov, O.A. Petrii, M. Probst, J. Solid State Electrochem. 10 (**2006**) 157-167; *see also* P.A. Zagrebin, M.I. Borzenko, S.Yu. Vasil'ev, G.A. Tsirlina, Rus. J. Electrochem. 40 (**2004**) 500-509; P.A.Zagrebin, R.R.Nazmutdinov, E.A.Spector, M.I.Borzenko, G.A.Tsirlina, K.N.Mikhelson, Electrochim. Acta 55 (**2010**) 6064-6072.

#### Model reactant [H<sub>2</sub>CeW<sub>10</sub>O<sub>36</sub>]<sup>6-</sup>, single electron reduction at mid overpotentials





## An attempt to apply for high overpotentials interval. Evidence of activationless reaction.

**I.** Sign of  $2.3RT(\log(\chi) - \log(i)) - Fz\psi_1$ 





#### D.J. Bieman, W.R. Fawcett, J. Electroanal. Chem. 34 (**1972**) 27-39:

Independence on the electrode metal nature in the absence of reactant specific adsorption is in favor of **equilibrium** 'double layer' On Ag(?), Au, and Pt, anions reduction is surely inner-sphere. However, it is also not so far from activationless region.

The most intriguing is current increase at essentially negative electrode charge. Under activationless conditions, it can probably result from increase of the overlap?



Can anions reduction be adiabatic? Solvent (in particular, viscosity) effects on peroxodisulfate reduction in sugar syrups



complex.

N.V. Titova, V.K. Laurinavichute, Z.V. Kuzminova, G.A. Tsirlina, Chem. Physics 352 (2008) 345-352

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Dielectric spectrum is also too



0

sucrose

glucose

0

-7

-7

22

10.8

-13

O

3,5-

Can anions reduction be adiabatic? Solvent effects on peroxodisulfate reduction in water-ethylene glycol (EG) mixtures having three relaxation times



P.A. Zagrebin, R. Buchner, R.R. Nazmutdinov, G.A. Tsirlina, J. Phys. Chem. B 114 (**2010**) 311-320

Anomalous viscosity/relaxation time effect is more pronounced than in sugar syrups and overpotentialdependent. This is a challenge for theory (at this stage explanation is switching to shorter relaxation times). **Can contribute to current growth at high overpotentials.**  Long distance (surely diabatic) electron transfer with alkane thiol spacers: free and attached reactants



V.A. Nikitina, A.V. Rudnev, G.A. Tsirlina, T. Wandlowski, J. Phys. Chem. C 118 (**2014**) 15970-15977; V.A. Nikitina, S.A. Kislenko, R.R. Nazmutdinov, M.D. Bronshtein, G.A. Tsirlina, J. Phys. Chem. C 118 (**2014**) 6151–6164



#### Weaver's attempt to figure out 'double layer' effects beyond Frumkin correction



Entropy difference between the ions that form redox couples (rc) can be estimated from the **temperature dependence** of rc **formal potentials.** 

It is the highest for aqua complexes because of the strongest ligand bonding to outersphere water. Additional contribution to solvent reorganization is expected.

E.L. Yee, R.J. Cave, K.L. Guyer, P.D. Tyma, M.J. Weaver, J. Amer. Chem. Soc. 101 (**1979**) 1131-1137

Hg, Ag, Au, Pt:

- compare complexes having different charges and yet similar ligand structure, so that the reaction sites are likely to be similar:  $[Co(NH_3)_6]^{3+}$ ,  $[Co(NH_3)_5F]^{2+}$ ,  $[Co(NH_3)_5OH]^{2+}$ ;

- compare various aqua-complexes.

The pronounced difference of the **apparent rate constants** does not always correlate with the difference of reactants charge/size and electrode charge as considered in frames of Frumkin correction concept.

