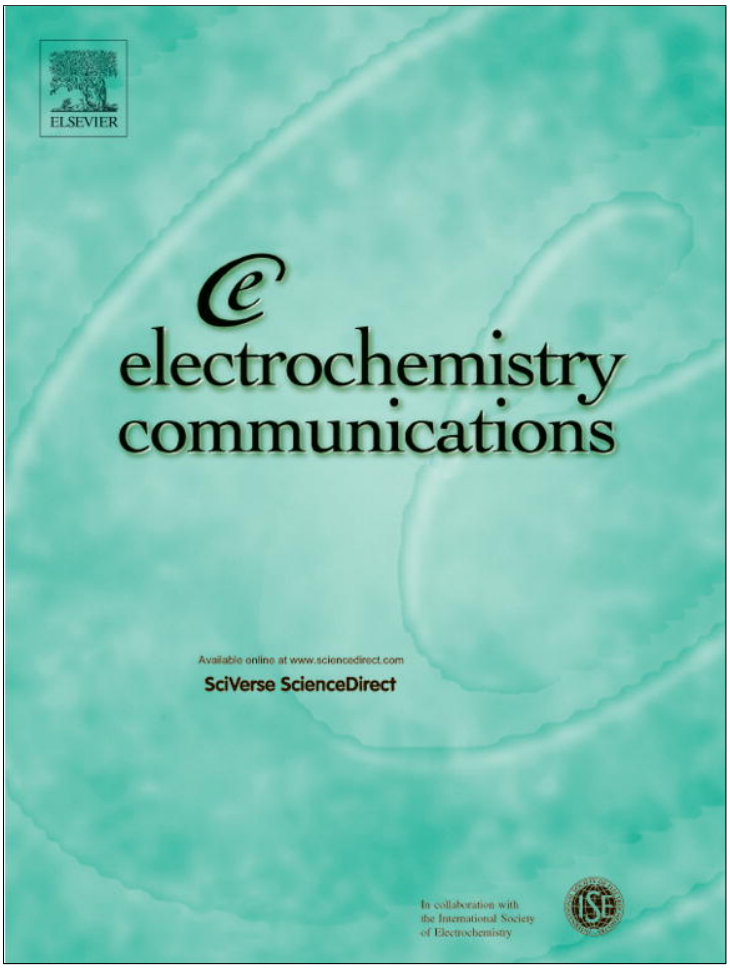
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Electroactive mixed self-assembled monolayers: Lateral interactions model updated to interactions between redox and non-redox species

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ABSTRACT

The lateral interactions model, dedicated to random and non-random distributed electroactive species on redox responsive self-assembled monolayers (SAM), was extended to interactions between redox and non-redox species. This approach supports an unusual result achieved in the field of electrochemical transduction without covalent links between redox and complexant units in mixed SAM.

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1. Introduction

Since their discovery in 1983 [1], self-assembled monolayers have become an ideal system for the theoretical study of interfacial phenomena [2], especially in the field of electrochemistry.

In a previous work [3], we have presented a theoretical study to complete the lateral interaction model proposed by E. Laviron [4], by extending this initial model to non-random distributions of electroactive sites adsorbed on surface. This model enables current-voltage behaviours to be simulated and allows extracting characteristics parameters (E_p, i_p and FWHM) of cyclic voltamograms (CVs) obtained from any surface distribution of electroactive self-assembledmonolayer(SAM).

Herein, we propose to update the lateral interaction model when interactions between redox and non-redox species are taking into account. Based on the same empirical numerical approach previously used, characteristic parameters (E_p, i_p and FWHM) of cyclic voltamograms (CVs) are extracted and discussed. In addition, this work supports an unusual result achieved in the field of electrochemical transduction without covalent links between redox and complexant units in electroactive mixed SAM [5].

