## RUBIN GULABOSKI
## Goce Delcev University, Stip, MACEDONIA

VOLTAMMETRY AT LIQUID-LIQUID INTERFACE
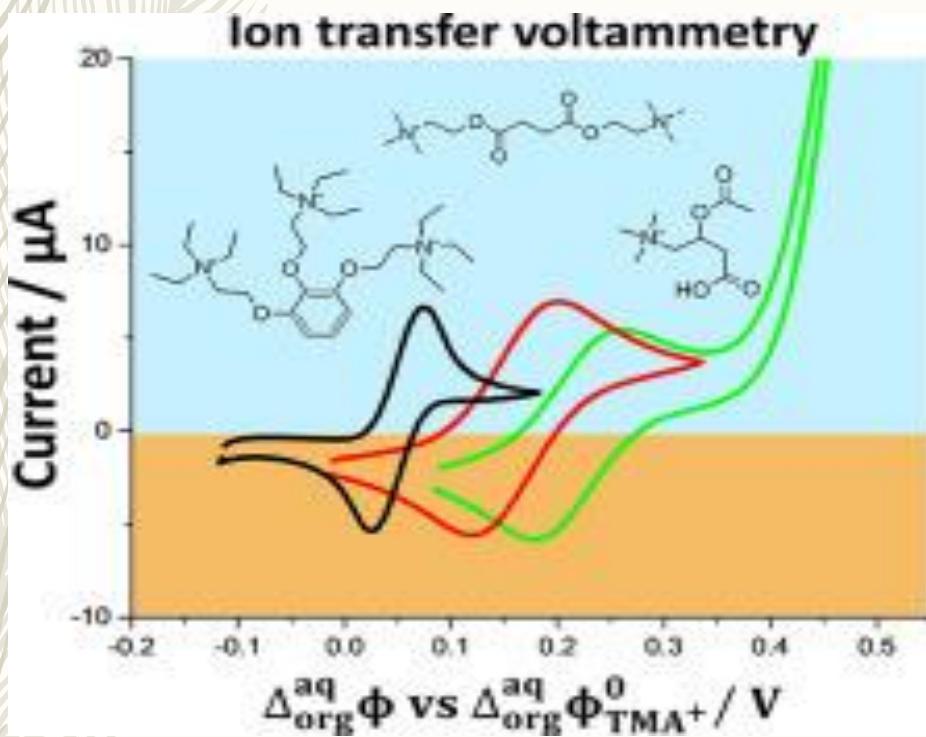
Seminar, School of PhD 2019

LIQUID-LIQUID INTERFACE between two immiscible liquids
# Crucial part for ionic transfer across membranes

FIGURE 3. Simulated voltammograms using different conditions of
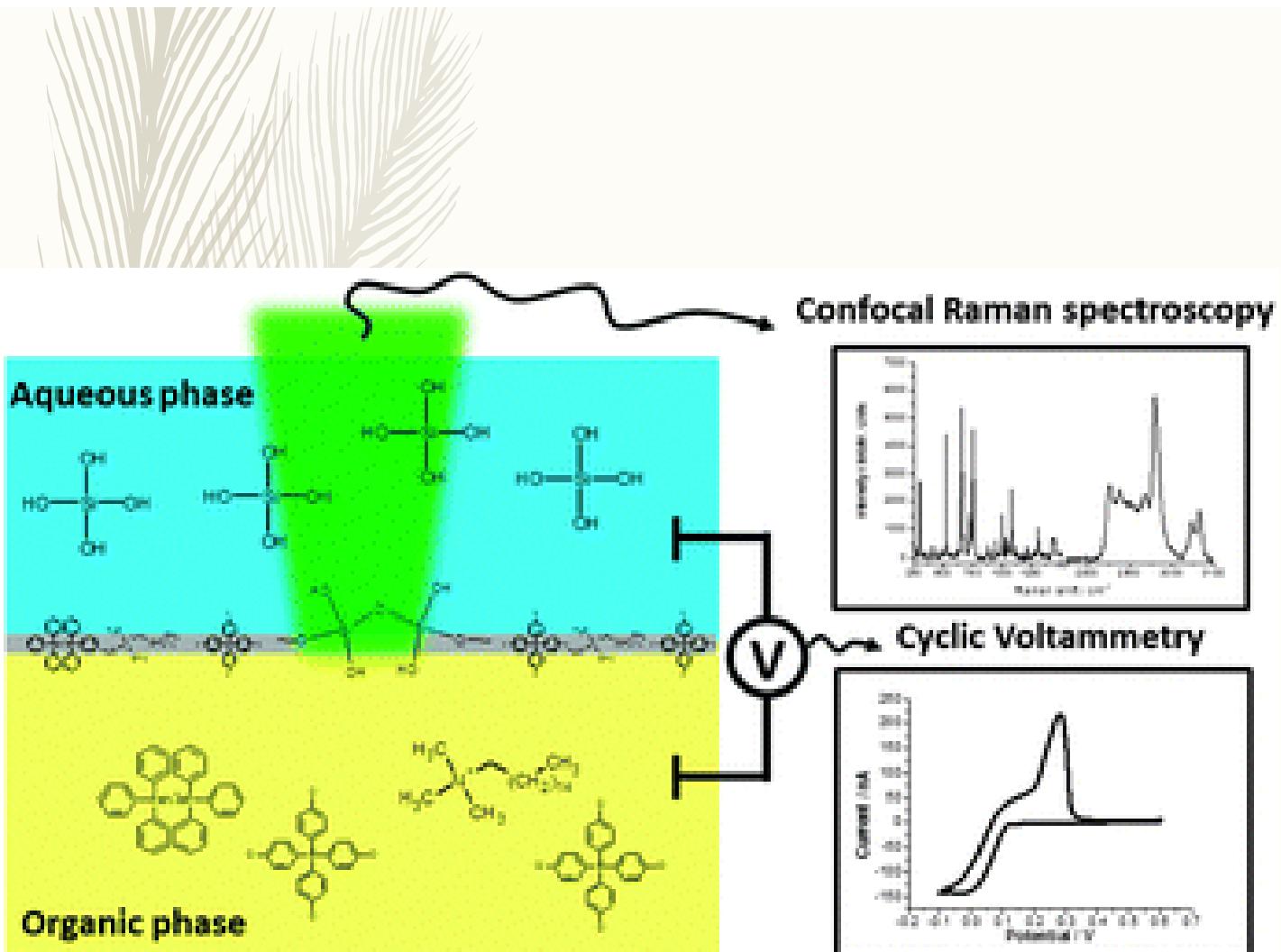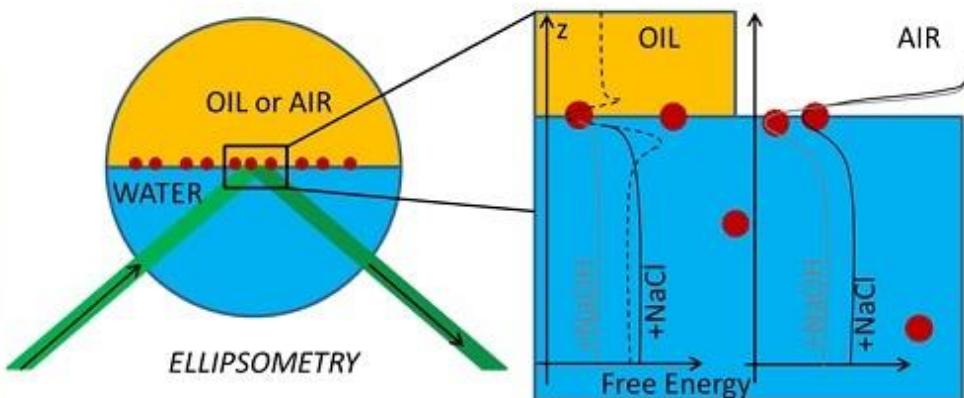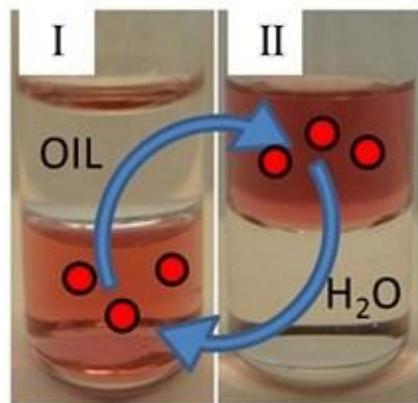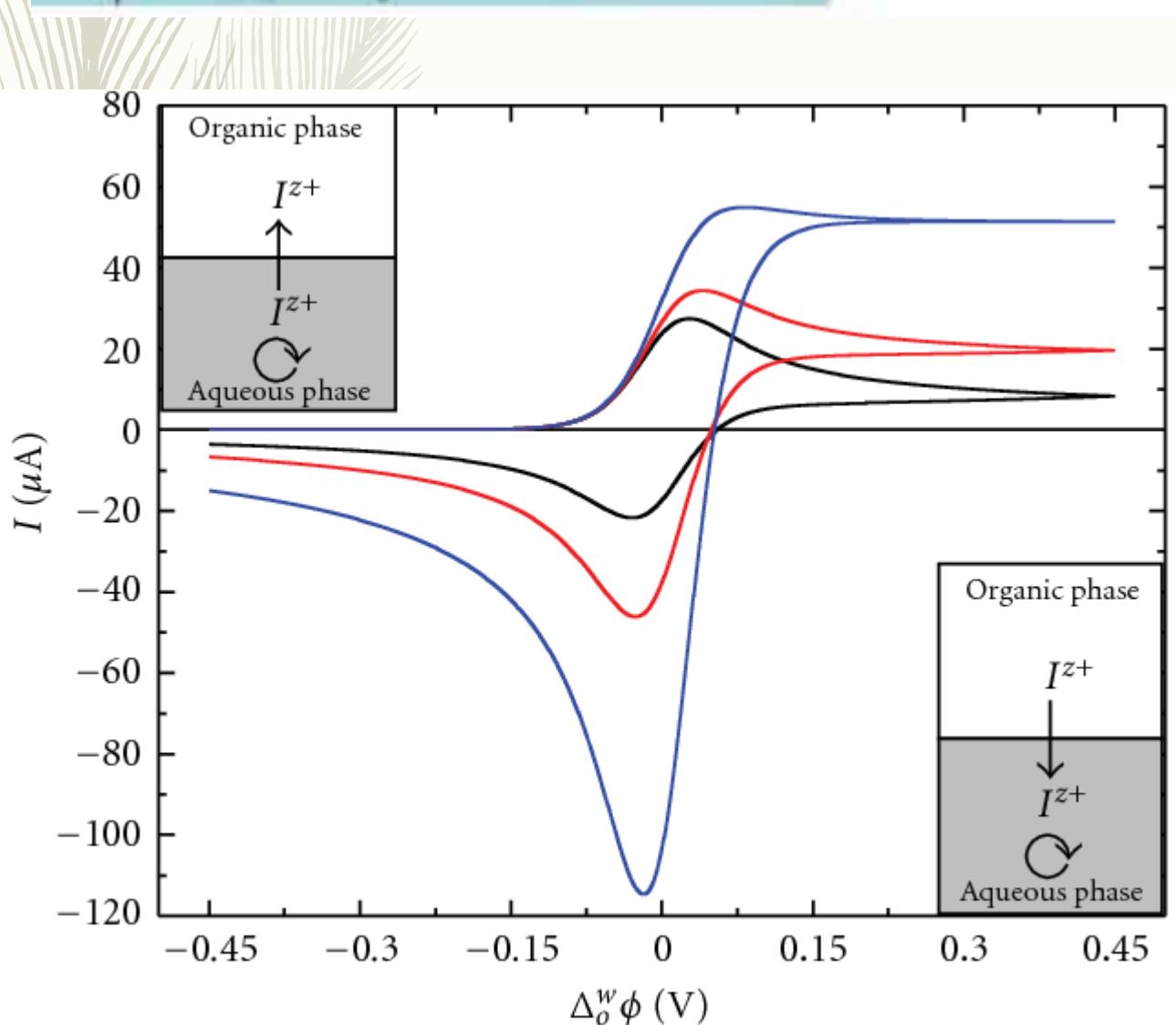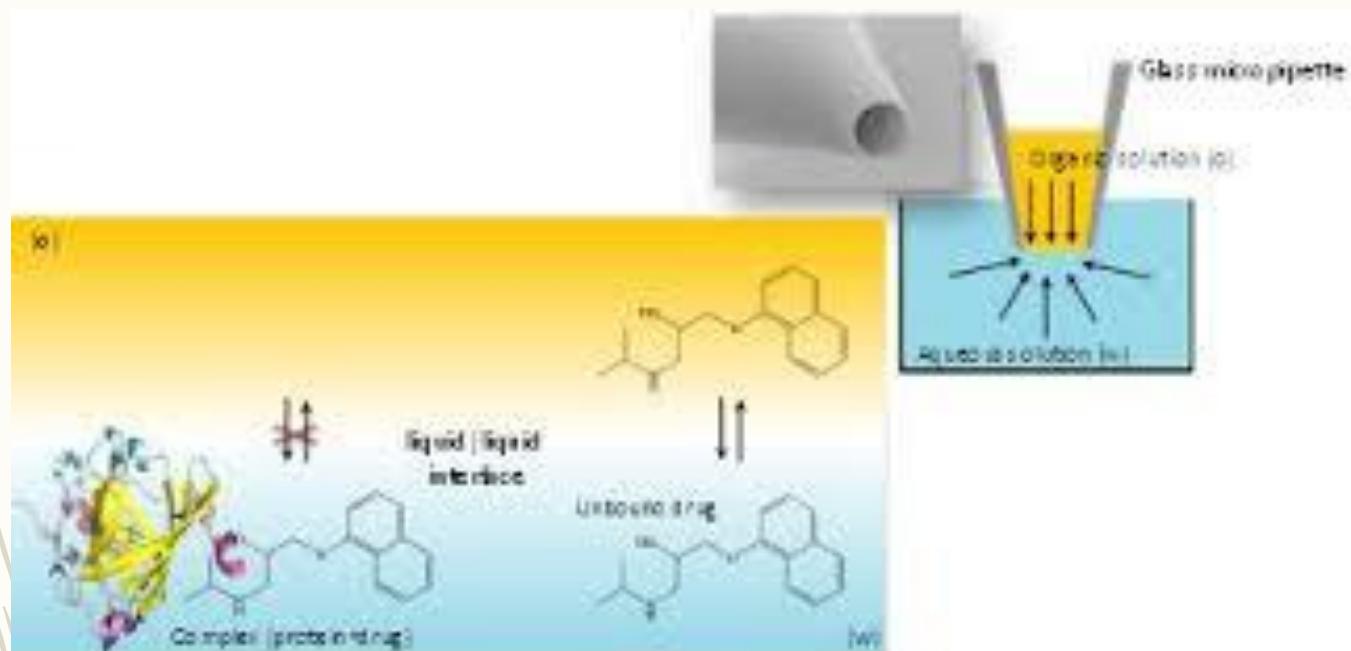
Voltammetry at LIQUID LIQUID INTERFACE gives insight Into the mechanism of ION TRANSFER
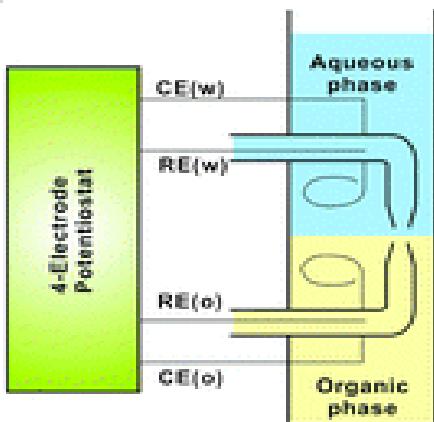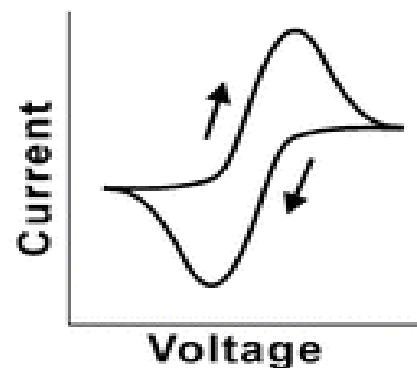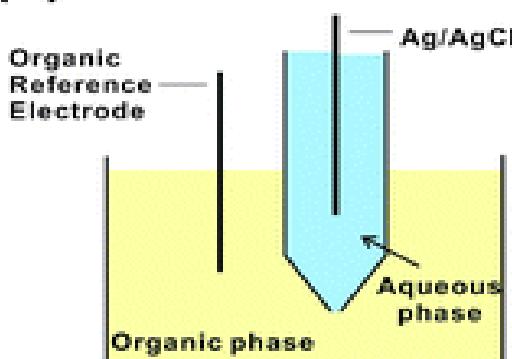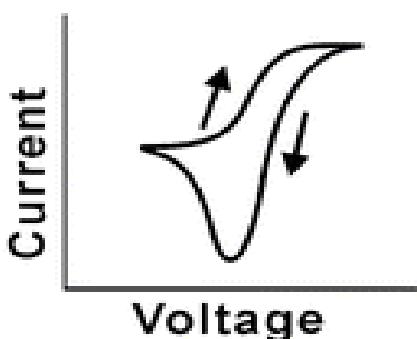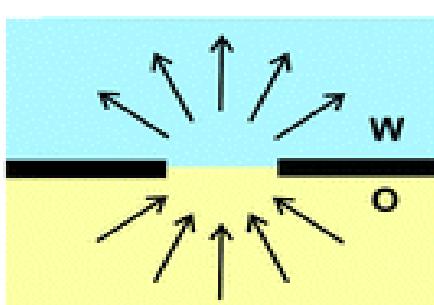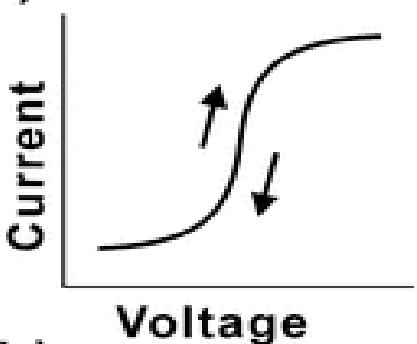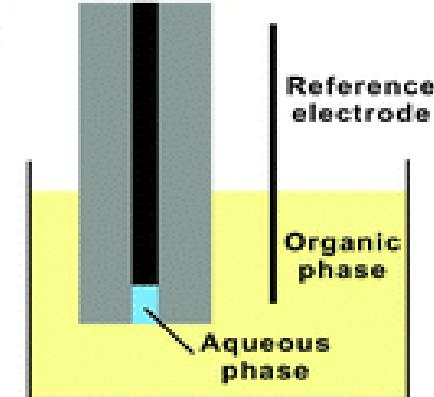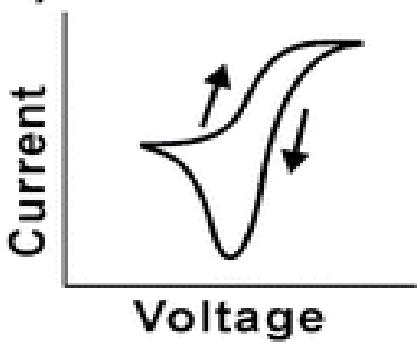
THREE-PHASE ELECTRODE

