Kinetic Implications of the Presence of Intermolecular Interactions in the Response of Binary Self-Assembled Electroactive Monolayers

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Supporting Information

ABSTRACT: Quantitative analysis of the influence of intermolecular interactions on the response of electroactive binary monolayers, incorporating the presence of electroinactive coadsorbed species and Marcus–Hush kinetic formalism, has been deduced as an extension of previous models. An expression for the current–potential relationship in terms of two global phenomenological interaction parameters and the apparent charge-transfer rate constant and formal potential has been obtained and applied to multipotential chronoamperometry for the analysis of intermolecular interaction effects on the kinetics of the charge transfer. Experimental verification of the theoretical framework has been performed with binary ferrocenylundecanethiol/decanethiol monolayers on gold and platinum substrates for different coverage degrees of the redox probe. The increase of the ferrocene coverage gives rise to a slowing down of the charge-transfer process through a decrease of the apparent rate constant above a 90% for gold and platinum electrodes when the surface coverage increases from 1–2 to 15–30%. Significant differences in the magnitude of intermolecular interactions and the symmetry degree of the charge-transfer process are observed between gold and platinum electrodes. Moreover, for high surface coverages of ferrocene, two different domains appear, from which it is possible to carry out a kinetic discrimination of the two responses. Values of the interaction and kinetic parameters have been obtained for the different monolayers under study, and the limit of applicability of this treatment is discussed.

1. INTRODUCTION

The interest and applications of redox molecular systems confined at conducting interfaces, and electroactive monolayers in particular, have grown remarkably in recent years. Among the increasing number of applications of these systems, the following can be cited: the design of new electrocatalytic platforms and bioplatforms for the development of new sensors and biosensors,1−3 molecular and organic electronics4−6 and energy storage systems,7,8 among many others, together with the possibility of exploring in detail fundamental aspects of charge-transfer processes as well as the chemical reactivity at electrified interfaces.9,10 To this purpose, it has been of great help in a number of procedures for immobilizing neutral and charged species at a wide range of conductive substrates,5,11−13 together with the use of instrumental techniques that allow for analyzing and in some cases controlling the structure of the modified interfaces.12,14,15

To improve the performance of these devices, it is necessary to get a detailed insight of the processes taking place, and with this aim, several theoretical models have been developed and tested with different electrochemical techniques, especially with cyclic voltammetry (CV).16−18 Unfortunately, in most practical situations, the experimental electrochemical responses deviate from the most used models that are based on an “ideal” behavior of the system, that is, a perfectly homogeneous 2-D electroactive monolayer with uniform solvation of the redox probes, local potential at the reactive molecules independent of the redox conversion degree, and the absence of intermolecular interactions.17−19 Unless rigorous procedures are followed for the synthesis of the monolayers to reasonably ensure the abovementioned requirements (i.e., low coverage degree of the redox probes and a reasonably rigid structure of the monolayer, among others), the ideal behavior is indeed a naive picture of the real experimental situation. Nonidealities, such as the presence of intermolecular interactions,19,20 the complex influence of the electrical double layer through the interfacial potential distribution,21,22 or the existence of different electrostatic environments leading to distinct structural (and therefore redox functional) domains, will cause a distortion of the electrochemical response of these systems.23−26

In this paper, we will focus on the influence of intermolecular interactions related to nonuniform solvation and ineffective electrostatic screening of the redox probes, together with the presence of noncovalent interactions.17,27 This gives rise to the appearance of different energetic landscapes surrounding the redox probes as a result of the balance between Coulombic (long range) and van der Waals (short range) interactions from which an attractive or repulsive global character of interactions
2. RESULTS AND DISCUSSION

In the following section, we will discuss the application of the simplified Laviron–Tokuda fully randomized model (s-LT-FR, see the Theory section) to a surface-confined redox pair when a single constant potential \( E \) or a sequence of \( n \) consecutive constant potentials \( E_1, E_2, \ldots, E_n \) is applied to the electrode, and the results will be compared with those corresponding to the ideal situation. For the sake of simplicity, henceforth, \( k_{\text{ap, global}}^{1292} \) will be denoted as \( k_{\text{ap}}^{1292} \).

1. Theoretical Results: Multipotential Pulse Chronoamperometry

The influence of parameters \( G \) and \( S \) on the current–time curves for the charge-transfer process given by (1) will be first analyzed. To simplify the analysis of the chronoamperometric responses, eqs 8 and 38 (or 41) can be rewritten as

\[
\Phi = \frac{I}{Q_{p}^{k_{\text{ap}}}} = -\frac{df_{k}}{df_{j}^{0}} = -\frac{df_{k}}{dT} = g\left(\eta_{i}\right) e^{-\theta_{i}S_{k}} \left( f_{r} e^{\theta_{r}G(1-f_{k})} - (1-f_{r}) e^{\theta_{r}G_{c}} \right)
\]

(1)

In the abovementioned expression, we have re-defined the time scale through the dimensionless time \( T = \frac{k_{\text{ap}}^{1292}}{k_{\text{ap}}^{0}} \). Both BV and MH kinetics formalisms have been considered (with a typical value of \( \alpha = 0.5 \) in the former and, unless specified, \( \gamma = 0 \) in the latter).

Equation 1 cannot be analytically solved, and therefore, standard numerical procedures have been employed (e.g., the fourth-order Runge–Kutta method). Nevertheless, analytical solutions can be obtained when some additional simplifications are introduced. Thus, in the absence of interactions (i.e., \( a_{ij} = 0 \)), and \( G = S = 0 \), the abovementioned equation presents a simple solution which takes the following expression for any potential \( E_{j} \) of an arbitrary sequence applied during a time \( t_{j}^{34} \)

\[
\Phi = \text{constant} \times e^{-k_{\text{eff}}(E_{j})t_{j}}
\]

(2)

with \( k_{\text{eff}}(E_{j}) \) being the effective rate constant at potential \( E_{j} \) given by

\[
k_{\text{eff}}(E_{j}) = k_{\text{ox}}(E_{j}) + k_{\text{red}}(E_{j})
\]

(3)

and \( k_{\text{ox}} \) and \( k_{\text{red}} \) being the rate constants for the oxidation and reduction processes, for which the particular mathematical form of the dependence with potential does not need to be established a priori and, therefore, both BV and MH kinetics formalisms can be directly applied.\textsuperscript{34,35} Thus, from eq 2, it is evident that the current shows a faster decay with time as the effective rate constant is higher, and the plots of ln(\( \Phi \)) versus time are linear with a slope equal to \( k_{\text{eff}}(E_{j}) \).

In Figure 1, several \( \Phi-T \) current–time curves have been plotted as obtained numerically from eq 1 for an applied potential \( (E - E_{\text{ap}}^{0}) = 0.15 \text{ V} \) assuming the BV formalism. These curves have been calculated for several values of \( \theta_{i}G \) (shown in the curves) and three values of \( \theta_{i}S \), (1, 0, and −1). The "ideal" behavior (absence of interactions, \( \theta_{i}G = 0 \), and \( \theta_{i}S = 0 \)) can be seen in Figure 1b (blue lines).