2. Generalized lateral interactions model

To summarize previous works, the generalized lateral interactions model can be defined according to the main following hypotheses [3,4,6,7]:

- The electroactive centers are distributed on substrate with a unimodal statistical distribution of electroactive neighbours. A parameter $\phi(\theta)$, between 0 and 1, defined for a normalized surface coverage θ, quantifies the segregation level of the electroactive centers. For a randomly distributed SAM, $\phi(\theta) = \theta$, and when a segregation exist on the surface, $\phi(\theta) > \theta$.
- The sum of normalized surface coverage θ_O and θ_R of oxidized (O) and reduced (R) species is constant and equal to θ,
- The surface occupied by one molecule of O is equal to the surface occupied by one molecule of R,
- The electrochemical rate constant k_s is independent of the coverage,
- a_{OO}, a_{RR} and a_{OR} are the interaction constants between molecules of O, molecules of R and molecules of O and R, respectively. a_{ij} is positive for an attraction and negative for a repulsion. The a_{ij} values are assumed to be independent of the potential and distribution.

For a full reversible reaction ($k_s \to \infty$), cyclic voltammograms are totally reversible, and the characteristic parameters as full width at half maximum (FWHM), peak potential (E_p) and peak current (i_p)) are defined as:

$$E_p(\phi(\theta)) = E_0^{'} + \frac{RT}{nF} S\phi(\theta) \quad (1)$$

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$$i_p(\phi(\theta),\theta) = \frac{n^2F^2vA\ \Gamma_m}{RT}\frac{\theta}{2(2-G\phi(\theta))} \quad (2)$$

$$FWHM(\phi(\theta)) \overset{|G\phi(\theta)<1|}{\approx} \frac{RT}{nF}\left(2ln\left(2\sqrt{2}+3\right)-\frac{3\sqrt{2}}{2}G\phi(\theta)\right) \quad (3)$$

with, $G = a_{OO} + a_{RR} - 2a_{OR}$ *et* $S = a_{RR} - a_{OO}$ $(|G|and|S| \leq 2)$

In this model, the interactions with non-electroactive species are not taken into account, because this model was created to perfectly fit with mixed SAMs where the diluent used does not interact with electroactive species. The typical example is the case of electroactive mixed SAMs diluted with alkanethiols.

Based on this fact, the purpose of this work is to introduce, in the model, interactions with the non-electroactive species (D) and to show if these interactions can influence the the i-E characteristics or not. Note that only one type of diluent is used in this study.