Is a SIMPLE CONCEPT for studying coupled electron-ion transfer reactions

Electron conductor, e.g. metal, graphite, etc.

droplet of org. solution of an electroactive compound

three-phase junction

three-phase junction

aqueous electrolyte solution

IT CAN BE APPLIED IN

Drug Synthesis	**Kinetics of Extraction**
Electrochemical Sensors	**Drug Delivery in Pharmacology**

Standard Gibbs energy of transfer

> **measure of the strenght of solvation interactions**

$$\Delta G_i^{\theta(A\to B)} = E_i \,\mathrm{solv}(B) - E_i \,\mathrm{solv}(A)$$

$$\Delta G_i^{\theta(w\to o)} = -\Delta_w^o \varphi_i^\theta zF$$

Link between **partition coefficient P**

and **standard Gibbs energy of transfer**

$$P_i = \exp\left(-\frac{\Delta G_i^{\theta(w\to o)}}{RT}\right) \qquad P_i = \frac{a_{i(o)}}{a_{i(w)}}$$

Importance of the partition coefficient

Measure of the **lipophilicity** of the compounds

Prediction of the transport through membranes

Toxicity

QSA-Relationships and QSP-Relationships

Drug design

Three-phase electrode approach

Scholz et all, *Electrochem. Commun.* *2*, **2000**, 112.
(**Awarded for „The Best Cited Paper"** **in 2003**)

reference electrode

counter electrode

working electrode

three-phase junction

three-phase junction

dmfc   **dmfc⁺ + 1e⁻**

$$dmfc \rightleftharpoons dmfc^+ + 1e^-$$

Organic solvent

$X^-_{(o)}$

CH₃   CH₃
CH₃ — CH₃
CH₃
Fe   CH₃
CH₃   CH₃
CH₃   CH₃

aqueous electrolyte   (Cat⁺, X⁻)

$X^-_{(aq)}$

$$\text{dmfc(o)} + A^-(w) \Leftrightarrow \text{dmfc}^+(o) + A^-(o) + 1e^-$$

$$E_f = E^{\theta}_{\text{dmfc}^+/\text{dmfc(o)}} - \frac{RT}{F}\ln(c_{(A^-)w}) + \Delta^o_w\varphi^{\theta}_{A^-} + \frac{RT}{F}\ln(\frac{c_{0(\text{dmfc})o}}{2})$$
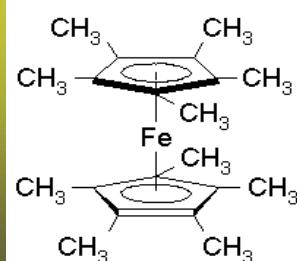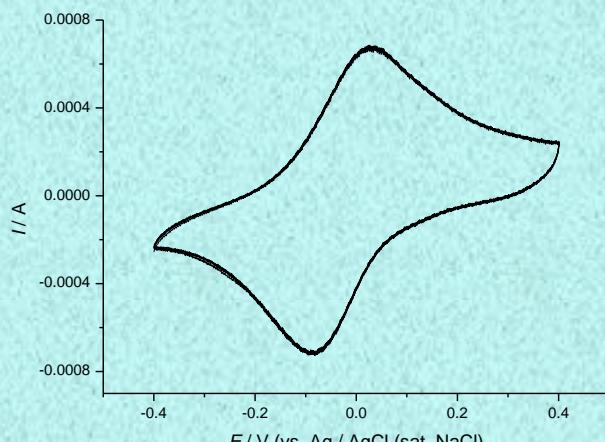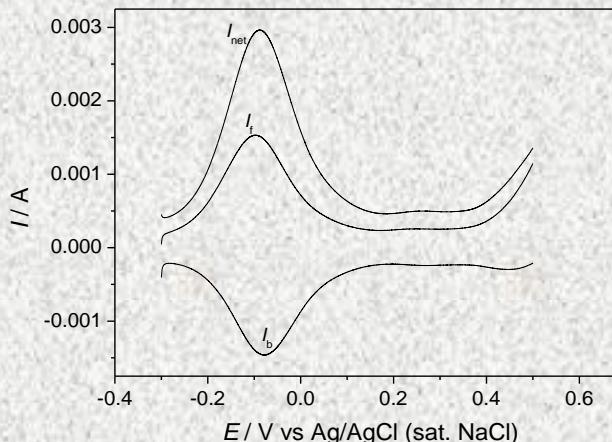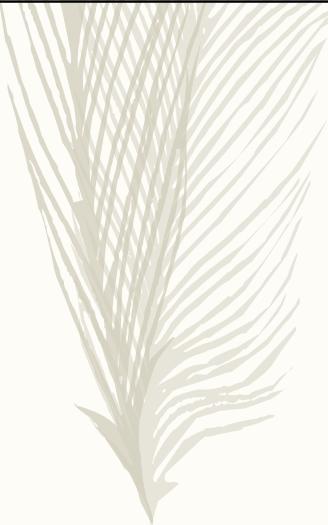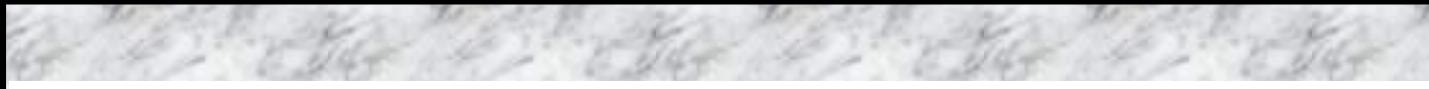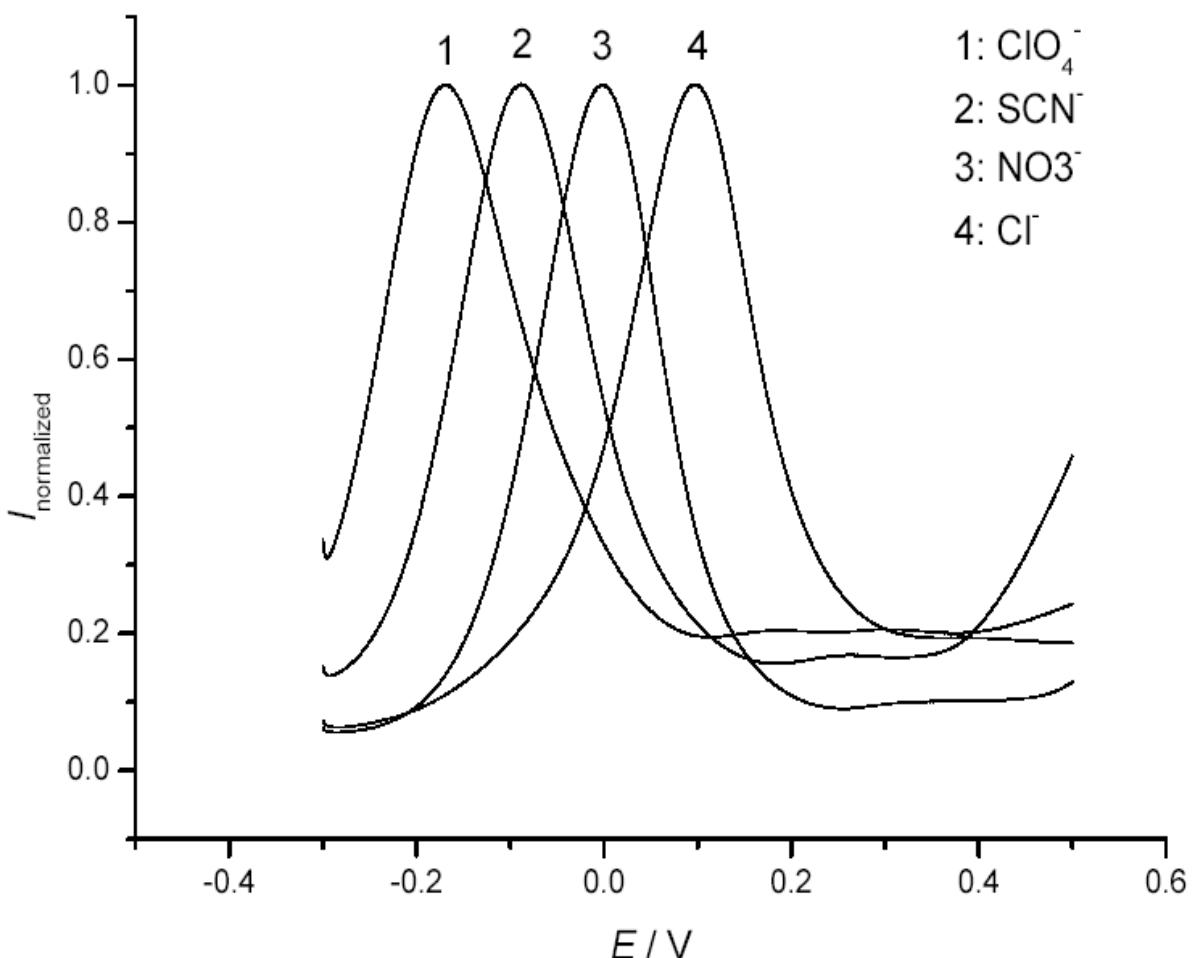
Square-wave voltammograms representing the redox reaction of dmfc at WE|NB|w three-phase electrode followed by transfer of common inogranic anions across the w|nitrobenzene interface