From the curves in this figure, it can be seen that the shape of the chronoamperograms is strongly affected by the values of the interaction parameters \( \theta_{i}G \) and \( \theta_{i}S \). Concerning the influence of \( \theta_{i}G \), when its value varies from negative (global repulsive character) to positive (global attractive character), the \( \Phi-T \)
curves show a slower temporal evolution for lower values of \( T \) (and even an increase with time for values of \( \theta_E G > 1 \) and \( \theta_E S \geq 0 \), Figure 1a,b), whereas the opposite behavior is observed for longer values of \( T \) (compare curves with \( \theta_E G = -1.5 \) and 1.5 in Figure 1a,c). On the other hand, the decrease of \( \theta_E S \) gives rise to a faster evolution of the current, whatever the value of \( \theta_E G \) (compare Figure 1a,c). For example, the value of \( T \) required for reaching a 10% of the initial current value is 0.043 for \( \theta_E S = -1 \), whereas it is more than three times higher for \( \theta_E S = 0 \) (\( T = 0.1322 \)), and in the case of \( \theta_E S = 1 \), the value is above 0.25 (\( T = 0.3615 \)).

The origin of the abovementioned influences lies in the differential character of the current for surface-confined species, that is, \( \Phi = -d\Delta Q/dT \). We have plotted in Figure S1 the dimensionless charge–time curves \( (Q/Q_0)−T \) corresponding to the current–time ones given in Figure 1, where it is clear that the increase of both \( \theta_E G \) and \( \theta_E S \) gives rise to a slower temporal increase of the charge. The current behavior observed at shorter \( T \) values is related to a change in the curvature of the \( (Q/Q_0)−T \) curves, mainly for positive values of \( \theta_E S \) and \( \theta_E G > 1 \). This is the responsible for the striking increase of the dimensionless current shown in Figure 1a,b.

When the MH formalism is considered, the global trends discussed above also hold, but the current–time curves show a slower time evolution as compared with those corresponding to BV for all the cases under study. In Figure S2, we have plotted the comparison between BV (lines) and MH treatments for \( \Lambda = 20 \) (i.e., a reorganization energy \( \lambda \simeq 0.5 \) eV, symbols) calculated for \( \theta_E G = 1 \), three values of \( \theta_E S \) (shown in the curves), and \( (E − E_{0p}^{\Delta}) = 0.15 \) V. The slower time evolution predicted by MH is based on the fact that the dimensionless effective global rate constant, defined as

\[
k_{\text{eff,D}}(E) = k_{\text{eff}}(E)/k_{ap}^0 = (k_{\text{eff}}(E) + k_{\text{ref}}(E))/k_{ap}^0
\]

is smaller for MH than that corresponding to BV because it is fulfilled that, under these conditions, \( \delta^{\text{MH}}(\phi_{ap}) < \delta^{\text{BV}}(\phi_{ap}) \) (see eq 36 and ref 36).

A usual procedure to obtain the values of the effective rate constant at each potential is to plot the logarithm of the current versus time (i.e., an exponential temporal decrease is assumed and, thus, from the values of the slopes of these lines, it is possible to obtain \( k_{\text{eff}}(E) \) (see eq 2 and refs 34 and 35). To know if this methodology can be applied when the influence of intermolecular interactions is significant, Figure 2a–c shows the logarithms of the currents shown in Figure 1 for the different cases under study (assuming the BV kinetic formalism). As can be seen, a good linearity is only observed for higher values of \( T \) (typically \( T \geq 0.15 \) values are recommended to carry out this kind of kinetic analysis, although for negative values of \( \theta_E S \) this limit time can be smaller). It should also be taken into account that, ideally, for a constant potential, the value of \( k_{\text{eff}}(E) \) should indeed be constant. However, although for negative values of \( \theta_E G \) there is no significant influence of the interactions parameters on the slope of the logarithm curves, for \( \theta_E G \geq 0 \), an increase of the absolute value of the slope is observed, being much more apparent as \( \theta_E S \) decreases (compare Figure 2a,c). Therefore, the value of \( k_{\text{eff}}(E) \) obtained from the logarithmic curves under these conditions is clearly affected by the presence of interactions and it should be considered as an apparent value.

When the MH formalism is considered, the linearity between \( \ln(\Phi) \) and \( T \) is also observed for values of \( T \geq 0.15 \) (see Figure S3), although the slopes of these straight lines are smaller than those obtained for BV curves, indicating a lower effective rate constant \( k_{\text{eff,D}}(E) \). As in the abovementioned case, one should be aware of the dependence of the values of \( k_{\text{eff}}(E) \) on the experimental conditions.

We will consider now the application of a staircase sequence of constant potentials of the form \( E_j = (E_{\text{initial}} − E_{\text{end}}^\Delta) + j\Delta E \) with \( j = 1, 2, \ldots, n \) with \( \Delta E \) being a constant potential amplitude. Each potential is applied during a dimensionless time \( 0 \leq T_j \leq \tau \), with the total time being \( T = T_j + (j - 1)\tau \). The current for each potential is obtained by solving eq 1 for the corresponding applied potential and boundary conditions. Thus, in Figure 3a, the \( \Phi–T \) curves obtained for the application of 31 potential pulses are plotted with \( (E_{\text{initial}} − E_{\text{end}}^\Delta) = -0.15 \) V, \( \tau = 0.25 \), and \( \Delta E = 0.01 \) V. Three values of the \( \theta_E G \) parameter have been
considered (−1, 0, and 1, corresponding to black, red, and blue lines, respectively) for \( \Theta_{ES} = 0 \). In Figure 3b, the \( \Phi - T \) curves are shown to be restricted to the potential interval (−0.1, 0.1) V.

The current transients in this figure show the typical sawtooth-shaped feature of surface-confined species (see, e.g.,34), with the increase of \( \Theta_{EG} \) causing the increase of the current at potentials around \( E_{ap}^0 \), whereas the opposite behavior is observed for \( |E_j - E_{ap}^0| > 0.075 \) V. This can also be observed in the linear plots of Figure 3b, from which it is clear that the slopes of the logarithmic curves increase with \( \Theta_{EG} \) (in the absolute value) for potentials far away from \( E_{ap}^0 \) whereas these slopes become practically independent of \( \Theta_{EG} \) for \( E \approx E_{ap}^0 \).