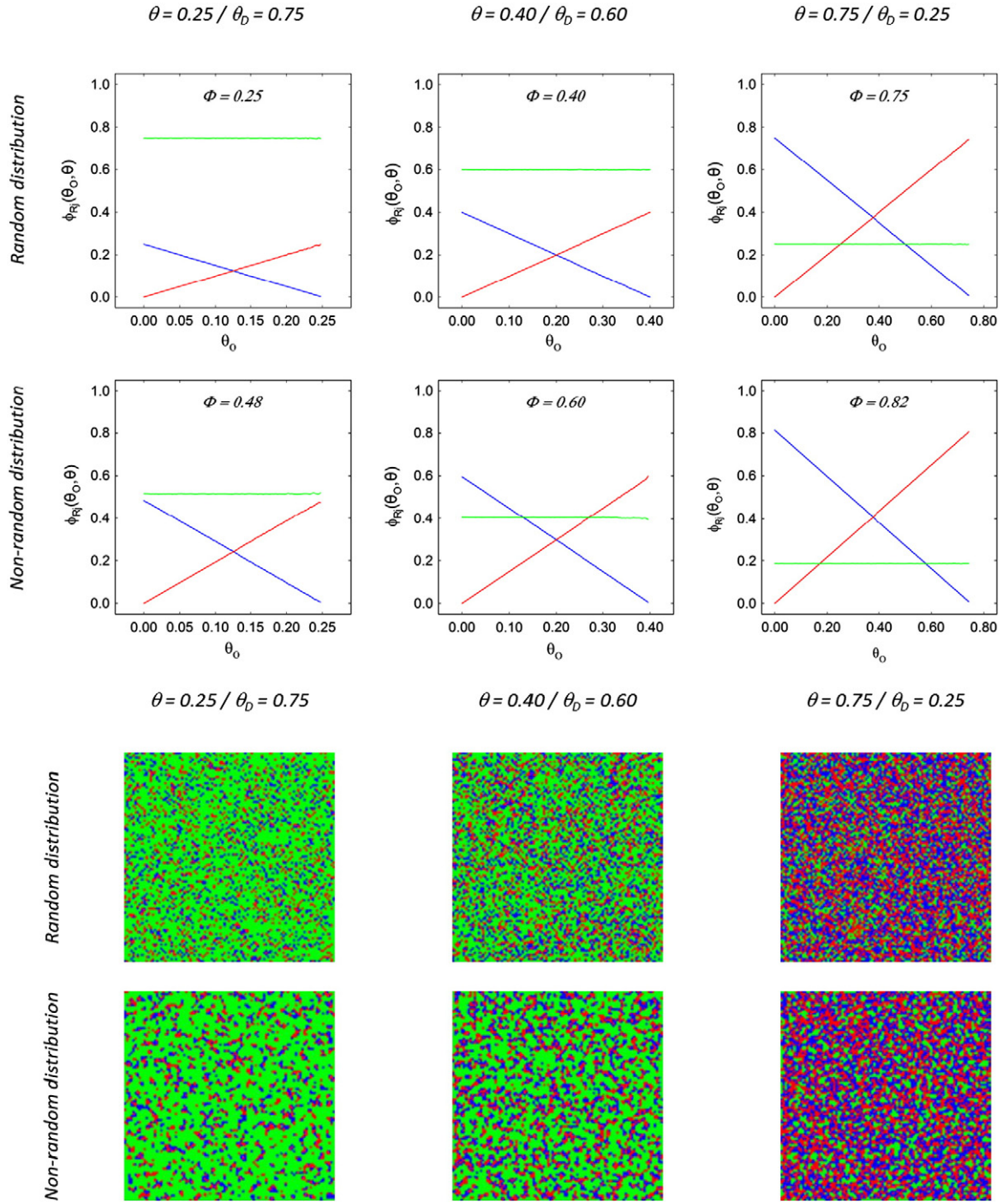


Fig. 1. (Top) Dimensionless quantities $\phi_{RR}(\theta_O,\theta)$ (blue), $\phi_{RO}(\theta_O,\theta)$ (red) and $\phi_{RD}(\theta_O,\theta)$ (green) vs. $\theta_O \in [0,\theta]$ for three various θ (0.25, 0.4 and 0.75) and two different surface distributions. (Bottom) Binary images obtained from calculated matrices during an oxidation step for $\theta_O/\theta = 50\%$ (intersection of the blue and red lines) and used for the calculation of dimensionless variables quantities $\phi_{ij}(\theta_O,\theta)$. For each matrix, R species are represented in blue, O species are represented in red and D species are represented in green. The size of the matrices is (100 × 100).

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3. Experimental

3.1. Numerical models

All procedures to model SAMs with matrix were clearly described in previous papers [8].

Essentially, the mixed SAMs with different molecular surface distributions (*i.e.* different $\phi(\theta)$ - Fig. 1), were numerically modeled (C++) by a square matrix M(X,Y) composed of "1" (site occupied by an electroactive specie initially in its reduced form) and of "0" (site occupied by a non electroactive specie, *i.e.* the diluent). The relation between the number of "1" and the "total number of sites" experimentally corresponds to the normalized surface coverage of electroactive species $\theta \in [0,1]$. Similarly, the relation between the number of "0" and the "total number of sites" experimentally corresponds to the normalized surface coverage of non-electroactive species $\theta_D \in [0,1]$. The relation, $\theta + \theta_D = 1$, is always true.

The oxidation process ($R_{ads} \rightleftarrows O_{ads} + ne^-$) is simulated by the random replacement of reduced species "1" by oxidized species "2". At each step of the oxidation process, the relation $\theta_O + \theta_R = \theta$ is always verified.

3.2. Interactions calculation during the numerical oxidation

At each step of the replacement (*i.e.* for various θ_O), we calculated interactions between all species by means of 9 dimensionless quantities:

$$\begin{aligned} &\bullet\ \textit{Interactions with } R: \phi_{RR}(\theta_O,\theta), \phi_{RO}(\theta_O,\theta), \phi_{RD}(\theta_O,\theta),\\ &\bullet\ \textit{Interactions with } O: \phi_{OR}(\theta_O,\theta), \phi_{OO}(\theta_O,\theta), \phi_{OD}(\theta_O,\theta),\\ &\bullet\ \textit{Interactions with } D: \phi_{DR}(\theta_O,\theta), \phi_{DO}(\theta_O,\theta), \phi_{DD}(\theta_O,\theta). \end{aligned} \quad (4)$$

$\phi_{ij}(\theta_O,\theta)$, is representative of the average number of interactions between species i (O, R or D) and species j (O, R or D) per species i.