"Structure-demanding" and "structureundemanding" reactants; for the former, substantial increase in solvent ordering when going from M(II) to M(III) induces the asymmetry of reaction terms.  $\mathbf{\nabla}$ 

Complex pathways (e.g., strong adsorption, ligand exchange chemical steps).

S.W. Barr, K.L. Guyer, M.J. Weaver, J. Electroanal. Chem., 111 (**1980**) 41-59; P.D. Tyma, M.J. Weaver, J. Electroanal. Chem. 111 (**1980**) 195-210 Some reactions that were previously considered as the outer-sphere, probably involve adsorbed intermediates: V(III/II) and some other flow battery reactions.



Can be hopefully separated now using interfacial spectroscopy.

If some structuredemanding reaction is really single-step, one can use it as a probe to test water structure effects in other systems.



N. Roznyatovskaya, J. Noack, K. Pinkwart, J. Tübke, Curr. Opin. Electrochem. 19 (**2020**) 42-48

H. Agarwal, J. Florian, D. Pert, B. R. Goldsmith, N. Singh, ACS Catal. 13 (**2023**) 2223–2233

#### **Gierst's classification of cations**



### Weaver's data on cations effects on cation reduction $\frac{Cr(OH_2)_6^{3+} reduction}{Cr(NH_3)_6^{3+} reduction} = \frac{Cr(NH_3)_6^{3+} reduction}{Cr(NH_3)_6^{3+} reduction}$

| Electrolyte <sup>a</sup> | $-\log k_{app}^{b}$ | $\alpha_{app}{}^{c}$ | $-\log k_{\rm corr}^{\rm GCS^d}$ | $\alpha_{\rm corr}^{\rm GCS^e}$ | $-\log k_{app}^{b}$ | $\alpha_{app}^{c}$ | $\sim \log k_{app}^{GCS^d}$ | $\alpha^{GCS^e}_{cott}$ |
|--------------------------|---------------------|----------------------|----------------------------------|---------------------------------|---------------------|--------------------|-----------------------------|-------------------------|
| 0.5 M LiNO3              | 2.26                | 0.65                 | 4.36                             | 0.48                            | 2.83                | 0.81               | 4.93                        | 0.66                    |
| 0.5 M NaNO3              | 2.41                | 0.63                 | 4.53                             | 0.46                            | 3.03                | 0.79               | 5.17                        | 0.63                    |
| 0.5 M KNO3               | 2.44                | 0.62                 | 4.57                             | 0.45                            | 3.06                | 0.78               | 5.19                        | 0.62                    |
| 0.5 M RbNO <sub>3</sub>  | 2.48                | 0.61                 | 4.63                             | 0.43                            | 3.10                | 0.77               | 5.25                        | 0.60                    |
| $0.5 M C_{\rm SNO_2}$    | 2.69                | 0.58                 | 4.89                             | 0.39                            | 3.29                | 0.76               | 5.49                        | 0.58                    |

2.5-3.5 times **decrease** of both apparent rate constants and the values after usual Frumkin correction in Li.....Cs sequence.

This can hardly be explained by either local electrostatics, or by cation effect on solvent reorganization, only by the **difference in** group of reactants.

Ammino complex is assumed to be closer to the surface because of partial penetration of ligands to the inner layer.



r<sub>h</sub>,Ă

hydrated cation radius



#### Michael J. Weaver (1947-2002)

The last article on outersphere electron transfer: M.J. WeaverJ. J. Electroanal. Chem. 498 (**2001**) 105-116

M.J. Weaver, H.Y. Liu, Y. Im, Canad. J. Chem. 59 (**1981**) 1944-1953 **Decrease of reorganization energy in the dense layer?** 



S.V. Borisevich, Yu.I. Kharkats, G.A. Tsirlina, Rus. J. Electrochem. 35 (1999) 675-682

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#### Alexander M. Kuznetsov (1938-2009)

2004, Christmas lecture "Theory of love"

#### 2001 (?), Halloween in Davis



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