In general, the influence of \( \Theta_{EG} \) and \( \Theta_{ES} \) on \( \Phi - T \) and in \( \Phi - T \), and therefore on the apparent reversibility degree of the process, is complex. When one considers the combined increase of both parameters (see Figure S4), the overall effect is the decrease of the slope of the logarithmic curve together with the shift of the response toward more positive potentials. The combined increase (in the absolute value) of \( \Theta_{EG} \) and \( \Theta_{ES} \) could be related to an overall increase of the attractive interactions due to a greater incidence of van der Waals interactions.20,37

To determine, or at least estimate, the values of \( k_{ap}^0 \) and \( E_{ap}^0 \) the most direct approach is that proposed by Chidsey,35 where the slopes of the logarithms of chronoamperometric curves obtained for different applied potentials are plotted versus the applied potentials, thus obtaining a V-shaped curve (Chidsey–Tafel plot) from which the values of \( 2k_{ap}^0 \) and \( E_{ap}^0 \) are extracted from the ordinate and abscissa of the minimum, respectively.

In Figure 4, three sets of Chidsey–Tafel plots (ln(k_{d(3)})-(E - E_{ap}^0)) are plotted, calculated from a multipotential sequence analogous to that used in Figure 3 for several values of \( \Theta_{EG} \) (shown in the curves) and three values of \( \Theta_{ES} \) (1, 0, and −1, Figure 4a–c, respectively). Both the Butler–Volmer (lines) and the symmetrical Marcus–Hush (γ = 0, symbols) models have
been considered. In the latter case, a dimensionless reorganization energy of $\Lambda = 40$ (i.e., $\lambda = 1$ eV) has been assumed.38 The values of $\ln(2)$ (horizontal dashed lines) and 0 (vertical dotted line) corresponding to the minimum ordinate and abscissa of an ideal situation have been included in the three figures.

From the abovementioned curves, it can be seen that intermolecular interactions cause a strong deviation of the Chidsey–Tafel curves from the ideal situation (see the curve with $\theta_e G = \theta_e S = 0$ in Figure 4b). In general, the increase of $\theta_e G$ gives rise to the approach of the cathodic and anodic branches of these curves in such a way that the electrochemical response will develop in a narrower potential interval.

Moreover, it is clear that when $\theta_e S \neq 0$, the estimation of $E^\alpha_{\text{ap}}$ and $E^\alpha_{\text{ep}}$ from the minima of these curves would lead to significant errors. Thus, for positive values of $\theta_e S$ (Figure 4a), the ordinate of the minima is below $\ln(2)$ for any value of $\theta_e G$ (being this value much smaller for $\theta_e G > 1$), whereas the opposite is observed for negative values of $\theta_e S$ (Figure 4c). As an example, for $\theta_e G = 0.5$ and $\theta_e S = 1$, there is a negative deviation of about $63\%$ in the value of $E^\alpha_{\text{ap}}$ whereas for the same value of $\theta_e G$ and $\theta_e S = -1$, there is a positive deviation of about $+53\%$. Concerning the abscissa of the minima, for $\theta_e S \geq 0$, it is located at negative overpotentials, and it shifts toward more positive values as $\theta_e G$ increases, whereas the opposite trend is observed for negative values of $\theta_e S$.

The influence of $\theta_e S$ is much more important for the cathodic branch of the Chidsey–Tafel plots, as can be seen in Figure S5, where these curves have been calculated for a given $\theta_e G$ and different values of $\theta_e S$. Thus, it can be seen that in the cathodic branch, there is a decrease of around one unit of $\ln(k_{\text{eff,D}})$ per unity of $\theta_e S$. In the anodic branch, the influence of $\theta_e S$ is lost at high overpotentials because the surface excess of species $R$ is practically null, and therefore $e^{-\theta_e S} \rightarrow 1$ (see eq 1).

When the MH formalism is used, although the minimum of Chidsey–Tafel plots logically coincides for both the MH and BV formalisms, the values of $\ln(k_{\text{eff,D}})$ obtained with the MH formalism are smaller than those corresponding to BV, especially at high overpotentials. In this sense, these deviations are more important for negative values of $\theta_e G$ (see, e.g., curves with $\theta_e G \leq 0$ in Figures 4a–c or in S5c).

Concerning the effect of the symmetry factor $\gamma$, in Figure S6, we have plotted the Chidsey–Tafel curves calculated for $\theta_e G = 0.5$, $\theta_e S = -0.5$, and different positive (S6a) and negative (S6b) values of $\gamma$. As previously reported,36 a nonnull value of $\gamma$ implies an asymmetry in the energy requirements for the direct and reverse redox half-reactions and, therefore, the increase of $|\gamma|$ will affect the relative slopes of the cathodic and anodic branches of the Chidsey–Tafel plots. In agreement with Figure S6a, a positive value of $\gamma$ gives rise to a decrease of the slopes of the anodic branch and an increase of the slopes of the cathodic branch (i.e., to a decrease of $k_{\text{eff,D}}|\xi-E_{\text{max}}|$ and to an increase of $k_{\text{eff,D}}|\xi-E_{\text{min}}|$ for a given value of $|\xi - E_{\text{min}}|$, with $E_{\text{min}}$ being the potential of the minimum), and the opposite is observed for a negative value of $\gamma$ (see Figure S6b). The decrease of the slope of one of the branches of the Chidsey–Tafel plots is related, in general, to stronger kinetic limitations for the corresponding redox conversion (i.e., with sluggish charge transfers).

It is important to remind that the distortions observed in the experimental Chidsey–Tafel plots will be related to the combined effect of the interaction parameters and the asymmetry of the rate constant (through the value of $\gamma$, see below).

As stated above, it is not possible to solve eq 1 analytically for any value of the applied potential, but approximate solutions corresponding to very negative and very positive potentials can be obtained in the way discussed in section S2 of the Supporting Information. Thus, the following expressions are obtained for these limits

$$\Phi_\alpha(T)|_{E_{\text{ap}}=E_{\text{ep}}} \approx \begin{cases} e^{q_\alpha - \theta_e G}(t_{\text{ap}}) & \text{for } E_{\text{ap}} = E_{\text{ep}} = E_{\text{ap}}^\alpha \\ e^{(q_\alpha - q_\gamma + \theta_e S) t_{\text{ap}}}(t_{\text{ap}}) & \text{for } E_{\text{ap}} = E_{\text{ep}} = E_{\text{ep}}^\alpha \end{cases}$$

$$\Phi_\alpha(T)|_{E_{\text{ap}}=E_{\text{ep}}} \approx \begin{cases} -g(t_{\text{ap}}) & \text{for } E_{\text{ap}} = E_{\text{ep}} = E_{\text{ap}}^\alpha \\ e^{(\theta_e S - \theta_e G + 1 + q_\gamma \theta_e S) t_{\text{ap}}}(t_{\text{ap}}) \end{cases}$$

(5)
from which the following expressions for the logarithms of the effective rate constants are deduced

\[ \ln(k_{\text{f,eff}}) = \ln(k_{\text{f,0}}) + \Delta \theta_S G - \theta_S S + \ln(g(\eta_{\text{ap}})) \]

Thus, a linear dependence of \( \ln(k_{\text{f,eff}}) \) with the overpotential is expected whenever the condition \( \ln(g(\eta_{\text{ap}})) \equiv \ln(g(\eta_{\text{ap}})) \) is fulfilled, and the intercepts of these lines, the interaction parameters could be determined. In the case of the BV formalism, the linear dependence will always be fulfilled because \( \ln(g(\eta_{\text{ap}})) = -\gamma \eta_{\text{ap}} \) (see eq 17), whereas in the case of the MH formalism, \( \ln(g(\eta_{\text{ap}})) \equiv A(\Lambda) \eta_{\text{ap}} \) with \( A(\Lambda) \) being a constant value for a given \( \Lambda \).