Taking into account only the nearest neighbours interactions, $\phi_{ij}(\theta_O,\theta)$ can be expressed by:

$$\phi_{ij}(\theta_O,\theta) = \frac{1}{N_{max,\theta=1}} \times \frac{\sum_x^X \sum_y^Y \sum_{M_{\theta_O,\theta}(x,y)=i} M_{\theta_O,\theta}(x,y) N_j(x,y)}{\sum_x^X \sum_y^Y \sum_{M_{\theta_O,\theta}(x,y)=i} M_{\theta_O,\theta}(x,y)} \in [0,1]$$

$$\text{with} \begin{cases} M_{\theta_O,\theta}(x,y): \textit{Matrix generated for given surface coverages } \theta_O \textit{ and } \theta.\\ N_j(x,y): \textit{Number of direct neighbours } j \textit{ close to } M(x,y).\\ N_{max,\theta=1}: \textit{Maximum number of direct neighbours.}\\ \quad 6 \textit{ in the case of hexagonal packing.} \end{cases}$$

4. Results and discussion

4.1. Numerical results

Fig. 1 shows the trend of the three dimensionless quantities corresponding to interactions with R when θ and $\phi(\theta)$ are modulated. As previously observed [3], $\phi_{RR}(\theta_O,\theta)$ and $\phi_{RO}(\theta_O,\theta)$ exhibited a linear dependence with θ and $\phi(\theta)$. The parameter $\phi_{RD}(\theta_O,\theta)$ is constant during the oxidation process and is only dependant of the segregation factor $\phi(\theta)$. This means that, the number of species D around each electroactive specie remains constant, just because D is not affected by the oxidation process.

To generalize, numerical simulations lead to:

$$\begin{aligned} &\phi_{ij}(\theta_O,\theta) = \frac{\phi(\theta)}{\theta}\theta_j \quad \textit{with } (i,j) = (O \textit{ or } R)\\ &\textit{and}\\ &\phi_{iD}(\theta_O,\theta) = 1-\phi(\theta) \quad \textit{with } (i) = (O \textit{ or } R) \end{aligned} \quad (5)$$

4.2. Modification of Laviron's interaction model

4.2.1. Surface activities

The theories of Laviron and Frumkin [9–12], using the mean field theory, suggest that the surface activities of the oxidized and reduced species are not exactly equal their surface concentrations but are modulated by an exponential term containing interaction constants:

$$\gamma_i = \Gamma_i exp\left[\sum_k -2a_{ik}\theta_k\right] \qquad \textit{with } i,\ k = O \textit{ and } R \quad (6)$$

Using the methodology applied in previous papers [3], the surface activities of the oxidized, reduced and non-redox species can be expressed with the term $\phi_{ik}(\theta_O,\theta)$, *i.e.* in function of lateral interactions between species. Eq. (6) can be formulated as following:

$$\gamma_i = \Gamma_i exp\left[\sum_k -2a_{ik}\phi_{ik}(\theta_O,\theta)\right] \qquad \textit{with } i,\ k = O,\ R \textit{ and } D \quad (7)$$

With Eqs. (5) and (7), the surface activity of the two states of the redox specie is given by:

$$\begin{cases} \gamma_O = \Gamma_O exp\left[-2a_{OO}\dfrac{\phi(\theta)}{\theta}\theta_O - 2a_{OR}\dfrac{\phi(\theta)}{\theta}\theta_R - 2a_{OD}(1-\phi(\theta))\right]\\ \gamma_R = \Gamma_R exp\left[-2a_{RR}\dfrac{\phi(\theta)}{\theta}\theta_R - 2a_{RO}\dfrac{\phi(\theta)}{\theta}\theta_O - 2a_{RD}(1-\phi(\theta))\right] \end{cases} \quad (8)$$

Using the same formalism, a_{OD} is the interaction constant between oxidized and diluent molecules. a_{RD} is the interaction constant between reduced and diluent molecules.