$$E_p / V = 0.95\Delta\phi_X^- - 0.259 \ (R^2 = 0.99)$$
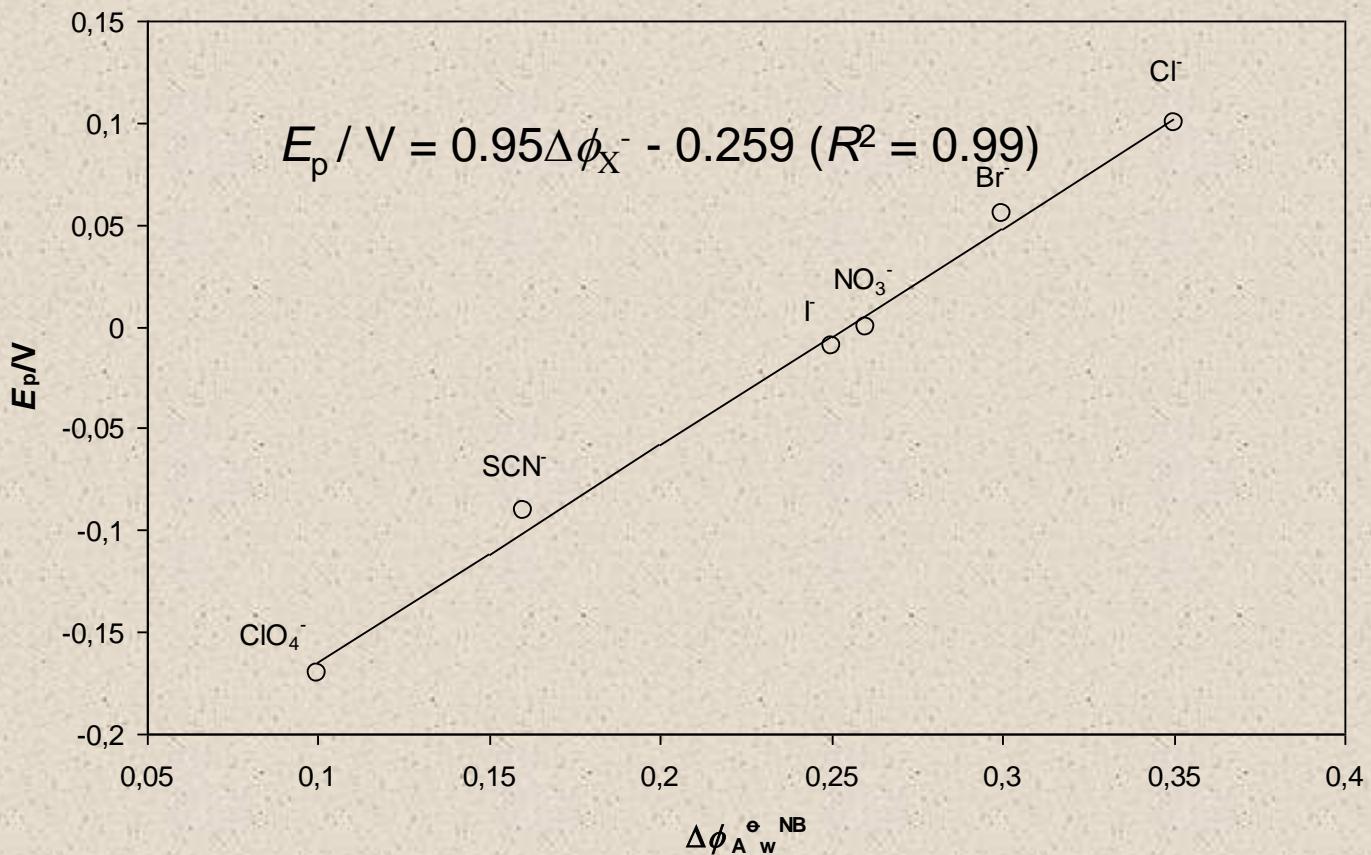
Peak potentials of the net SW voltammetric responses of dmfc in NB as a function of **the standard potentials of transfer of anions across water | nitrobenzene interface**

$$E_f = E_{\mathrm{dmfc^+/dmfc(o)}}^{\theta} - \frac{RT}{F}\ln(a_{\mathrm{(A^-)w}}) + \Delta_w^o\varphi_{\mathrm{A^-}}^{\theta} + \frac{RT}{F}\ln(\frac{a_{0\mathrm{(dmfc)o}}}{2})$$

– I. *Inorganic anions*

– II. *Organic anions-Monoanionic forms of*:

- – A. *Phenols*
- – B. *Cyclo-, Mono, Di-,* and *halogen substituted carboxylic acids*
- – C. *Amino acids*
- – D. *Peptides*
- – E. *Medicaments*

Š. Komorsky-Lovric, K. Riedl, **R. Gulaboski**, V. Mirceski and F. Scholz, *Langmuir* 18 (2002) 8000-8005,

R. Gulaboski, K. Riedl, F. Scholz, *Phys. Chem. Chem. Phys.* 5 (2003) 1284-1289

R. Gulaboski, K. Caban, Z. Stojek, F. Scholz; *Electrochem. Commun.* 6 (2004) 215

V. Mirceski, **R. Gulaboski**, F. Scholz; *Electrochem. Commun.* 4 (2002) 813-818

V. Mirceski, **R. Gulaboski**, F. Scholz, *J. Electroanal. Chem.* 566 (2004) 351

1-Trp
2-Tyr
3-Met
4-His
5-Lys
6-Pro
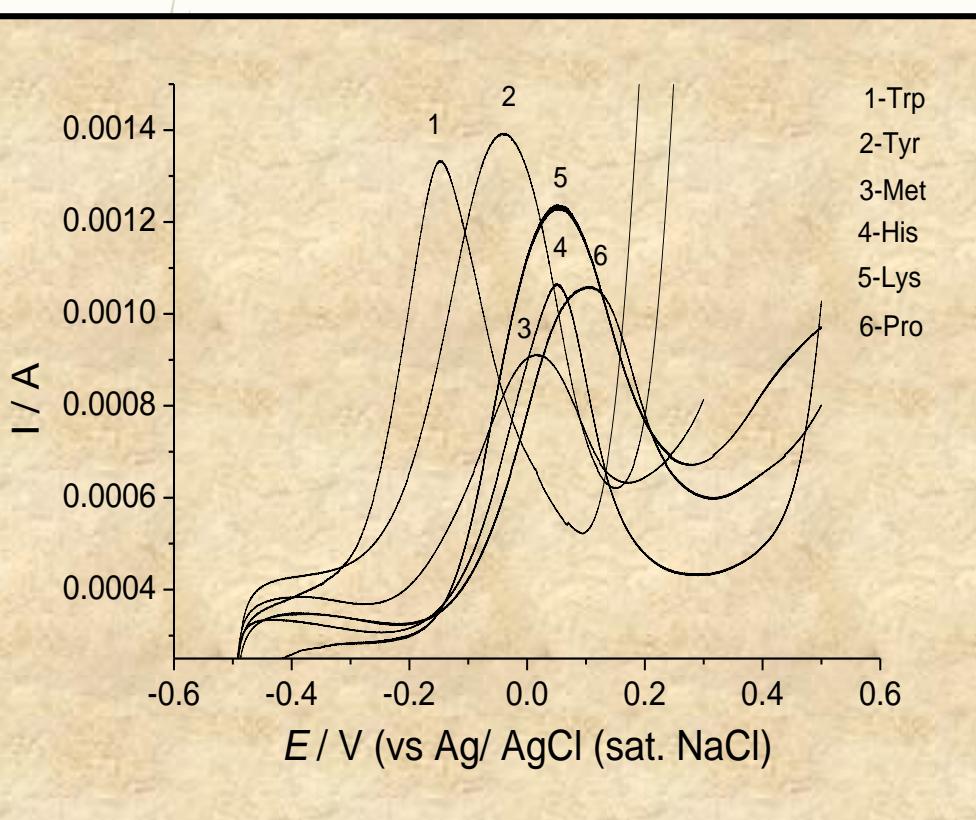
Transfer of monoanions of aminoacids
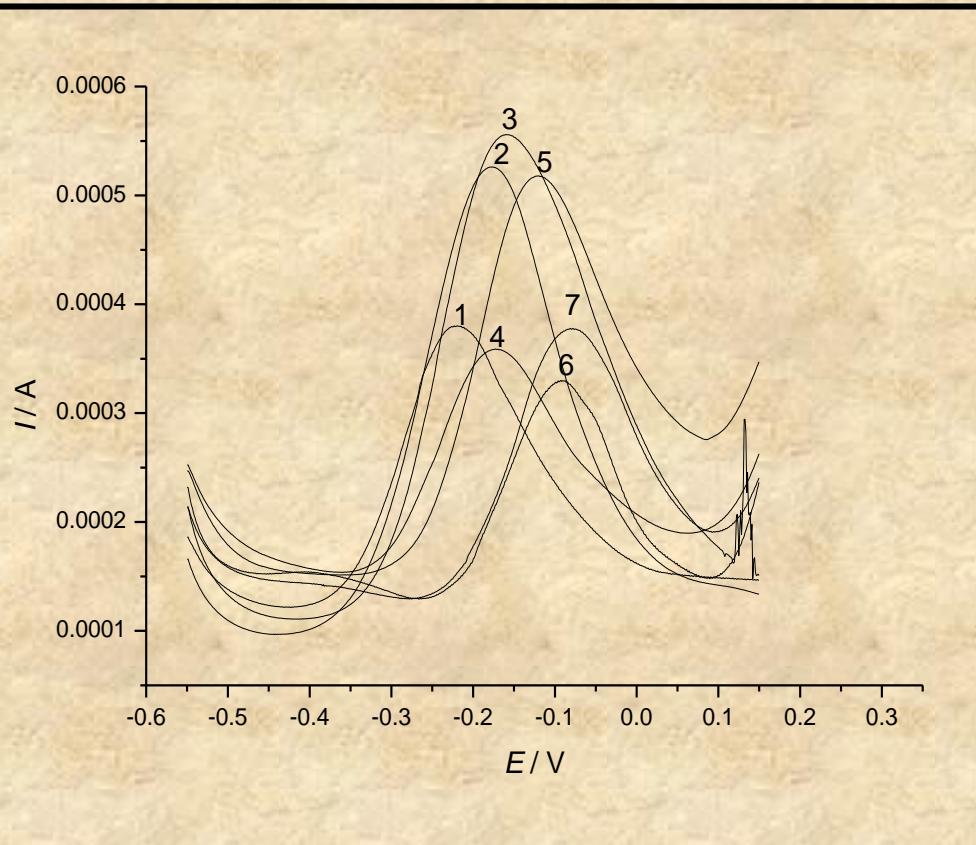
Transfer of monoanions of some Trp-X peptides