Nevertheless, it should also be taken into account that the experimental measured current always presents a capacitive component that, for the application of a potential jump of magnitude \( \Delta E \), is given by \[ \psi_{\text{eff}} = \frac{R_{\text{f}}}{Q_{\text{f}}} \frac{\Delta E}{R_{\text{f}}} \quad \text{e}^{-t/(R_{\text{f}}C_{\text{f}})} \]

with \( R_{\text{f}} \) and \( C_{\text{f}} \) being the uncompensated resistance and double layer capacitance of the monolayer/solution interface. The inverse of the product \( (R_{\text{f}}C_{\text{f}}) \) is a characteristic time below which the nonfaradaic component of the current becomes dominant (see section S3 of the Supporting Information and Figures S7 and S8). Thus, the value of \( (R_{\text{f}}C_{\text{f}}) \) fixes a practical limit value of the effective rate constant that can be determined and, therefore, the applicability of approximate solutions given by eq 6 is very restricted.

2.2. Experimental Results: Binary Ferrocenylundecanethiol/Decanethiol Monolayer. We have validated the theory presented with the analysis of the chronoamperometric responses of binary monolayers of ferrocenylundecanethiol/decanethiol (FcC11SH/C10SH) at gold and platinum electrodes. These monolayers have been prepared by using mixtures of ethanolic solutions 1 mM of the redox probe 1,1’-(ferroceny1)-undecanethiol and electroinactive 1-decanethiol in the following ratios (v/v): 1:15, 1:10, 1:5, and 1:2.5 (see the Experimental Conditions section). The influence of an increasing presence of the redox probe on the electrochemical response of the system will be analyzed. We will consider in our treatment that under working conditions, there is a single type of ferrocene moiety at the different monolayers and, therefore, the differences observed between them are solely due to changes in the microenvironment of the redox probe related to the different amount of redox probes but not with the appearance of different domains of ferrocenes. The validity of this assumption will be tested below.

The electrolyte medium chosen is EtOH/ClO4NBu4 0.1 M, and the supporting electrodes are polycrystalline gold and platinum. As discussed in previous refs 19, 31, and 41, one of the main pitfalls of the LMT model is the “fully randomized” (FR) assumption for the redox probes in the monolayer, which seems to be noncompatible with the presence of strong attractive interactions resulting in a global quasordering of the 2D system. Nevertheless, the polycrystalline nature of the substrates will give rise to an average current corresponding to different surface microenvironments such that the overall response should be reasonably coincident with an FR one, even though there could be some local order in some of the microenvironments.\(^e\)

Although, as far as we know, only a few contributions in the literature have been devoted to the analysis of the electrochemical behavior of monolayers at nonaqueous media (see, e.g., refs 42 and 43), ethanolic medium has been chosen to avoid phase transitions or reordering processes in the binary monolayer, which are frequent for medium-high coverages of the redox probe when aqueous media are used, giving rise to the full coverage of ferrocene of around \( \Gamma_{\text{M}} \leq 4.8 \times 10^{-10} \) mol cm\(^{-2}\). The percentage of the surface-confined redox probe, \( \theta_{\text{Fc}} \), has been maintained below 30% in all the cases (see data in Tables 1, S2 and S3).

| \( \chi_{\text{Fc}} \) | (in %) of Ferrocene in the Assembling Solutions of FcC11SH/C10SH in Proportions (\( V_{\text{FcC11SH}}/V_{\text{C10SH}} \)) and \( \theta_{\text{Fc}} \) | \( \theta_{\text{Fc}} \) | \( \theta_{\text{Fc}} \) |
|-----------------|-----------------|-----------------|
| 6.25/(1:15)     | 1.4             | 1.9             |
| 9.10/(1:10)     | 5.8             | 3.7             |
| 16.70/(1:5)     | 8.4             | 6.9             |
| 28.60/(1:2.5)   | 29.1            | 14.0            |

Figure 5 shows the CV responses of the four monolayers under study corresponding to gold electrodes for different values of the scan rate (v = 50, 100, 200, and 300 mV s\(^{-1}\)), with the analogue curves for platinum electrodes given in Figure S9. The values of the peak parameters (peak current, peak potential, and full width at the half maximum (fwhm)) for the different scan rates, corresponding to the direct anodic scan, are given in Tables S2 and S3 of section S4 of the Supporting Information.

From the CV curves in Figures 5 and S9, it can be seen that they present a single pair of peaks in all the cases with a typical Gaussian-like feature for the lower ferrocene coverages, \( \theta_{\text{Fc}} \leq 2\% \) for the 1:15 monolayers, which is distorted as \( \theta_{\text{Fc}} \) increases up to 30% in the case of 1:2.5 monolayers at gold, for which the distortion is very evident (see Figure 5cd).

The experimental studies of the influence of intermolecular interactions on the CV curves have been mostly devoted to Nernstian processes for which, in agreement with,\(^{17,12}\) fwhm values different from the ideal 90 mV value (for \( T = 298 K \)) and peak potentials dependent on the surface coverage of the redox molecules are expected. Under these conditions, the value of parameter \( \theta_{\text{G}} \) is crucial for determining the global character of these interactions. We have calculated the values of \( \theta_{\text{G}} \) directly from the experimental CV curves of the anodic scan of the four systems under study by using eqs 18 and 19 of ref 29, which are valid only for Nernstian conditions (see Tables S2 and S3 of section S4 of the Supporting Information).

On the basis of the abovementioned criteria and the peak parameters values, it is evident that the CV curves for gold and platinum electrodes are affected by intermolecular interactions. Thus, the fwhm values for the lower \( \theta_{\text{Fc}} \) are greater than 90 mV (105–107 mV for gold and 98–102 mV for platinum, with \( \theta_{\text{Fc}} = -0.27 \) and \( -0.16 \), respectively), revealing the predominance of repulsive interactions in the CV curve. When the ferrocene coverage and therefore the surface redox charge increases, the fwhm values begin to decrease, indicating a change in the global
character of interactions from repulsive to attractive (e.g., for the 1:2.5 monolayer, fwhm is in the range 44−53 mV for gold and 57−59 mV for platinum, with $\theta_{EG} = 0.84$ and 0.62, respectively). Concerning the influence of the ferrocene coverage on the position of the CV curves, there is a shift of the responses toward higher potentials at both gold and platinum electrodes as $\theta_{Fc}$ increases, which is more important for the latter electrode.