4.2.2. Cyclic voltammetry parameters for a reversible system

The i-E characteristic (IUPAC convention) can be expressed:

$$\begin{aligned} i(t) &= nFAk_s\left(\gamma_O exp\left[-\alpha\frac{nF}{RT}\left(E-E^{0'}\right)\right] - \gamma_R exp\left[(1-\alpha)\frac{nF}{RT}\left(E-E^{0'}\right)\right]\right)\\ &= nFAk_s\left(\gamma_O\eta^{-\alpha} - \gamma_R{}^{1-\alpha}\right) \textit{with } \eta = exp\left[\frac{nF}{RT}\left(E-E^{0'}\right)\right] \textit{ and } E^{0'}\\ &= E^0 + \frac{RT}{nF}ln\left(\frac{b_R}{b_O}\right) \textit{ with } b_R \textit{ and } b_O \textit{ the adsorption coefficients} \end{aligned} \quad (9)$$

Using surface activity of the two redox states, Eq. (10), we reach:

$$\begin{cases} i(t) = nFAk_s\Gamma_{max}\begin{pmatrix} \theta_O(t)\eta^{-\alpha}exp\left[-2a_{OO}\dfrac{\phi(\theta)}{\theta}\theta_O - 2a_{OR}\dfrac{\phi(\theta)}{\theta}\theta_R - 2a_{OD}(1-\phi(\theta))\right]\\ -\theta_R(t)\eta^{1-\alpha}exp\left[-2a_{RR}\dfrac{\phi(\theta)}{\theta}\theta_R - 2a_{RO}\dfrac{\phi(\theta)}{\theta}\theta_O - 2a_{RD}(1-\phi(\theta))\right] \end{pmatrix}\\ i(t) = nFA\dfrac{d\Gamma_O}{dt} = nFA\Gamma_{max}\dfrac{d\theta_O}{dt}\\ \textit{with } n,F,A,k_s,R,T,E,\ E_0^{'} \textit{ and } t \textit{ have their usual meanings} \end{cases} \quad (10)$$

For a fast reversible system ($k_s \rightarrow \infty$), the Nernst equation is applicable:

$$\frac{\gamma_O}{\gamma_R} = \eta = exp\left[\frac{nF}{RT}\left(E-E^{0'}\right)\right] \quad (11)$$

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From Eqs. (8) and (11) and, we obtain:

$$exp\left[\frac{nF}{RT}\left(E-E^{0'}\right)\right]=\frac{\theta_O}{\theta-\theta_O}exp\left[-2\frac{\phi(\theta)}{\theta}(G\theta_O+\theta(a_{OR}-a_{RR}))-2(1-\phi(\theta))(a_{OD}-a_{RD})\right]$$

$$exp\left[\frac{nF}{RT}\left(E-E^{0'}\right)\right]=\frac{\theta_O}{\theta-\theta_O}exp\left[-2\frac{\phi(\theta)}{\theta}(G\theta_O+\theta(a_{OR}-a_{RR}))-2(1-\phi(\theta))D\right] \quad (13)$$

$$with\ interaction\ parameters\begin{cases}G=a_{OO}+a_{RR}-2a_{OR}\\S=a_{RR}-a_{OO}.\\D=a_{OD}-a_{RD}\end{cases}\quad(a_{OR}=a_{RO})$$

In order to extract the i-e characteristic (cyclic voltammetry, $E = E_i + vt$), the differentiation of Eq. (13) in t and θ_O respectively leads to:

$$\left(\frac{nF}{RT}v\right)dt=\left(\frac{\theta}{\theta_O(\theta-\theta_O)}-2G\frac{\phi^n(\theta)}{\theta}\right)d\theta_O \quad (14)$$

From Eqs. (10) and (14), the current can be expressed:

$$i(\theta_O)=\frac{n^2F^2Av\Gamma_{max}}{RT}\frac{\theta\theta_O(\theta-\theta_O)}{\theta_T{}^2-2G\theta_O\phi(\theta)(\theta-\theta_O)} \quad (15)$$

From Eqs. (13) and (15), peak potential (E_p) and peak current (i_p) can be extracted for $\theta_O = \theta/2$.

$$E_p(\phi(\theta))=E^{0'}+\frac{RT}{nF}S\phi(\theta)-2\frac{RT}{nF}(1-\phi(\theta))D \quad (16)$$

$$i_p(\phi(\theta),\theta)=\frac{n^2F^2vA\Gamma_{max}}{RT}\frac{\theta}{2(2-G\phi(\theta))} \quad (17)$$

