Phase segregation on electroactive mixed SAMs: a numerical approach for describing interactions

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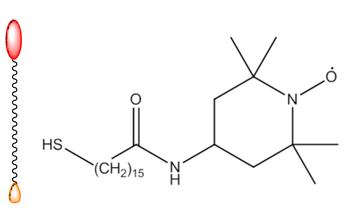
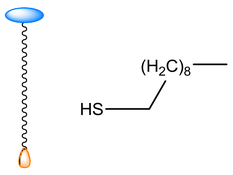
The Laviron's interaction model, dedicated to randomly distributed electroactive adsorbed species, was extended to a non-random distribution in order to extract the current–voltage characteristics from any surface distribution of electroactive centers on self-assembled monolayer (SAM). Confronted to electrochemical behaviour of nitroxyl radical SAMs, the agreement observed between theory and experiments provides evidence of a distribution independence of the interaction parameters.

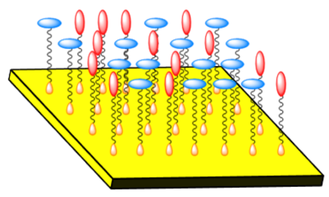
Nitroxyl radical self-assembled monolayers on gold



C15-TEMPO
Electroactive

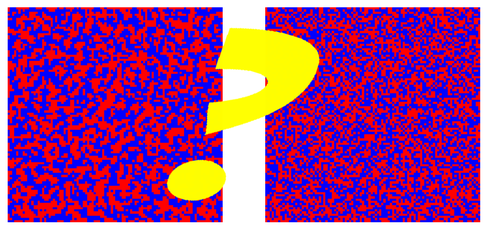


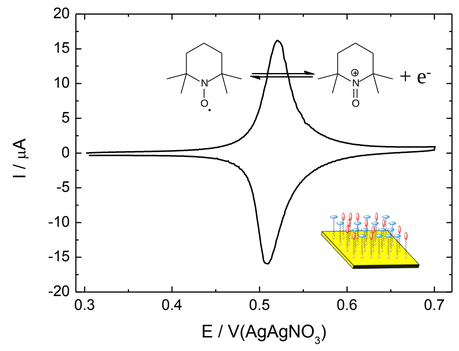
$C_{10}SH$
Non electroactive



Surface distribution is controlled by several factors like the elaboration protocol and the binary used

Phase segregation Random distribution



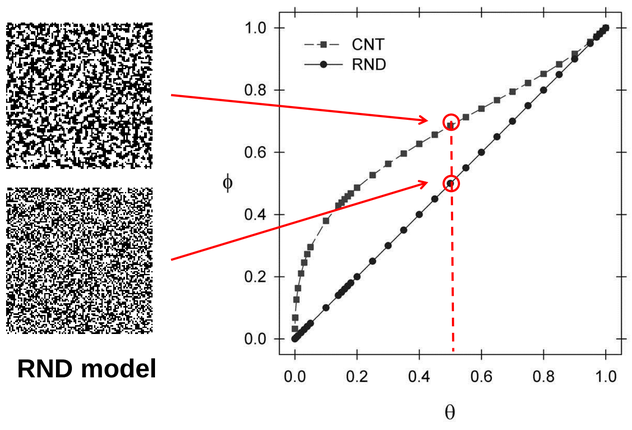


Can we obtain informations about the surface distribution with the shape of cyclic voltammograms ?

Generalization of Lateral Interaction Model for any surface distribution

FIRST STEP : NUMERICAL MODEL

CNT model



RND model

Generation of two surface distributions with two numerical models simulating the phase of adsorption :

- A "constraint" model (**CNT**) which simulates preferential adsorption of a molecule in interaction with a similar molecule.
- A "random" model (**RND**) which simulates the absence of interaction between molecules.