Moreover, the influence of intermolecular interactions affects not only the shape of the response but also the reversibility of the same. Thus, the CV curve for a redox molecule confined at the electrode surface can be considered as Nernstian on the basis of the following features: a scan rate-independent peak potential and $(I_{CV, peak}/v)$ ratio and a fwhm value of 90 mV as stated above. In the case of non-Nernstian ideal systems (i.e., for log($k_0'$/(Fv/RT)) ≤ 1), the increase of the scan rate affects the three peak parameters (with a decrease of the peak height, a shift of the peak potentials toward more positive/negative potentials depending on the anodic/cathodic character of the charge transfer, and an increase of the fwhm values).

For the lower coverages ($\theta_{Fc} \leq 2\%$, Figures 5a and S9a), the two first features of ideal Nernstian systems hold but, as $\theta_{Fc}$ becomes higher, the decrease of $(I_{CV, peak}/v)$ and the shift toward more positive potentials of the direct peak as the scan rate increases are observed (compare Figure 5a−d corresponding to gold electrodes). The higher sensitivity of the CV curves to the scan rates, together with the distortion of the typical Gaussian-like shape the CV curves, points to a decrease of the apparent rate constant $k_0'$ (and therefore of the reversibility of the charge transfer) from 1:15 to 1:2.5 monolayers due to the increase of the interaction parameters $\theta_{EG}$ and $\theta_{ES}$ (in the absolute value).

In the case of platinum electrodes, the CV curves shown in Figure S9 follow the general trends indicated for gold electrodes, although the CV curves corresponding to the most diluted monolayers ($\theta_{Fc} = 2$ and 3.7% for 1:15 and 1:10 monolayers, respectively) are severely distorted because of a low faradaic to background signal ratio. Moreover, the influence of the scan rate on the peak currents and potentials for the most concentrated monolayers is smaller than that observed for gold, indicating a higher value of the apparent rate constant.

Now, to determine, or at least to make an estimation, of $k_0'$ of the different monolayers under study, the $I$−$t$ and ln($I$)−$t$ curves for gold (Figure 6a,b) and platinum (Figure S10a,b) electrodes are obtained, corresponding to the application of a staircase potential of the form $E_j(V) = 0.15 + j\Delta E$ with $j = 1, 2, \ldots, 35$ and $\Delta E = 0.01 V$, for different values of the time lengths of the potential steps in the range 1−100 ms. The curves in Figures 6 and S10 show sawtooth features in line with the theoretical predictions given in Figure 3, with sharper decays of the current for the lowest ferrocene coverage (see black lines in Figure S9).
decrease in the slope of the straight lines can be clearly seen as CV, is clearly related to the increasing oxidation. This result, in an analogous way to that observed for k parameters to be determined. The values of gold and platinum electrodes), and almost linear time difference of the current would allow us to obtain the value of (\( \Lambda \)) and therefore of the kinetics of the ferrocene charge-transfer process would present a rate similar or faster dominates the response. In practice, under these conditions, the most diluted ferrocene monolayers, especially for the 1:15 case (Figures 7a and 8a), and they are related to the double layer charging process taking place, which contaminates or even dominates the response. In practice, under these conditions, the charge-transfer process would present a rate similar or faster than that corresponding to the charge of the double layer. Therefore, the values of the slopes of the logarithmic chronoamperograms corresponding to these regions are not valid for the estimation of the kinetic and interaction parameters because they correspond to (\( R_{\text{C}_{1}} \)) (see eq 7).

To determine a practical potential limit above which no reliable kinetic information can be obtained, we have analyzed the current transients at such extreme potential regions. By assuming that the response is purely nonfaradic, the logarithm of the current corresponding to a fully reduced and fully oxidized monolayer shown in Table S1 have been obtained. We have marked in Figures 7 and 8 the values of \( R_{\text{C}_{1}}(\gamma) \) given in this table as horizontal dashed lines that delimit the potential interval valid to carry out kinetic measurements.

Concerning the values obtained from the different fittings shown in Table 2, it can be concluded that the value \( \Lambda = 30 \) for the dimensionless reorganization energy (corresponding to \( \lambda = 0.75 \text{ eV} \)) gives rise to satisfactory fittings for both gold and platinum electrodes. The values of the apparent rate constant \( k_{\text{app}} \) obtained from these fittings are smaller than those obtained from the minima ordinate with deviations of around 20–22% for gold and 13–16% for platinum, indicating a negative value of the \( \theta \) parameter in line with Figure 3. Moreover, the

Figure 6. Chronoamperometric \( I-t \) (a) and \( \ln(I)-t \) (b) curves corresponding to FcC11SH/C10SH monolayers on gold electrodes for different surface coverages \( \theta_{\text{Fc}} \) (in %): (a) 1.3, solution 1:15, black lines; (b) 5.8, solution 1:10, red lines; (c) 8.3, solution 1:5, green lines; (d) 29, solution 1:2.5, blue lines. \( E(V) = 0.15 + j\Delta E \) with \( j = 1, 2, ..., 35, \tau = 0.010 \text{ s} \) and \( \Delta E = 0.01 \text{ V} \). EtOH/0.1 M CIQNB, \( T = 298 \text{ K} \).

Figures 6a and S10a, corresponding to \( \theta_{\text{Fc}} = 1.3 \) and 2% for gold and platinum electrodes), and almost linear time dependence for the higher \( \theta_{\text{Fc}} \) value (see blue lines in Figures 6a and S10a obtained for \( \theta_{\text{Fc}} = 29 \) and 14% for gold and platinum electrodes).

Concerning the logarithmic curves in Figures 6b and S10b, a decrease in the slope of the straight lines can be clearly seen as \( \theta_{\text{Fc}} \) increases, evidencing a decrease of the effective rate constant \( k\text{eff}(E) \) and therefore of the kinetics of the ferrocene oxidation. This result, in an analogous way to that observed for CV, is clearly related to the increasing effect of intermolecular interactions.

Thus, the Chidsey–Tafel plots at gold and platinum electrodes will be used for the four systems under study to determine the effective rate constants at each potential and, from these values, the apparent rate constant and formal potential of the ferrocene monolayers as well as the interaction parameters. The MH formalism will be considered and, therefore, \( \Lambda, \gamma, k_{\text{app}}(E), E_{\text{app}}, \theta_{\text{C}}, \text{and } \theta_{\text{S}} \) will be adjustable parameters to be determined. The values of \( k_{\text{app}} \) and \( E_{\text{app}} \) obtained from the minima of the Chidsey–Tafel plots will be used as seeds for these parameters, whereas \( \Lambda \) will be restricted to the range 25–40, which corresponds to typical values for redox probes at alkanethiol monolayers. \( ^{36,42,43} \) As stated in section 2.1, to assure a good linearity of the \( \ln(I)−t \) curves, time values fulfilling the condition \( (k\text{eff}(t) \geq 0.15 \) should be employed (although this limit could be smaller for negative values of \( \theta_{\text{S}} \)). For the experimental conditions used here, pulse time lengths of 10 and 50 ms have been used.