From Eqs. (13), (15), (16) and (17), full width at half maximum (FWHM) can be extracted for $i = i_p/2$.

$$FWHM(\phi(\theta))=\frac{2RT}{nF}\left[ln\left(\frac{1+\sqrt{\frac{G\phi(\theta)-2}{G\phi(\theta)-4}}}{1-\sqrt{\frac{G\phi(\theta)-2}{G\phi(\theta)-4}}}\right)-G\phi(\theta)\sqrt{\frac{G\phi(\theta)-2}{G\phi(\theta)-4}}\right] \quad (18)$$

$$\overset{|G\phi(\theta)<1|}{\approx}\frac{RT}{nF}\left(2ln\left(2\sqrt{2}+3\right)-\frac{3\sqrt{2}}{2}G\phi(\theta)\right)$$

4.3. Discussion

4.3.1. Differences between the two models

A comparison between Eqs. (16), (17) and (18) and Eqs. (1), (2) and (3) shows that only the peak potential (Ep) of cyclic voltamograms (CVs) is affected, when the interaction between redox and non-redox species are taken into account.

The difference between Eqs. (1) and (16) is equal to:

$$\left|\Delta E_p(\theta)\right|=2\frac{RT}{nF}|D|[1-\phi(\theta)] \qquad with\ |D|\leq 2 \quad (19)$$

This means that, if the molecules used to dilute a SAM can interact with the redox species, a maximum variation of 103 mV ($T = 298$ K, $D = 2$ and $\phi(\theta) \approx \theta \to 0$) on the peak potential can be obtained from the previous model, whatever the distribution is. This extreme variation makes the previous generalized lateral interactions model unusable.

This phenomenon is clearly shown on Fig. 2. The shapes of the CVs are identical whereas the peak potentials are affected by a_{OD} when the surface coverage of electroactive molecules decreases.

The determination of D is not very easy and can be made only if the interaction constants G and S are precisely known (case of a non-interacting diluent). In that case, the value of D is determined by adjusting the experimental points with Eq. (16).

4.3.2. Potential applications

Blanchard et al. [5] provides evidence of electrochemical transduction without a covalent link between redox (ferrocene) and complexant (crown ether) units in mixed SAMs and demonstrates, without giving further explanation, that the electrochemical transduction (*i.e.* the potential shift) depends on the crown ether/ferrocene ratio (*i.e.* the surface coverage of ferrocene).

Considering that the crown ethers act as, either a "neutral" diluent (*i.e.* free) or a diluent which interacts with the redox molecules (*i.e.* complexed), this unusual result can be interpreted by the lateral interactions model including interactions between redox and non-redox species. The peak potential shift can be expressed as:

$$\Delta E_p(\theta)=E_p(complexed)-E_p(free)=-2\frac{RT}{nF}D[1-\phi(\theta)] \quad (20)$$