K2·K1 + $\left(\text{H}_i\right)$ + H$_i$·K1
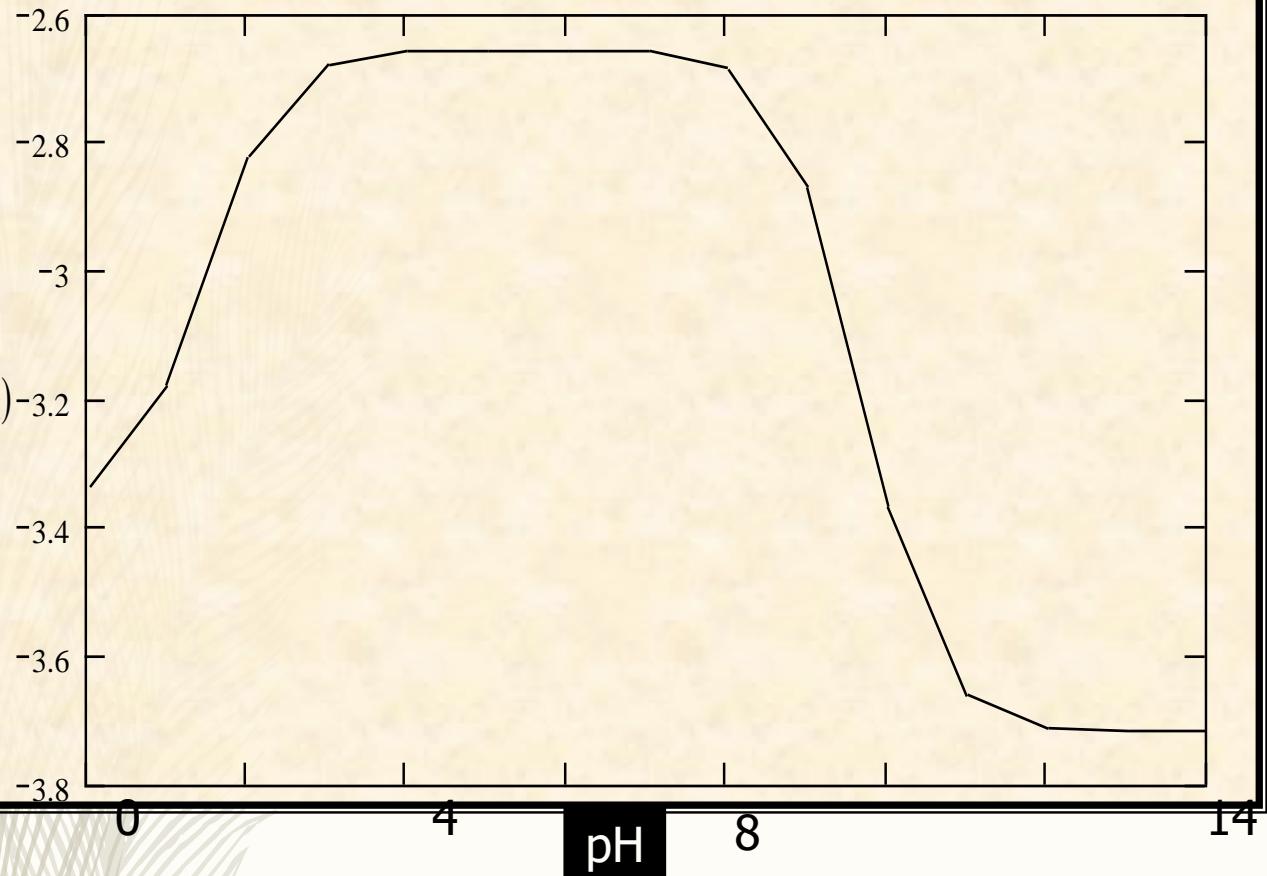
Distribution diagram of Phenyalanine

R. Gulaboski, V. Mirceski, F. Scholz; *Amino Acids* 24 (2003) 149–154

R. Gulaboski, F. Scholz, *J. Phys, Chem. B* 107 (2003) 5650-5657

➤ among the organic solvents used for studying the lipophilicity of solutes, *n*-OCTANOL is certainly the most important one

➤It is an ideal mimic for the biological membranes *(amphipathic nature similar to those of the lipides in biological membranes,* long alkyl side chain and OH group)

n-Octanol

➤**No data** in the literature about the standard *ion potentials* of transfer across the interface **water|*n*-octanol**:

Reason: *non-polarizability* of the interface water|n-Octanol

R. Gulaboski, V. Mirceski, F. Scholz; *Electrochem. Commun.* 4 (2002) 277-283

G. Bouchard, A. Galland, P.-A. Carrupt, **R. Gulaboski**, V. Mirceski, F. Scholz, H. H. Girault, *Phys. Chem. Chem. Phys.* 5 (2003) 3748-3751

$$dmfc(n\text{-}oct) + A^-(w) \Leftrightarrow dmfc^+(n\text{-}oct) + A^-(n\text{-}oct) + 1e^-$$
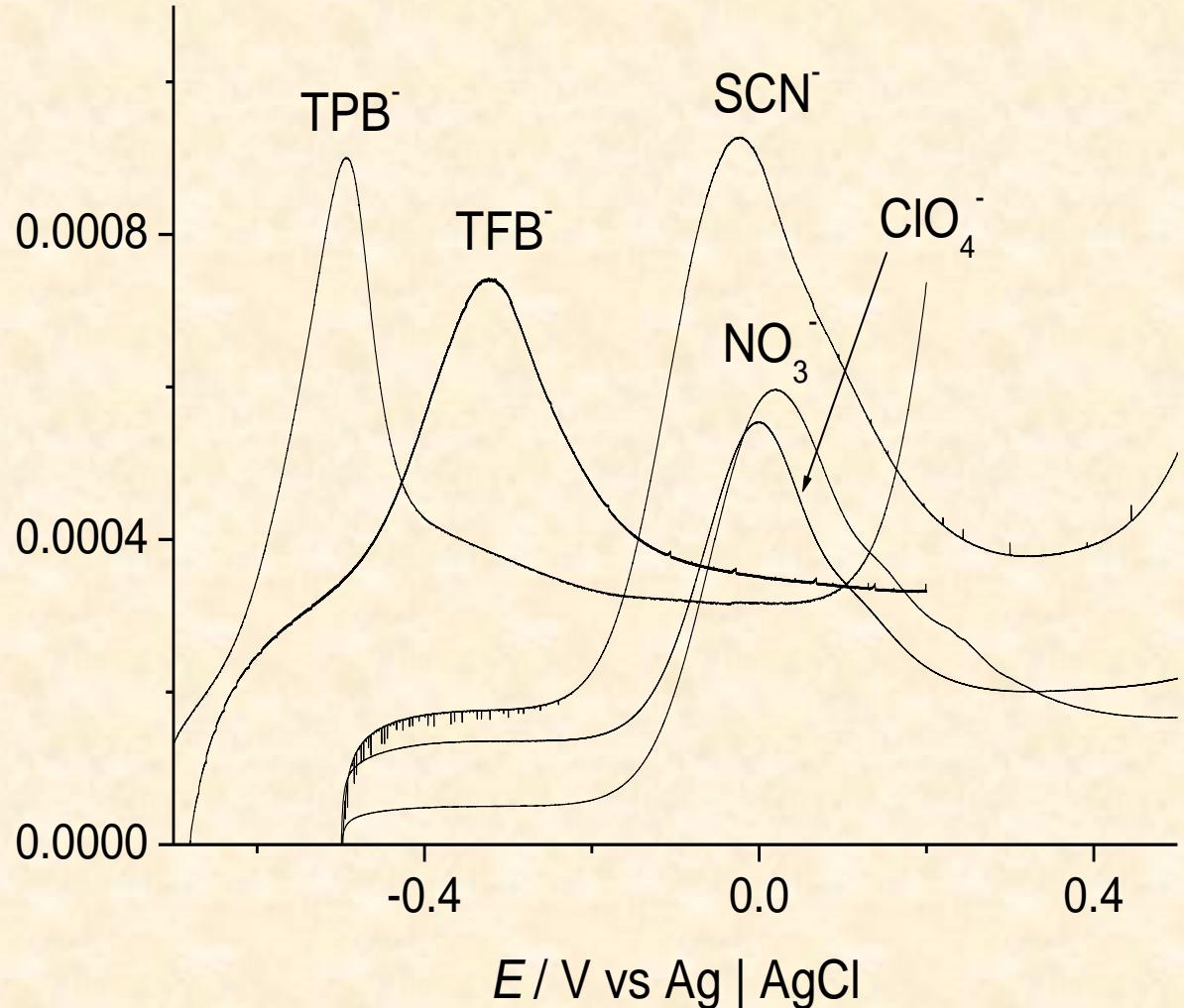
Transfer of some common anions across water|**n-octanol** interface

18

1

2

3

4

5

6

7

8

9

10

11

12- Naphtoic acid

13-Ketoprofen

14-Suprofen

15-Naproxen

16-Pirprofen

17-Flurbiprofen

18-Ibuprofen

19-Carprofen

20-Indomethacin

21-Phenylbutazone

22-Sulfinpyrazone

23-Warfarin

24-Phenobarbital

25-Phenytoin

26-Maleic acid
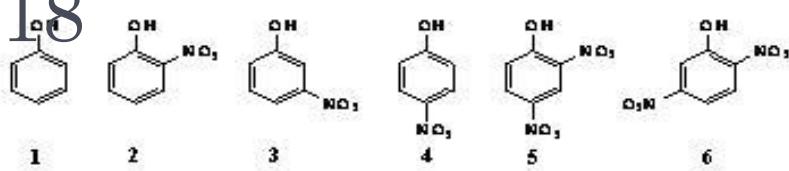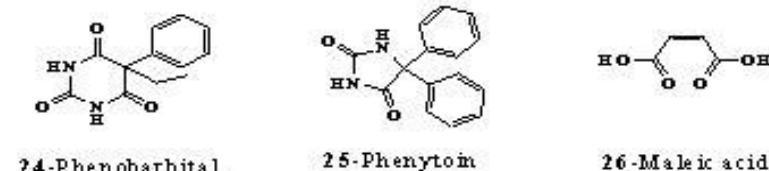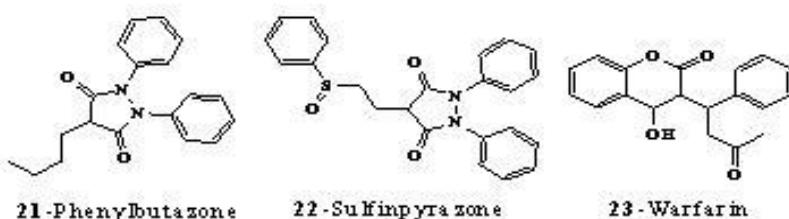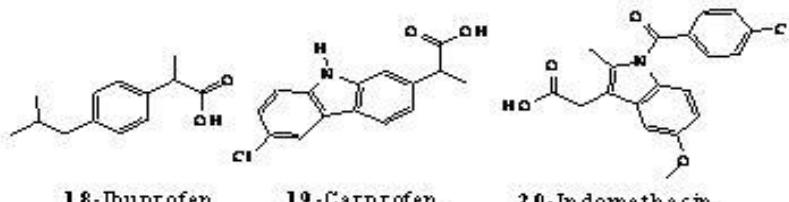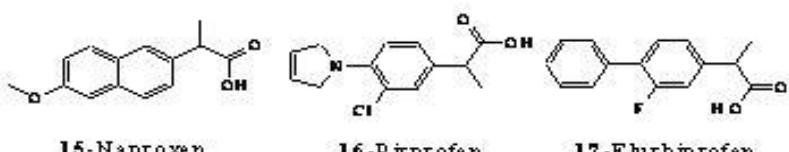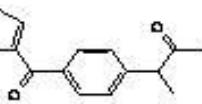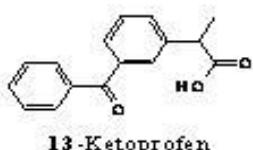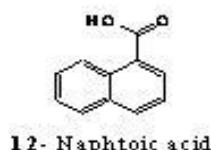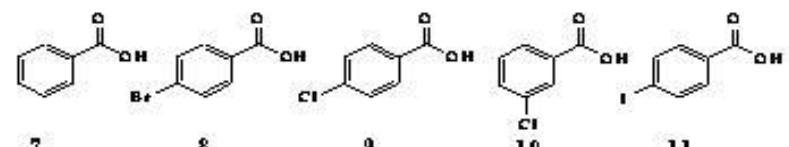
G. Bouchard, A. Galland, P.-A. Carrupt,
B. Testa, R. Gulaboski, V. Mirčeski,
F. Scholz, H. H. Girault