The \( \ln(k\text{eff})−E \) curves for the four systems considered are shown in Figures 7 and 8 (black circles) for gold and platinum electrodes, respectively, for the 1:15, 1:10, and 1:5 monolayers (with a pulse time \( \tau = 10 \text{ ms} \)). Because of their special features, the 1:2.5 ones (corresponding to a pulse time \( \tau = 50 \text{ ms} \) are plotted separately in Figure 9 for both gold and platinum electrodes. The theoretical curves corresponding to the best fittings obtained have been included, by using eq 1, with the parameters listed in Table 2 (diamonds). In this table, we have also included the values corresponding to the effective rate constant and formal potential obtained directly from the coordinates of the minima of the curves.

The Chidsey–Tafel plots in Figure 7 corresponding to gold electrodes show a practically symmetrical V-shape, whereas those corresponding to platinum electrodes in Figure 8 are clearly nonsymmetrical, showing a distortion at positive overpotentials, with the experimental values of \( \ln(k\text{eff}) \) tending to a constant limit value for potentials above 0.40 V, especially for the 1:15 case (Figure 8a).

Moreover, at more positive and negative overpotentials, the experimental values of the slopes of the logarithms of current versus time curves deviate from the theoretical \( \ln(k\text{eff}(E)) \) ones (i.e., potentials below 0.23–0.24 V and above 0.4 V for gold electrodes and below 0.20–0.22 V and above 0.4 V for platinum electrodes). These deviations are more apparent for the most diluted ferrocene monolayers, especially for the 1:15 case (see Figures 7a and 8a), and they are related to the double layer charging process taking place, which contaminates or even dominates the response. In practice, under these conditions, the charge-transfer process would present a rate similar or faster than that corresponding to the charge of the double layer. Therefore, the values of the slopes of the logarithmic chronoamperograms corresponding to these regions are not valid for the estimation of the kinetic and interaction parameters because they correspond to \( (R_{\text{C}_{1}})^{−1} \) (see eq 7).
apparent rate constant $k_{ap}^0$ decreases with the increase of $\theta_Fc$ from 355 to 80 s$^{-1}$ for gold and from 521 to 165 s$^{-1}$ for platinum when moving from 1:15 to 1:5 monolayers. The decreases of $k_{ap}^0$ indicate a progressive slowing down of the charge-transfer process associated with the increase of attractive interactions ($\theta_FG$ varies from 0.2 to 0.6 for gold and from 0.2 to 0.3 for platinum) together with a decrease of the parameter $\theta_FS$ (which varies from $-0.3$ to $-0.8$ for gold and from $-0.1$ to $-0.3$ for platinum). This is in agreement with the s-LT-FR

Figure 7. Experimental (black circles) and theoretical (red diamonds) Chidsey–Tafel plots ($\ln(k_{eff}(E))$–$E$ curves), corresponding to FeC11SH/C10SH monolayers on gold electrodes for different surface coverages: (a) solution 1:15; (b) solution 1:10; and (c) solution 1:5. $E_i(V) = 0.15 + j \Delta E$ with $j = 1, 2, ..., 35$, $\tau = 0.010$ s and $\Delta E = 0.01$ V. EtOH/0.1 M ClO4NBu$_4$, $T = 298$ K. Theoretical curves have been obtained by solving eq 1 numerically with the parameters shown in Table 2. Horizontal dashed lines correspond to the values of $-\ln(R_uC_{dl})$ for fully reduced and fully oxidized monolayers given in Table S1.

Figure 8. Experimental (black circles) and theoretical (red diamonds) Chidsey–Tafel plots ($\ln(k_{eff}(E))$–$E$ curves), corresponding to FeC11SH/C10SH monolayers on platinum electrodes for different surface coverages: (a) solution 1:15; (b) solution 1:10; and (c) solution 1:5. $E_i(V) = 0.15 + j \Delta E$ with $j = 1, 2, ..., 35$, $\tau = 0.010$ s and $\Delta E = 0.01$ V. EtOH/0.1 M ClO4NBu$_4$, $T = 298$ K. Theoretical curves have been obtained by solving eq 1 numerically with the parameters shown in Table 2. Horizontal dashed lines correspond to the values of $-\ln(R_uC_{dl})$ for fully reduced and fully oxidized monolayers given in Table S1.
model, that predicts that the decrease of the term $\theta_F (S - G)$ will cause a decrease of the apparent rate constant (see eq 42).

Together with the strong decrease of the apparent rate constant for the ferrocene oxidation as $\theta_F$ increases with both supporting electrodes, there are important differences between the monolayers at gold and platinum. Thus, for the case of gold, the symmetry of the Chidsey–Tafel plots in Figure 7 is evident, and therefore, a value of $\gamma = 0$ has been used in the three plots shown in this figure. However, the $\ln(k_{eq}) = E$ curves for platinum, especially the 1:15 case, are strongly asymmetrical, and positive values of $\gamma$ parameter are necessary to achieve satisfactory fittings. The value of $\gamma$ employed for platinum electrodes decreases as $\theta_F$ increases (this effect can be clearly seen in the anodic branch of the Chidsey–Tafel plots that “elevates” as the coverage of the redox probe increases). As stated in Theory section, the positive value of $\gamma$ indicates greater force constants for the oxidized species than for the reduced ones (or smaller slopes for the anodic branches of the Chidsey–Tafel plots, see Figure S6). Moreover, for platinum electrodes, the interaction parameters take low values as compared with gold electrodes (see Table 2). Both facts suggest that at low ferrocene coverage (for which small absolute values of $\theta_F G$ and $\theta_F S$ are obtained), the “accommodation” of the oxidized redox probes in the monolayer is more difficult at platinum than at gold, for which intermolecular interactions are more intense. This “accommodation” refers to the energetics of the processes taking place when ferrocene is oxidized, that is, changes in solvation, conformation, and interactions with the surroundings. Thus, the increase of these interactions, linked to that of $\theta_F$, seems to cause a more favorable electrostatic environment within the monolayer (i.e., the energetic requirements are lower). The different magnitude of interactions at both metals can be related to a different structure of the alkanethiol monolayers, which changes as a function of the ferrocene coverage. If the abovementioned assumption is correct, for higher values of $\theta_F$ (and therefore higher absolute values of parameters $\theta_F G$ and $\theta_F S$), the ferrocene state of the redox probe in the monolayer would be more stable, and lower (or even negative) values of $\gamma$ should be required at platinum and gold electrodes (see below).