ϕ is representative of lateral interactions per electroactive site.
θ is the normalized surface coverage of electroactive species

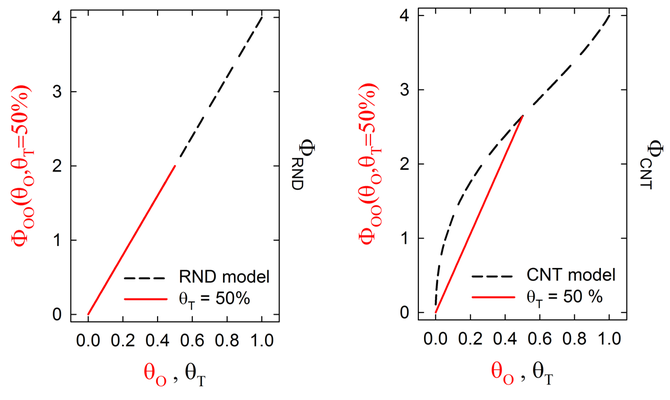
For a given θ_T matrix image, with random (RND) or non random (CNT) distribution, and initially composed of R species ($\theta_R = \theta_T$), we :

- simulate an oxidation process (left)
- follow the interactions between redox species (right) (here $\phi_{OO}(\theta_O,\theta_T)$ for θ_T = 50%).

In both models, numerical simulations exhibited a linear dependence of $\phi_{ij}(\theta_O, \theta_T)$, leading to :

$$\phi_{ij}(\theta_O,\theta_T) = N\frac{\phi(\theta_T)}{\theta_T}\theta_j \quad \text{with} \begin{cases} N \text{ the maximum possible neighbors} \\ i \text{ and } j \text{ are species O or R} \end{cases}$$

For a random distribution : $\phi_{ij}(\theta_O,\theta_T) = \frac{N\phi_{RND}(\theta_T)}{\theta_T}\theta_j = \frac{N\theta_T}{\theta_T}\theta_j = N\theta_j$



SECOND STEP : GENERALIZATION OF THE MODEL

$$\begin{cases} i(t) = nFAk_s\Gamma_{max}\left(\theta_O(t)\eta^{-\alpha}\exp\left[-2a_{OO}\frac{\phi(\theta_T)}{\theta_T}\theta_O(t) - 2a_{OR}\frac{\phi(\theta_T)}{\theta_T}\theta_R(t)\right] - \theta_R(t)\eta^{1-\alpha}\exp\left[-2a_{RR}\frac{\phi(\theta_T)}{\theta_T}\theta_R(t) - 2a_{RO}\frac{\phi(\theta_T)}{\theta_T}\theta_O(t)\right]\right) \\ i(t) = nFA\frac{d\Gamma_O}{dt} = nFA\Gamma_{max}\frac{d\theta_O}{dt} \end{cases}$$

where $\eta = \exp\left(nF\frac{(E - E_0')}{RT}\right)$ and $E_0' = E_0 - \frac{RT}{nF}\ln\left(\frac{b_O}{b_R}\right)$

and n, F, A, R, k_s, T, $E^{0'}$ have their usual meanings.

We generalized the LAVIRON's interaction model by introducing the ϕ parameter calculated in the first step.

θ_O and θ_R, normalized surface coverage of oxidized and reduced species
$\theta_T = \theta_O + \theta_R$, normalized surface coverage

a_{OO}, a_{RR}, a_{OR} and a_{RO} are the interaction constants between molecules of O, molecules of R and molecules of O and R respectively.
a_i is positive for an attraction and negative for a repulsion.
The a values are assumed to be independent of the potential.

$\phi(\theta_T)$, "segregation factor", is representative of the average number of lateral interactions per electroactive site

For a fast reversible system ($k_s = \infty$), the i-E characteristics can be expressed as :

$$E_p(\theta_T) = E^{0'} - \frac{RT}{nF}S\phi(\theta_T)$$

$$i_p(\theta_T) = \frac{n^2F^2vA\Gamma_{max}}{RT}\frac{\theta_T}{2(2 - G\phi(\theta_T))}$$