2-Nitrophenyl octyl ether-used as an alternative solvent for *n*-octanol

It *shares* the structures of Nitrobenzene and *n*-octanol
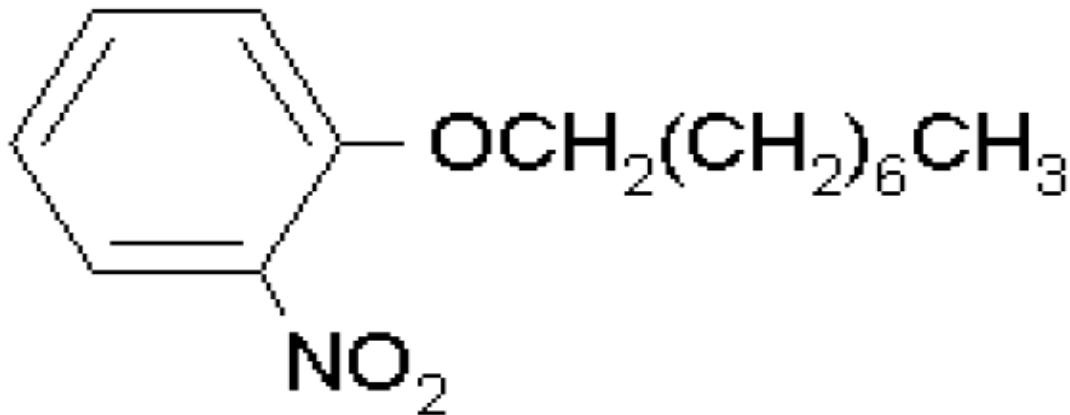
2-Nitrophenyl octyl ether

11. **R. Gulaboski**, A. Galland, G. Bouchard, K. Caban, A. Kretschmer, P.-A. Carrupt, Z. Stojek, H. H. Girault, F. Scholz, *J. Phys. Chem. B*, 108 (2004) 4565

Table 2 Standard Gibbs energies of transfer and partition coefficients of the studied anions.

| n°	Compound	$\Delta G_{tr,A}^{0,w \to NB}$ [a]	$\Delta G_{tr,A}^{0,w \to NPOE}$ [a]	$\Delta G_{tr,A}^{0,w \to OCT}$ [a][b]	log $P_{NB}^{0,A}$	log $P_{NPOE}^{0,A}$	log $P_{OCT}^{0,A}$ [b]	r (Å)[c]
1	Phenol	20.45	19.50	23.13	-3.62	-3.46	-4.10	2.78
2	2-Nitrophenol	14.60	18.00	22.56	-2.59	-3.19	-4.00	2.98
3	3-Nitrophenol	20.00	18.75	23.70	-3.54	-3.32	-4.20	2.98
4	4-Nitrophenol	21.48	17.20	24.82	-3.81	-3.05	-4.40	2.98
5	2,4-Dinitrophenol	8.70	11.62	24.25	-1.54	-2.06	-4.30	3.15
6	2,5-Dinitrophenol	14.00	14.85	25.40	-2.48	-2.63	-4.50	3.15
7	Benzoic acid	21.00	18.95	32.72	-3.72	-3.36	-5.80	2.97
8	4-Bromobenzoic acid	12.00	17.32	28.20	-2.13	-3.07	-5.00	3.15
9	4-Chlorobenzoic acid	12.25	15.23	31.59	-2.17	-2.70	-5.60	3.09
10	3-Chlorobenzoic acid	15.25	16.65	27.08	-2.70	-2.95	-4.80	3.09
11	4-Iodobenzoic acid	14.00	12.00	28.77	-2.48	-2.13	-5.10	3.21
12	Naphtoic acid	15.50	17.80	31.05	-2.74	-3.15	-5.50	3.77
13	Ketoprofen	19.33	18.05	28.20	-3.42	-3.20	-5.00	3.84
14	Suprofen	15.80	16.47	32.15	-2.80	-2.92	-5.70	3.79
15	Naproxen	11.50	12.86	28.77	-2.04	-2.28	-5.10	3.70
16	Pirprofen	5.65	9.55	28.75	-1.00	-1.69	-5.10	3.76
17	Flurbiprofen	10.50	12.35	24.80	-1.86	-2.19	-4.40	3.75
18	Ibuprofen	17.40	15.34	28.77	-3.08	-2.72	-5.10	3.59
19	Carprofen	-14.80	-3.85	18.05	2.62	0.68	-3.20	3.82
20	Indomethacin	11.00	15.05	26.50	-1.95	-2.67	-4.70	4.06
21	Phenylbutazone	3.70	12.85	24.25	-0.65	-2.28	-4.30	4.13
22	Sulfinpyrazone	7.10	12.85	24.25	-1.26	-2.28	-4.30	4.40
23	Warfarine	9.80	12.30	23.13	-1.74	-2.18	-4.10	4.05
24	Phenobarbital	26.75	24.10	31.02	-4.74	-4.27	-5.50	3.64
25	Phenytoine	17.70	19.65	30.45	-3.14	-3.48	-5.40	3.78
26	Maleic acid	20.30	19.50	31.02	-3.60	-3.46	-5.50	2.75
27	Picric acid	-3.00	3.65	n.m.[d]	0.53	-0.65	n.m.[b]	3.28

a) in kJ.mol^{-1} b) taken from reference [35] c) van der Waals radius of the ion, d) non measured
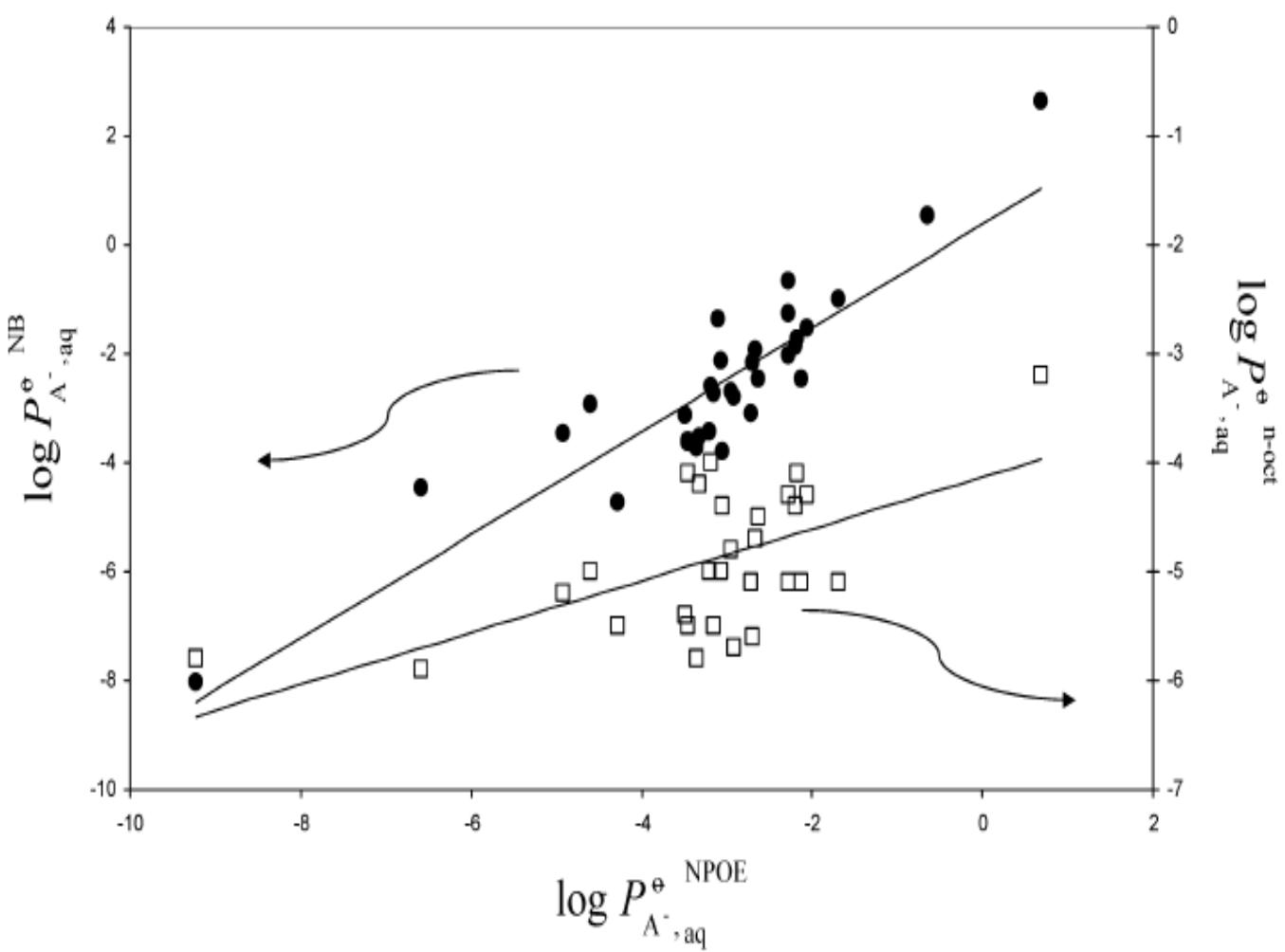
Comparison between partition coefficients in w|NB and w|NPOE, and w|*n*-oct and w|NPOE

F. Scholz, **R. Gulaboski**, *ChemPhysChem* 2005, 6, 16–28 (**Review**)

22

graphite electrode

e⁻

chiral solvent

⁻mfc   mfc⁺

COOH

H   C   R

NH₂

chiral⁻(org)

chiral⁻(aq)

COOH

R   C   H

NH₂

aqueous electrolyte
(Cat⁺, chiral⁻)

(Racemic mixtures can be separated)
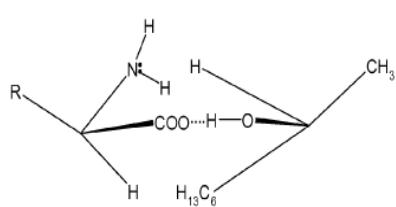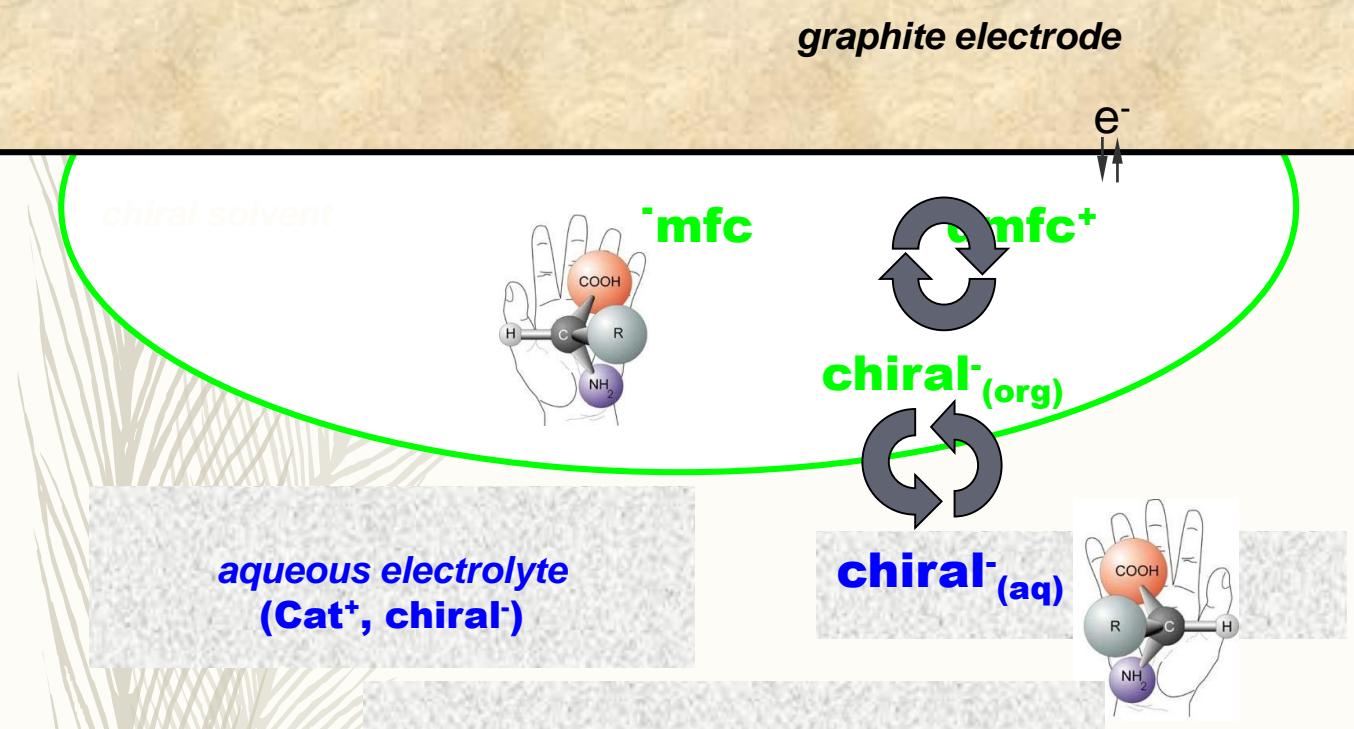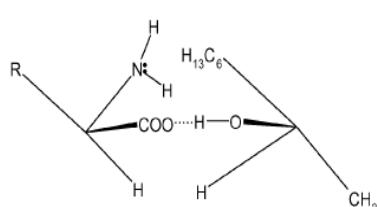
D-ion/D-solvent   D-ion/L-solvent

F. Scholz, **R. Gulaboski**, *Faraday Discuss*., 2005, 129, 169–177
F. Scholz, **R. Gulaboski**, V. Mirceski, P. Langer; *Electrochem. Commun*. 4 (2002) 659-662