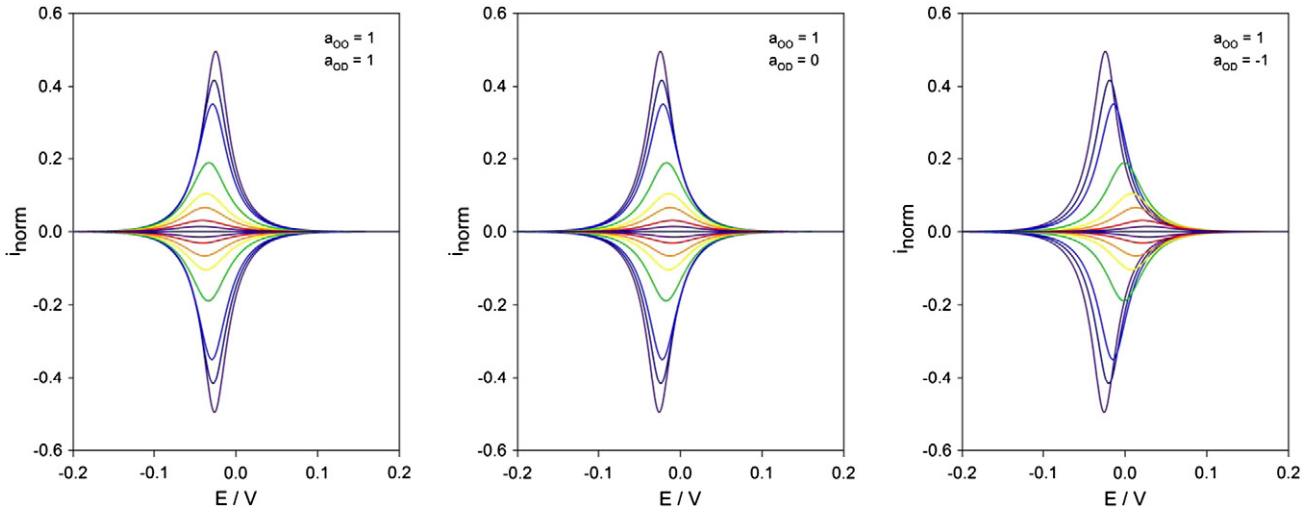


Fig. 2. i-E characteristics of cyclic voltamograms, calculated from Eq. (10), as a function of $\theta = \{1, 0.9, 0.8, 0.5, 0.3, 0.2, 0.1, 0.05, 0.0001\}$, for a random distribution of electroactive species and for given values of $G = -S = a_{OO} = 1$ and $D = a_{OD} = \{-1, 0, 1\}$. Others parameters: $k_s = 100000 \to \infty$ (full reversible reaction), $E^{0'} = 0$ V, $v = 0.1$ V.s^{-1} and $T = 293$ K. The currents are normalized according to $i_{norm} = i/(n^2F^2vAFT/RT)$ [7].

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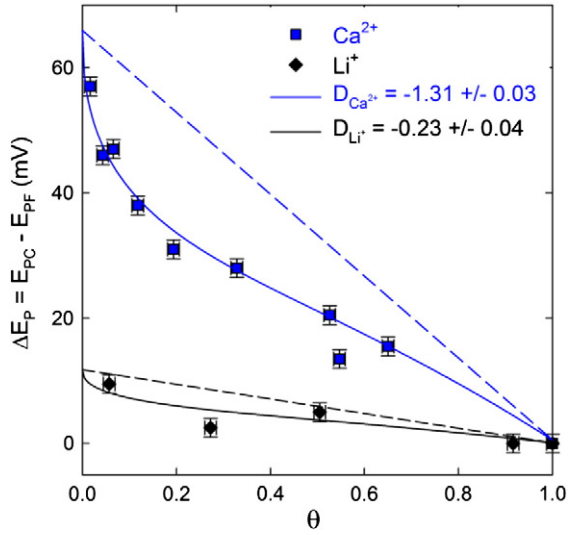


Fig. 3. Peak potentials shift (ΔE_p) before and after complexation with Ca^{2+} (Blue square) and Li^+ (Black diamond), as a function of the surface coverage. (Blue and black lines) Adjustments of experimental data using Eq. (19), with a non-random distribution $\phi(\theta)$ and a parameter D depending of each cation. (Blue and black dash lines) Variations in the case of a random distribution.

Because potential shifts are not linear in ferrocene surface coverage (θ), the interaction parameter D was estimated from experimental data with a non-random surface distribution of the electroactive centers. Fig. 3 compares model outputs (*i.e.* variation of peak potential before and after complexation from Eq. (20)) with the results of Ca^{2+} and Li^+ complexations on mixed SAMs (*i.e.* borderline cases of the Fig. 3 in reference [5]). As the model predicts, the trend is monotonic, the electrochemical transduction is most effective when redox molecules are highly diluted in the matrix of diluent and a segregation phase of ferrocene sites on mixed SAMs is suggested. In these cases, the peak potential shift can be understood by the establishment of interaction between the oxydized species and complexed crown ether ($D = a_{OD}$). By way of reminder, the interaction between cations or anions are possible, because lateral interactions are governed by the interplay of intermolecular forces, electrostatic interactions [13], pairing ions between charged states of redox molecules and electrolytic ions [14,15], and solvatation.

It is important to note that the model matches with the trend observed despite different experimental conditions (quartz crystal microbalance experiments suggest that the crown ether occupies the surface of two ferrocenes, *i.e.* two cell of the matrix).

5. Conclusion

This work updates the lateral interactions model to interactions between redox and non-redox species. Compared with published experimental data, the model seems effective in the case of electrochemical transduction.

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