The curves corresponding to 1:2.5 monolayers at gold and platinum in Figure 9 show more complex responses compared to monolayers that are more diluted in ferrocene. A first

![Figure 9. Experimental (circles) and theoretical (diamonds) Chidsey–Tafel plots ($\ln(k_{eq}(E)) = E$ curves), corresponding to FeC11SH/C10SH monolayers on gold (a) and platinum (b) electrodes for a 1:2.5 monolayer. $E(\text{V}) = 0.15 + j \Delta E$ with $j = 1, 2, \ldots, 35$, $\tau = 0.010$ s, and $\Delta E = 0.01$ V. EtOH/0.1 M ClO$_4$NBu$_4$, $T = 298$ K. Theoretical curves have been obtained by solving eq 1 numerically with the parameters shown in Table 2. Horizontal dashed lines correspond to the values of $\ln(R_C)$ for fully reduced and fully oxidized monolayers given in Table S1.](image)

Table 2. Best Fitting Values of $\Lambda$, $k_{eq}^0$, $E_{eq}^0$, $G$, and $S$ Parameters for the Chidsey–Tafel Plots in Figure 7

| Ferrocene proportion $\theta_F/(\nu/v)$ | Gold electrode/fitting parameters | Gold electrode/values from the minima |
|---------------------------------------|-----------------------------------|--------------------------------------|
|                                       | $\theta_F G$ | $\theta_F S$ | $k_{eq}^0/s^{-1}$ | $E_{eq}^0$ V vs Ag QRE | $\Lambda$ | $\gamma$ | $k_{eq}^0/s^{-1}$ | $E_{eq}^0$ V vs Ag QRE |
| 1:15                                 | 0.2          | -0.3         | 355             | 0.325             | 30 0         | 426 | 0.326 |
| 1:10                                 | 0.5          | -0.4         | 155             | 0.310             | 30 0         | 189 | 0.318 |
| 1:5                                  | 0.6          | -0.8         | 80              | 0.302             | 30 0         | 96  | 0.310 |
| 1:2.5                                | 1.3, 1.3     | -2.0, -1.9   | 12, 9.5         | 0.287, 0.286      | 30 -0.8, -0.9 | 14, 12.5 | 0.296, 0.294 |

| Ferrocene proportion $\theta_F/(\nu/v)$ | Platinum electrode/fitting parameters | Platinum electrode/values from the minima |
|----------------------------------------|---------------------------------------|----------------------------------------|
|                                       | $\theta_F G$ | $\theta_F S$ | $k_{eq}^0/s^{-1}$ | $E_{eq}^0$ V vs Ag QRE | $\Lambda$ | $\gamma$ | $k_{eq}^0/s^{-1}$ | $E_{eq}^0$ V vs Ag QRE |
| 1:15                                  | 0.2          | -0.2         | 515             | 0.277             | 30 1.0 | 521 | 0.304 |
| 1:10                                  | 0.3          | -0.3         | 215             | 0.275             | 30 0.7 | 233 | 0.294 |
| 1.5                                   | 0.3          | -0.3         | 165             | 0.257             | 30 0.4 | 182 | 0.266 |
| 1:2.5                                 | 0.95, 1.05   | -0.8, -0.7   | 43, 36          | 0.247, 0.245      | 30 0.0 | 54.7, 41.5 | 0.256, 0.251 |

*The first and second values in the row for 1:2.5 monolayers correspond to blue and red symbols, respectively,*

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evidence of this fact comes from the analysis of the logarithms of the current for both gold and platinum electrodes because they show two very defined linear domains with slopes that change with the applied potential (for some examples of these plots, see Figures S11 and S12). This suggests the existence of two different types of ferrocenes that will be denoted as types I and II, with different kinetic and interaction parameters arising from different environments (and as a consequence different redox functionality), a known fact for monolayers with medium–high values of $\theta_{Fc}^{0,20,24,25}$.

This fact has not been considered until now because of the lower values of $\theta_{Fc}$ of monolayers in Figures 7 and 8. Note that under these conditions, the analysis of the Chidsey–Tafel plot curves cannot be performed unless the apparent rate constants of the two redox processes taking place were different enough such that a kinetic discrimination between them was advisable in the way discussed in ref 44. In any other case, the logarithm of the chronoamperometric current would not be coincident with $k_\text{app}$ because the plots of the logarithm of $I_{\text{app}}(=I_t + I_0)$ versus time would not be linear or, if linearity holds, the slopes would be a combination of $k_{\text{app}}$ and $k_{\text{app}}\gamma$.

Bearing the above in mind, on the basis of the experimental $\ln(k_\text{app})−E$ plots, it is clear that, because two clearly separated linear sections are obtained for the 1:2.5 monolayers, it is possible to decouple both responses, and therefore, it is possible to obtain two Chidsey–Tafel plots. For this, the chronoamperograms corresponding to pulse times of 10 and 50 ms have been considered to assure a good linearity of the resulting logarithms curves, and the results for both electrodes are plotted in Figure 9. The blue and red dots correspond to the slopes obtained at shorter (1–5 ms) and longer (2–30 ms) times, respectively. In both cases, the Chidsey–Tafel plots are of a similar shape, with differences in the cathodic branch (suggesting different values of $\theta_{S,S}$, see Figure S3), the presence of two different minima, and the overlapping in the right anodic branch, reaching a constant limit at very anodic potential. The fitting parameters for the two curves at each electrode, given in Table 2, show differences of 2 mV in the apparent potential and around 24–30% in the apparent rate constant, pointing out the great sensitivity of chronoamperometry (CA) for kinetic discrimination.

Moreover, the Chidsey–Tafel plots for gold electrodes shown in Figure 9a are clearly asymmetrical, unlike what is observed at lower ferrocene coverages (Figure 7), and they present high absolute values of the interaction parameters (2.6 and $\theta_{S,S}$ = −2.0 and −1.9) with negative values of $\gamma$ (−0.8 and −0.9) being necessary to get satisfactory fittings. As stated above, negative values of $\gamma$ indicate that the reduction of the ferrocenium state of the redox probe in the monolayer is now more sluggish. This evidence for medium–high coverages of the electroactive probe has been previously reported for several redox groups at gold.$^{20,24,45}$

In the case of platinum electrodes, much more symmetrical Chidsey–Tafel plots than those corresponding to lower values of $\theta_{Fc}$ (see Figure 8) are obtained. Indeed, we have used the value $\gamma = 0$ for the fitting of both curves. This fact points again to a monolayer structure for which intermolecular interactions are progressively destabilizing the oxidized species as compared with the results for lower ferrocene coverages, such that for the coverage used, there are no kinetic “asymmetries” between the ferrocene oxidation and the ferrocenium reduction. As in the case of gold electrodes, this result is in agreement with previous data that show symmetrical Marcus–Hush plots for high ferrocene coverages at platinum.$^{45}$

As a summary, the magnitude of intermolecular interactions is different at gold and platinum electrodes, a fact that suggests different structures for the corresponding alkanethiol monolayers. The increase of the ferrocene coverage causes changes in the structure, much more apparent for gold, which gives rise to a strong slowing down of the charge-transfer process together with the appearance of different domains and a change in the relative stability of reduced and oxidized states of the redox probe in the monolayer.