Transfer of cations across the water|Nitrobenzene interface

Fe(III)TPhP R =
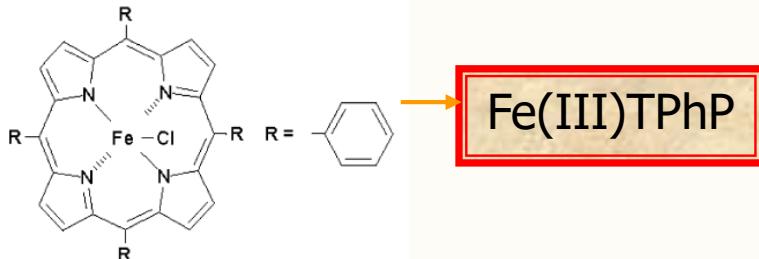
→ **Fe(III)TPhP**

graphite electrode

NB **Fe(III)TPhP +e-** ⇄ **Fe(II)TPhP⁻**

Cat⁺

aqueous electrolyte
(Cat⁺, A⁻)

Cat⁺(aq)

TButN⁺

Transfer of TButN⁺ across w|NB interface
scan rate/ mv s⁻¹ = 10, 20, 50, 100, 200, 300, 400

F. Scholz, **R. Gulaboski**, K. Caban, *Electrochem. Commun.* 5 (2003) 929

Considering theoretically the reaction occuring at the Three-Phase Electrode:

$$Ox_{(nb)} + X^-_{(nb)} + e \rightleftharpoons Red^-_{(nb)} + X^-_{(w)}$$

the **_apparent reversibility_** depends on dimensionless kinetic parameter

$$K' = \frac{k'_s c^*_{X^-_{(w)}} \exp(\beta \ln(c^*_{X^-_{(nb)}}/c^*_{X^-_{(w)}}))}{\sqrt{Df}}$$

(A) (B)
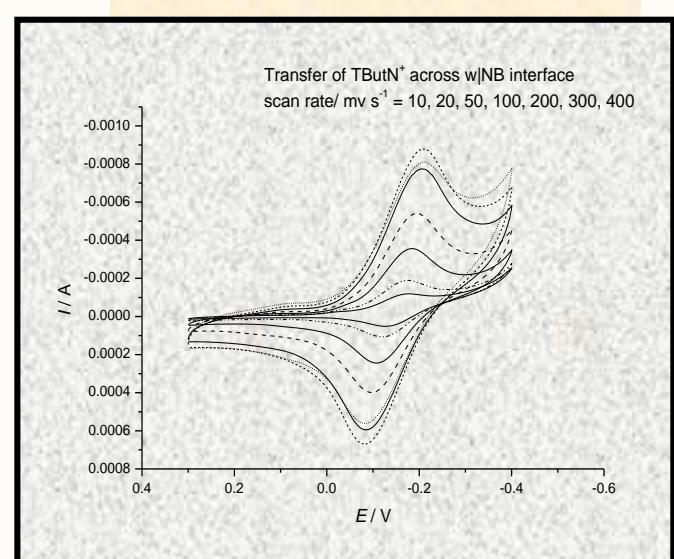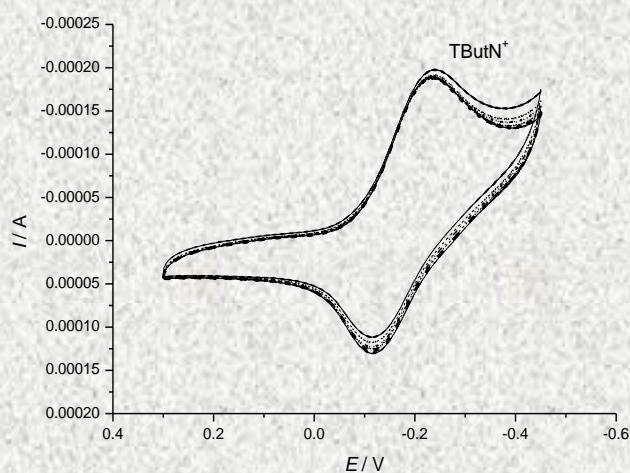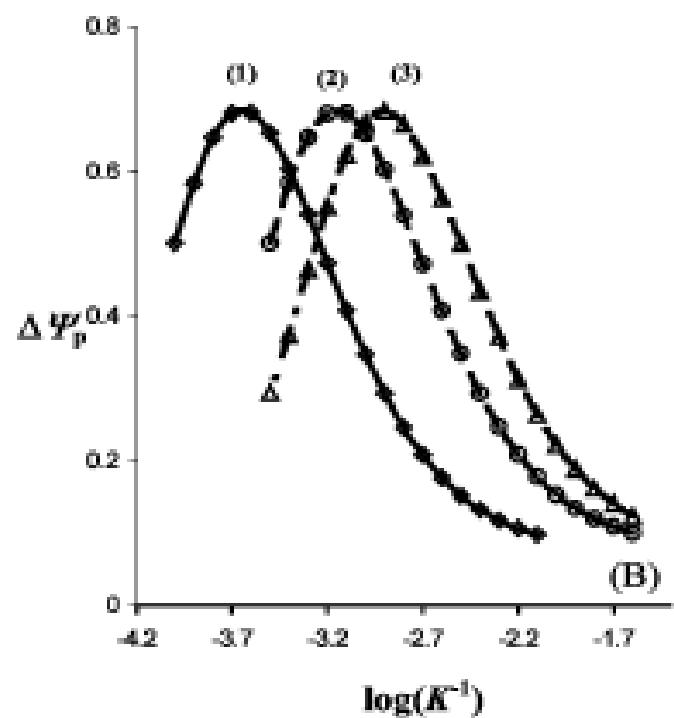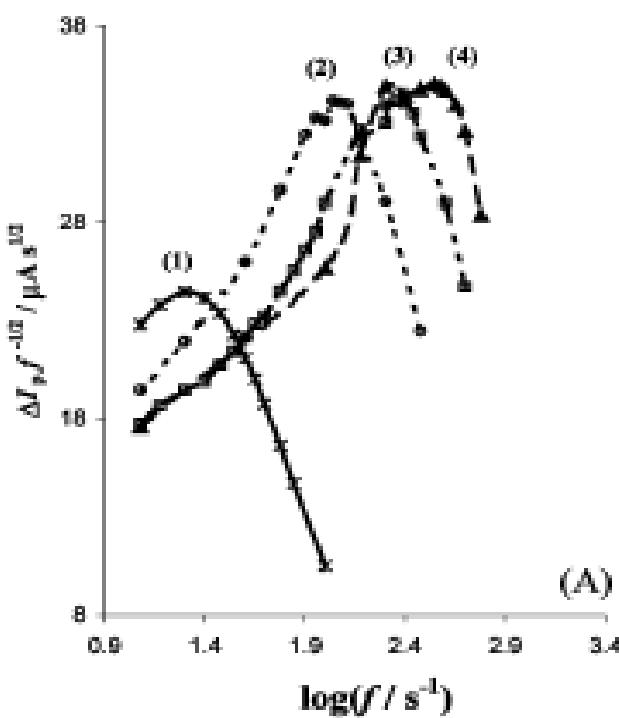
Kinetics of Ion Transfer measured by Electrochemical Impedance Spectroscopy (EIS)

R. Gulaboski, V. Mirceski, C. M. Pereira.
M. N. D. S. Cordeiro et al. *Langmuir* **(submitted)**
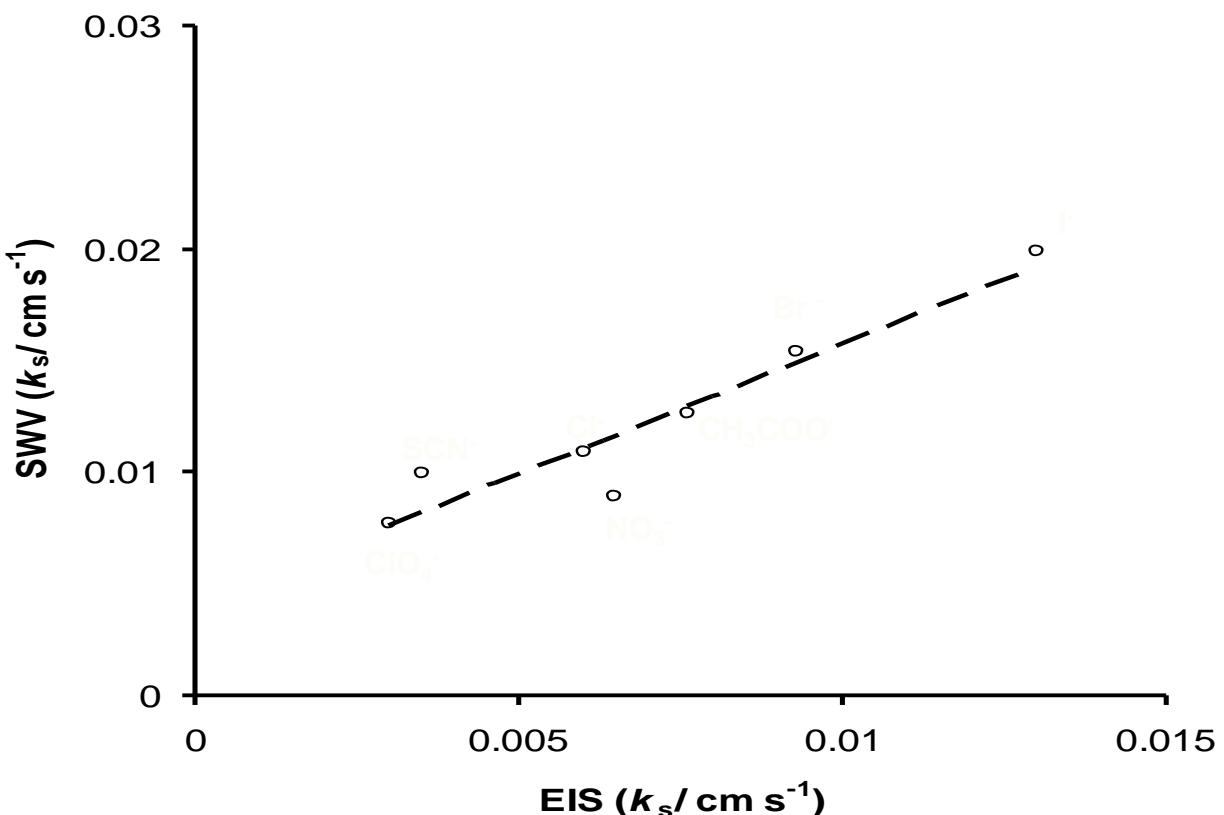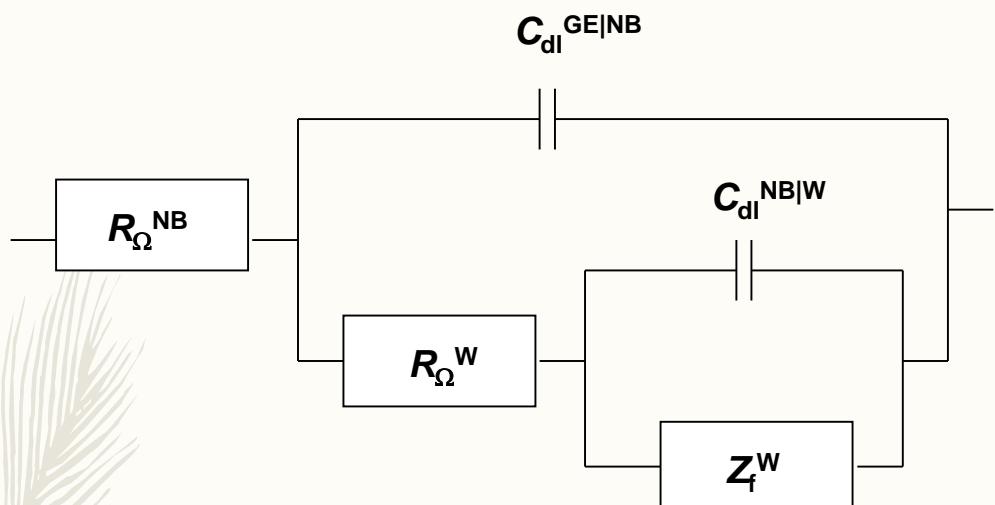
26