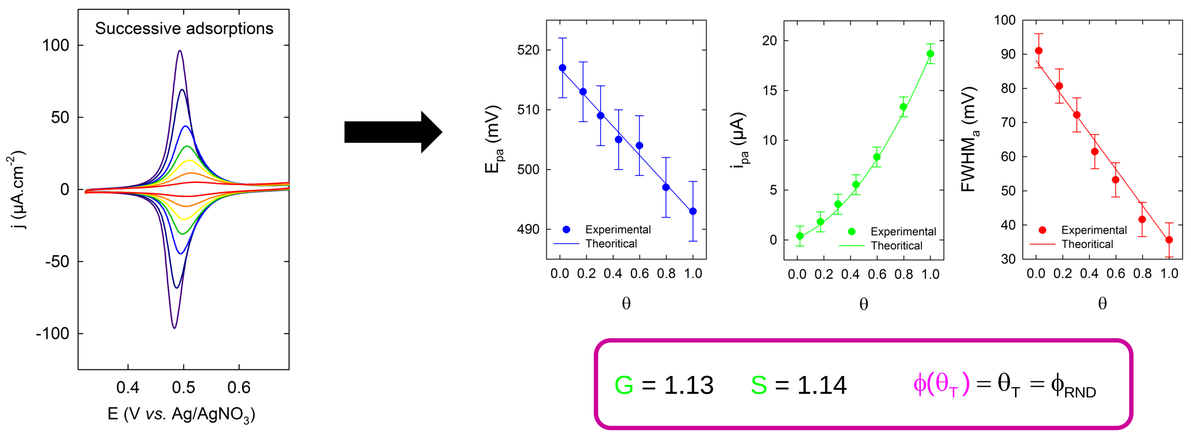
$$FWHM(\theta_T) \simeq \frac{RT}{nF}\left[2\ln(2\sqrt{2}+3) - \frac{3\sqrt{2}}{2}G\phi(\theta_T)\right]$$

with $G = a_{OO} + a_{RR} - a_{OR} - a_{RO}$ and $S = a_{OO} - a_{RR} + a_{OR} - a_{RO}$

Application

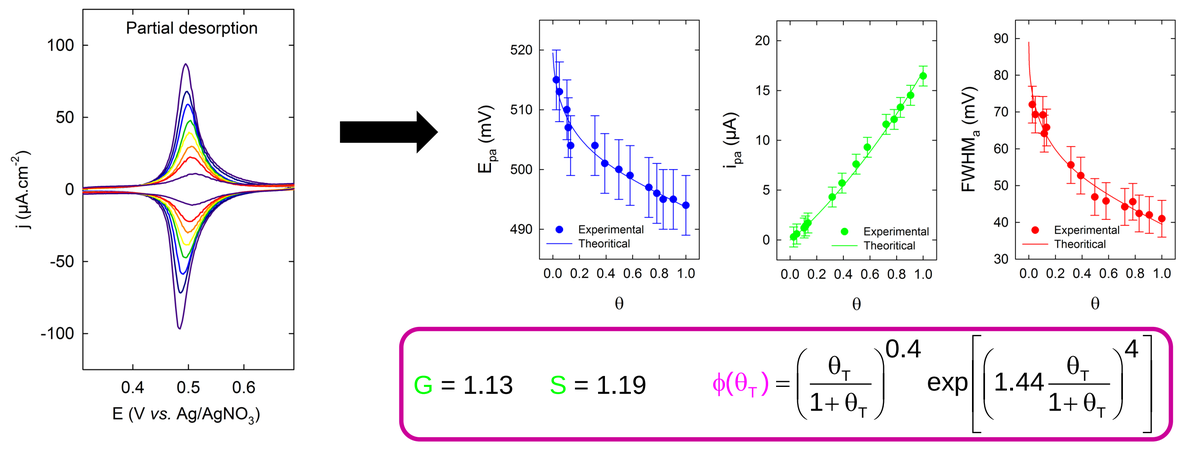
In order to test this new model, we elaborate C15-TEMPO mixed SAMs using two protocols leading to two surface distributions.

Successive adsorptions of C15-TEMPO and $C_{10}SH$
*Favors **random distribution***



G = 1.13 S = 1.14 $\phi(\theta_T) = \theta_T = \phi_{RND}$

Partial desorption of a densely packed SAM of C15-TEMPO under ultrasonication
*Favors **surface segregation***



G = 1.13 S = 1.19 $\phi(\theta_T) = \left(\frac{\theta_T}{1+\theta_T}\right)^{0.4}\exp\left[\left(1.44\frac{\theta_T}{1+\theta_T}\right)^4\right]$

Distribution independence of G and S parameters. The surface distribution ϕ can be deduced with the shape of cyclic voltammograms.

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4] Alévêque O., Gautier C., Dias M., Breton T., Levillain E., **Phys. Chem. Chem. Phys.**, 2010, DOI: 10.1039/C0CP00085J..
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