Working electrode

-e⁻

TButN⁺TPB⁻

dmfc **dmfc⁺**

organic film

Gluconate⁻

Aqueous electrolyte

b) Gluconic acid → Gluconate⁻ + H⁺

GlOx

a) Glucose → Gluconic acid (Enzymatic reaction)
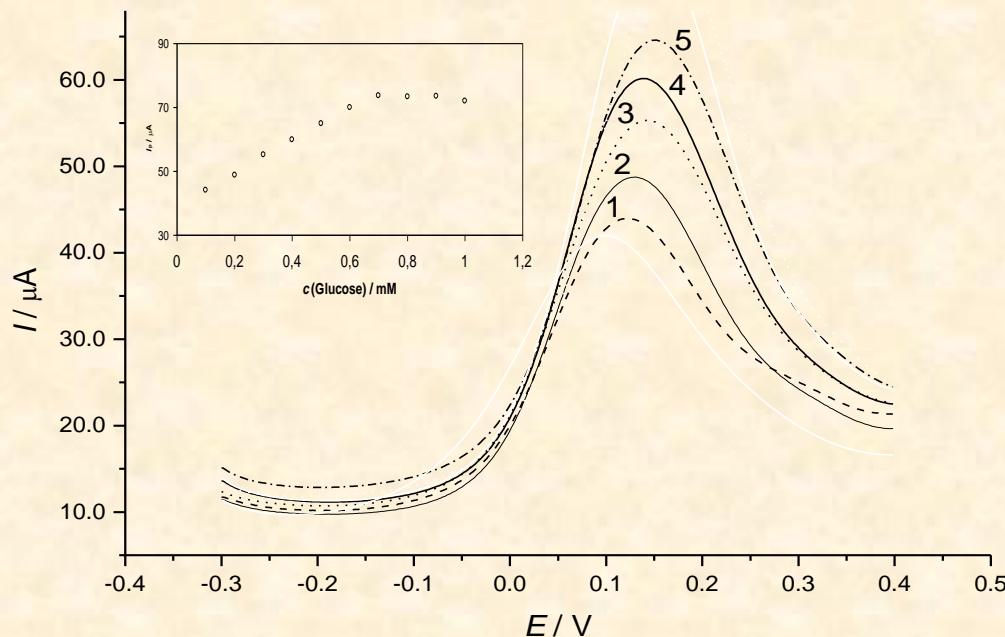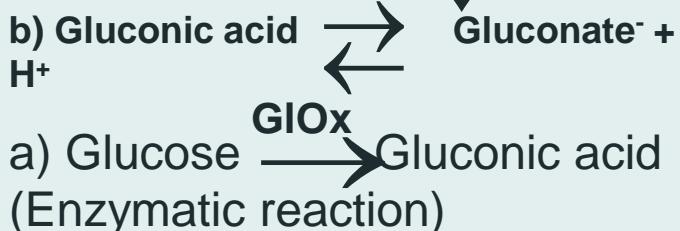
R. Gulaboski, C. M. Pereira. M. N. D. S. Cordeiro, et al. *J. Solid State Electrochem.* **9 (2005) 469-474**

R. Gulaboski, C. M. Pereira. M. N. D. S. Cordeiro, et al., *J. Phys. Chem B* 109 (2005) 12549

e-

dmfc $\rightleftharpoons$ dmfc$^+$

aqueous electrolyte
solution

Ag$^+$ $\rightarrow$ Ag-nanoparticles at
the L|L interface

Gulaboski R, Mirceski V, *J Phys Chem B 2005*
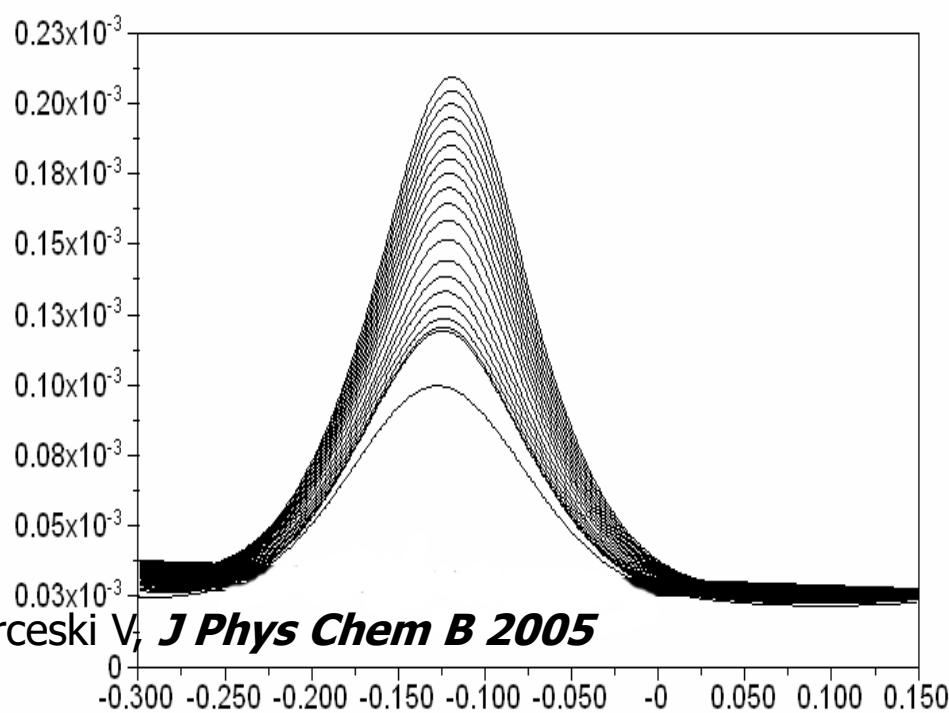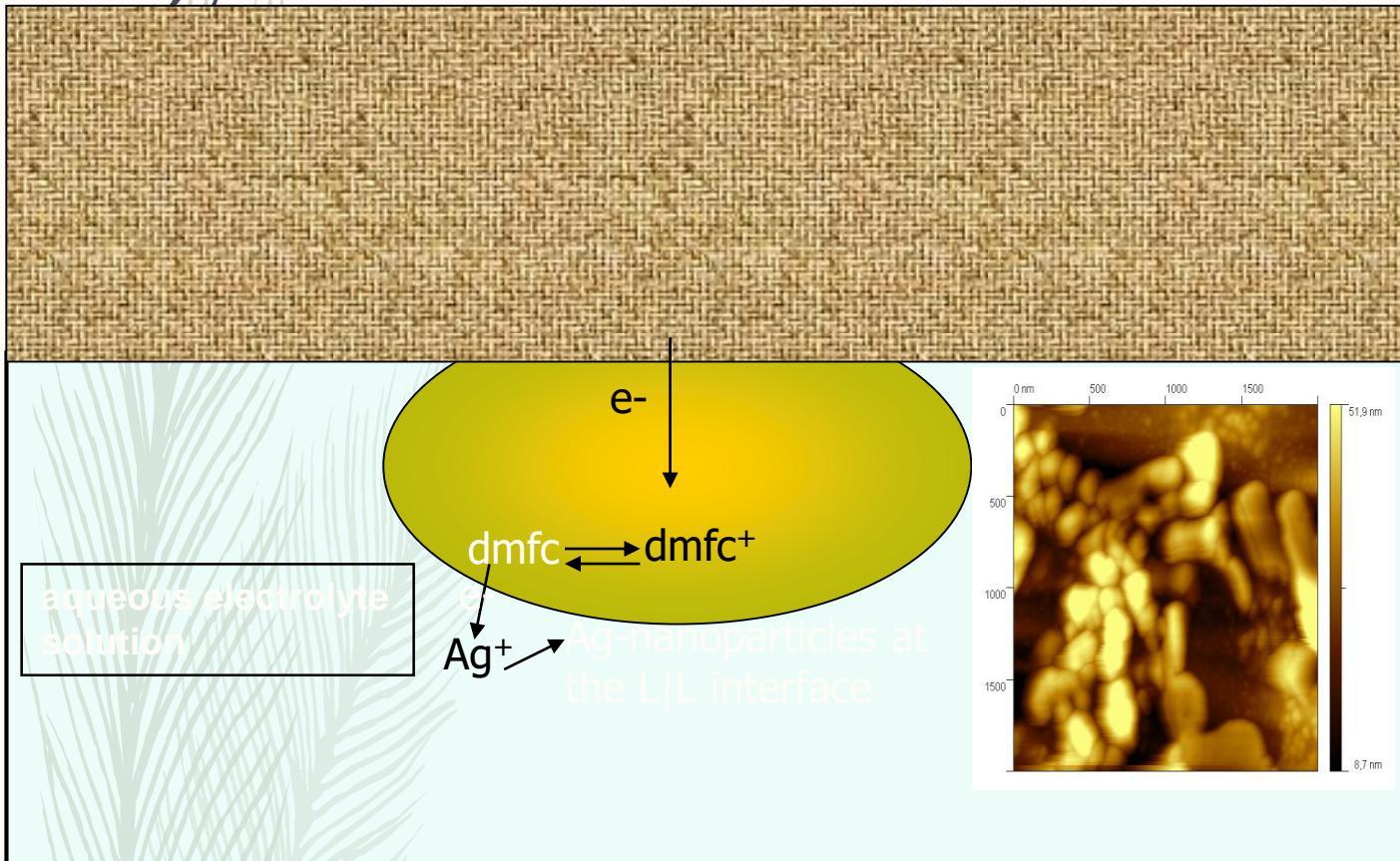
28

Energy of solvation=

| Energy of making a cavity in the solvent to accomodate the solute | Energy of reorganization of solvent molecules |

Short-term interactions
(H-bonds, van der Walls interactions, electrostatic interactions)

First model of ion-solvent interaction:

Born electrostatic theory:

$$\Delta_w^o G_{Born}^\theta = -\frac{N_A z^2 e^2}{8\pi\varepsilon_0 r}\left(\frac{1}{\varepsilon_{(w)}} - \frac{1}{\varepsilon_{(o)}}\right)$$

Major
weaknesses:

Neglects the
charge
delocalization
effects

Neglects the
energy
of cavity
formation

Influence of the energy of making a cavity to the lipophilicity of the ions

$$E_{cav.} = 4\sigma_w^o \, A_i \, N_A$$
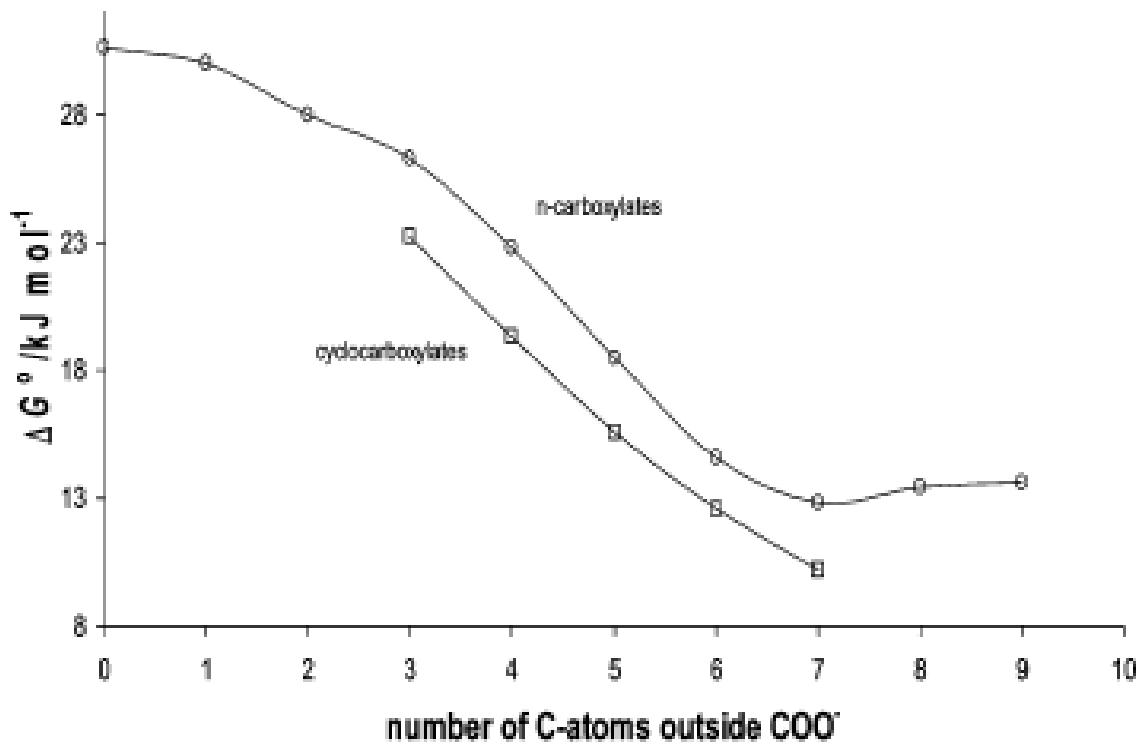
Summary:

Ion transfer processes studied by *three-phase electrodes:*

   -common three-electrode setup
   -simple, precise and fast determinations of *thermodynamic and kinetic parameters*
    -the approach applicable to different organic solvents (octanol(s), menthol, nitrobenzene, dichlorethan, nitrophenyl   octyl   ether, ...)
    -a huge data base of new determined   standard Gibbs energies of transfer of   various ions as well as of k_s values
    -Potential applications as a sensor
    and by the ion separation processes
    -MD Simulations needed for   molecular understanding
    (N. Cordeiro, J. Miguel)

Limitations of the 4-electrode voltammetry at ITIES:
➢**Narrow potential windows**
➢**Applicable to few organic solvents only,
mainly to 1,2 dichlorethan and Nitrobenzene**
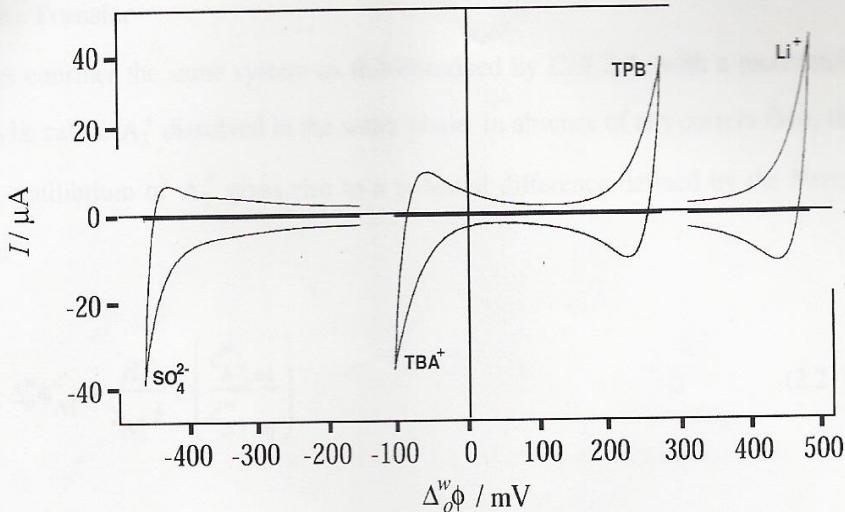
Figure: blank voltammograms obtained by four-electrode measurements
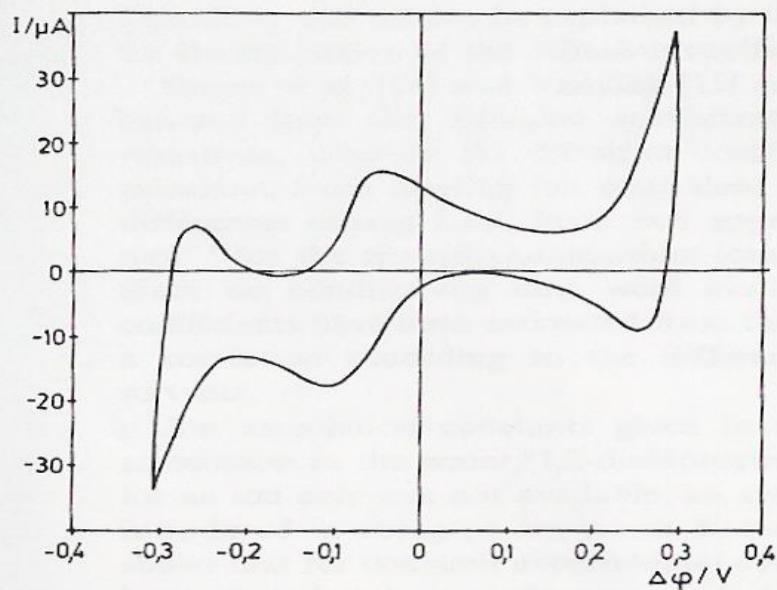
Transfer of perchlorate across water/NB interface
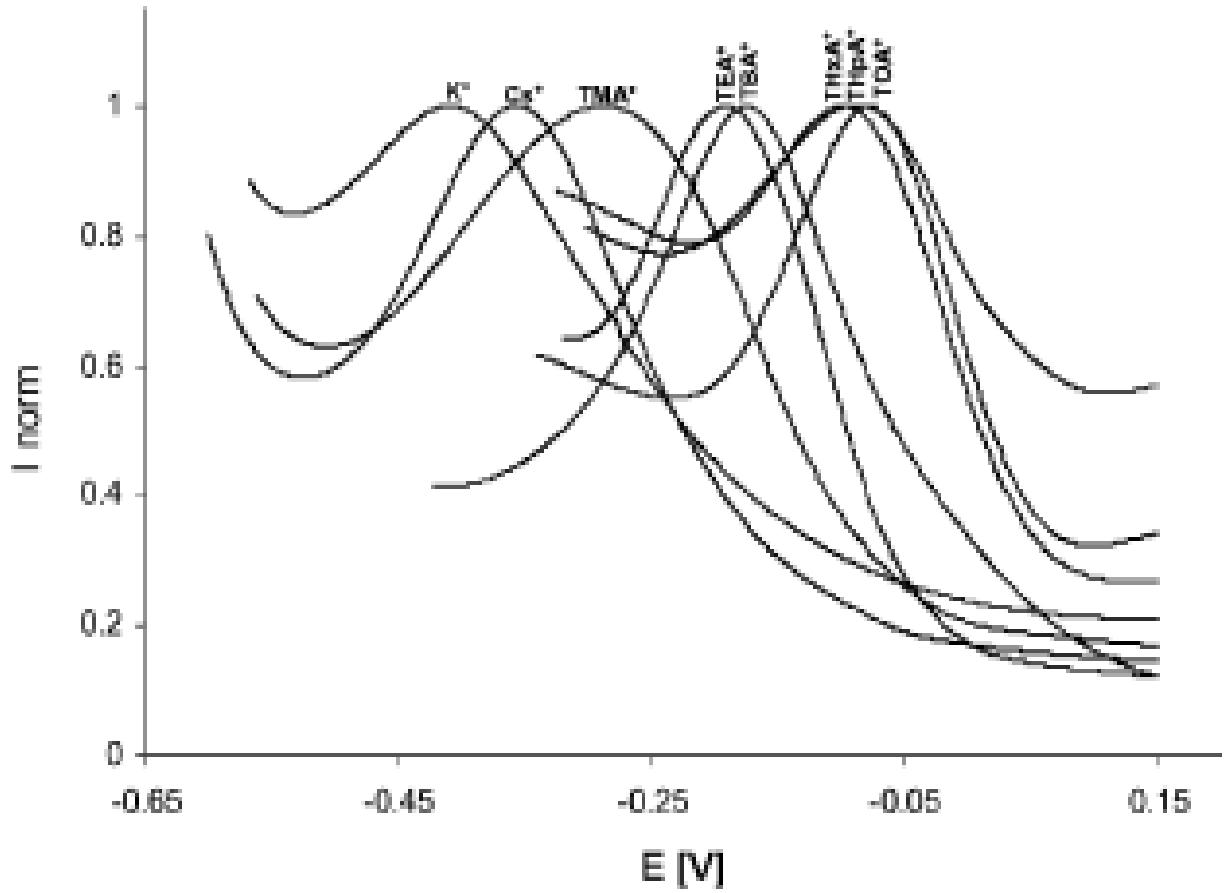
SW voltammograms showing transfer of some monocations across the w|nitrobenzene interface

$$dmfc(o) + A^-(w) \Leftrightarrow dmfc^+(o) + A^-(o) + 1e^-$$

-Once the reaction in the organic phase starts, then significant ammount of ions is being created in the organic phase

The Ionic content in organic solvent
at potential that is 250 mV more negative
than the formal potential of the redox system
(i.e. at $E(<0) - E^0$ = -250 mV):

$$c(dmfc+X-)o = c(Salt)w*\varepsilon/2 \, [-1+(1+(4*c(dmfc)o/e*c(salt)w)^{0.5}]$$

$$\varepsilon = exp(F(E(<0) - E^0)/RT)$$

<u>**c(dmfc+X-)org. phase = 5 mM!!!**</u>

(for c(dmfc)o = 0.05 M, and c(salt)w = 0.5 M)
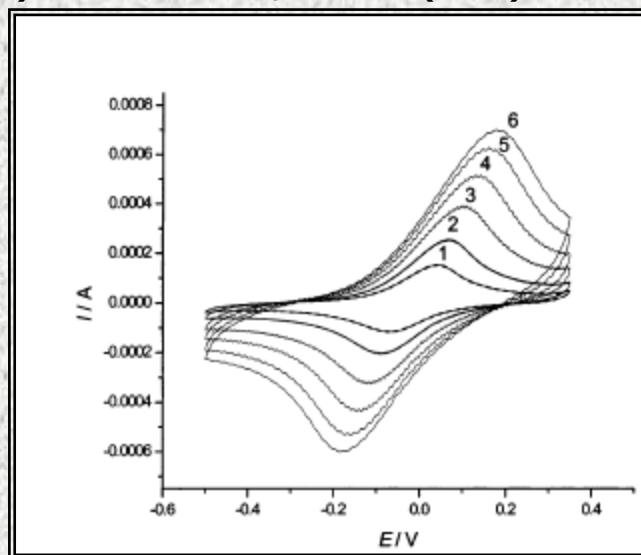
➤Expanding of the active organic layer
(through diffusion of the ions) :

$$L = k \, (Dt)^{0.5}$$
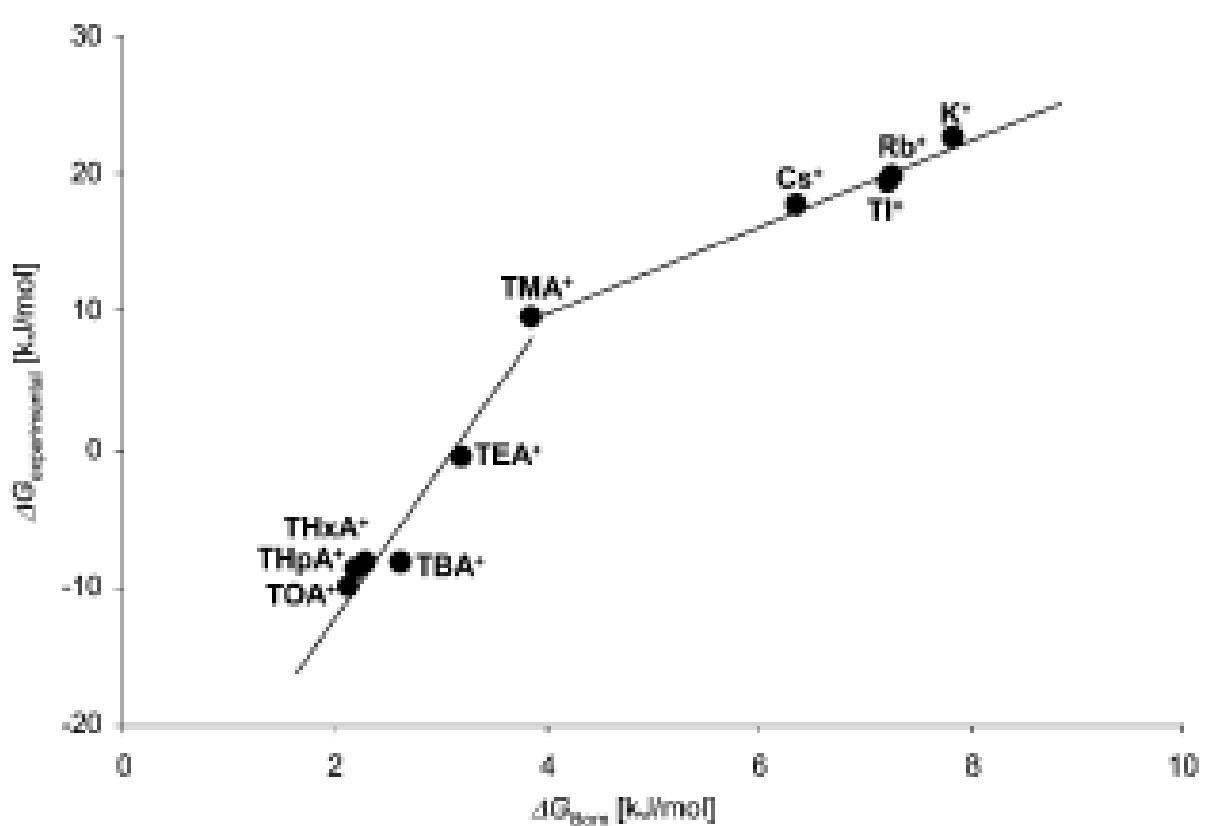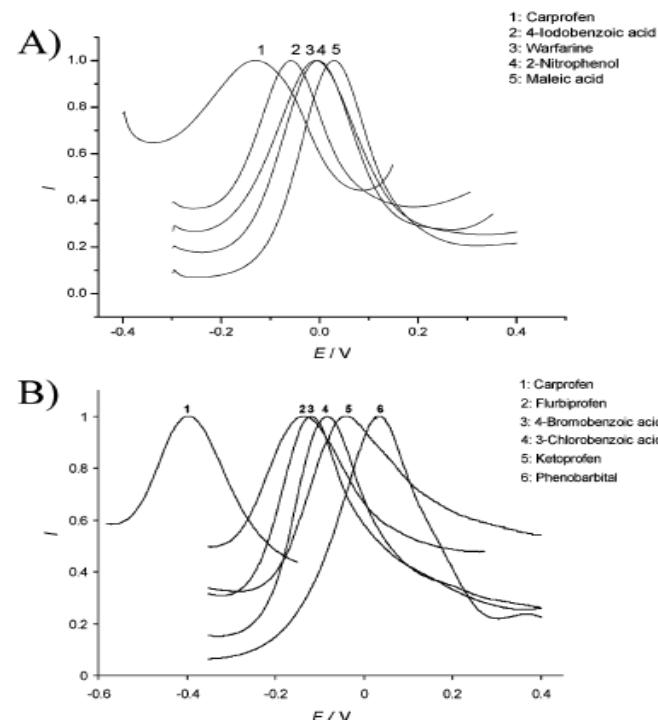
Comparison between experimentally determined $\Delta G_{W'Cat^+}^{NB^0}$ and the estimated values by using the electrostatic Born theory

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