3. CONCLUSIONS

We have presented the theoretical and experimental analysis of the influence of intermolecular interactions on the kinetics of the response of binary electroactive monolayers. The theoretical model expands previous efforts by including relevant novelties such as the presence an electroinactive coadsorbate and asymmetric Marcus–Hush kinetic formalism, and it presents an expression for the current–potential relationship in terms of two interaction parameters and apparent values of the formal potential and rate constants. We have considered the application of a single constant potential and of a sequence of constant potentials, with special interest in the so-called Chidsey–Tafel plots. The theoretical framework predicts a clear influence of the intermolecular interactions on the apparent formal potential of the redox probe and also on the apparent rate constant for the charge transfer. To validate these theoretical results, experimental analysis of the response of binary ferrocenylundecanethiol/decanethiol monolayers at gold and platinum electrodes in ethanolic media has been performed. A decrease of around 90% in the value of the apparent rate constant for the ferrocene oxidation has been observed for the abovementioned monolayers when the surface coverage of the redox probe increases by one order of magnitude. Moreover, for the monolayers with higher surface coverage, two functional domains appear for which different rate constants, formal potentials, and interaction parameters have been determined by means of a kinetic discrimination of the corresponding current–time transients. The data also suggest the existence of different monolayer structures at gold and platinum, for which the increase of the ferrocene coverage causes changes in the relative stability of reduced and oxidized states of the redox probe.

These results clearly show the great applicability of CA to get a deeper insight into the processes taking place, although it should be noted that, because the influence of intermolecular interactions changes with time, the time window of the different techniques could lead to different values of the interaction parameters (e.g., compare the values of $\theta_{S,Fc}$ obtained for CV and CA). Both the apparent rate constant and formal potential reflect the environmental influences on the redox centers, an energetic landscape that is affected by both $\theta_{Fc}$ and the nature of the supporting electrode. Thus, the values of $k_{\text{app}}^{\text{up}}$ and $E_{\text{app}}^{\text{up}}$ obtained with the different techniques should be placed in the specific context (potential perturbation, time window) where they have been obtained.

Because the knowledge of interaction parameters could be of great interest for an appropriate design of new functional materials$^{46}$ as well as for a better understanding of the mechanisms of charge-transfer processes at different interfaces of technological relevance,$^{46}$ it is clear that an adequate diagnosis and quantification of these influences is required, and
further analysis devoted to other techniques beyond CV is necessary.

The validity of CA as a tool for the kinetic analysis of electroactive monolayers is beyond doubt because it reveals a much more complex framework than CV does. In this sense, the use of multipotential pulse techniques would be very helpful, such as square wave voltammetry and voltammetry, as complementary techniques.

4. EXPERIMENTAL CONDITIONS

4.1. Reagents and Chemicals. Ethanol (Merck), 11-(ferrocenyl)undecanethiol \((C_{11}H_{22}FeS)\), 10-decanethiol \((C_{10}SH)\), and tetrabutylammonium perchlorate \((\text{Sigma-Drich})\) were reagent grade and used as received.

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4.2. Electrochemistry. Multipotential pulse CA and CV were performed using a home-made computer-driven potentiostat—galvanostat.

A three-electrode cell was employed in the experiments with gold and platinum disc electrodes of diameter 0.3 cm as working electrodes (CH Instruments). The counter electrode was a Pt foil, and the quasireference electrode was a silver wire (Ag QRE). Solutions were prepared with distilled deionized water (Milli-Q filtering system). Ethanol-saturated nitrogen gas was passed through solutions for de-aeration for 20 min prior to measurements, with nitrogen atmosphere maintained over the solution during all the experiments.

The coverages of the ferrocene moiety have been calculated by numerical integration of the baseline-corrected voltammograms of freshly prepared monolayers corresponding to the direct anodic scan and are given in Tables S2 and S3 of section S4 of the Supporting Information.

4.3. Preparation of the Binary Ferrocene Monolayers at Gold and Platinum Electrodes. Monolayers of ferrocene were formed by the self-assembling technique on gold and platinum substrates. The gold and platinum electrodes were mechanically polished on alumina slurry (0.05 \(\mu\)m, Buellier), washed, and electrochemically cleaned by cycling the potential between 0 and \(-1.4\) V (vs SCE) in 2.0 M NaOH and then between 1.6 and 0.4 V (vs SCE) in 1.0 M H\(_2\)SO\(_4\) until stable voltammograms were obtained. They were then washed with ethanol and water, and after that, they were soaked in solutions 2 mM of 11-(ferrocenyl)undecanethiol \((\text{FcC}_{11}\text{SH})\) and 1-decanethiol \((\text{C}_{10}\text{SH})\) in 4 different proportions (ratio v/v) for 48 h at room temperature. The proportions chosen were as follows: 1:1.5, 1:10, 1:5, and 1:2.5, with the total volume of the assembling solution being 5 mL in all the cases. Upon removal from this solution, the electrode was thoroughly rinsed with ethanol and left in the organic solvent for 48 h before use.

The variation of the surface coverage of ferrocene probes \((\theta_{\text{Fc}})\) as a function of the mole fraction \(x_{\text{Fc}}\) is shown in Figure 10. Thus, the surface coverage of ferrocene increases linearly with the mole fraction for the case of platinum, whereas for gold, the evolution of \(\theta_{\text{Fc}}\) is not linear and, for medium-high coverages, it is fulfilled that \(\theta_{\text{FcAu}} > \theta_{\text{FcPt}}\). These results are in line with previous data for gold substrates.\(^{53}\)

Moreover, the monolayers at both electrodes are very stable, and no significant loss of signal is observed during four-five weeks, especially at platinum.
10, it is possible to define the surface coverage in terms of $\Gamma_M$ or $\Gamma_E$:

$$\theta_i = \frac{\Gamma_i}{\Gamma_M} = \frac{\Gamma_i}{\Gamma_E \Gamma_M} = \frac{\Gamma_i}{\Gamma_E \Gamma_M} = \theta_{f_i}$$  \hspace{1cm} (12)

5.1. Ideal Behavior. If we assume that all the surface sites are equivalent, the oxidized and reduced species occupy the same area and are uniformly solvated, the local electric potential at the reaction site is independent of the charge-transfer extent, and the interactions between adsorbed species can be neglected, "ideal" conditions hold.\textsuperscript{16,17,19} The relationship between the surface coverage of species O and R and the electrochemical potential $\eta$ defines the Langmuir’s isotherm\textsuperscript{16,39,47}

$$\exp\left(\frac{\mu_i}{RT}\right) = \frac{\theta_O}{1 - \theta_O - \theta_R - \theta_P}$$

$$\exp\left(\frac{\mu_R}{RT}\right) = \frac{\theta_R}{1 - \theta_O - \theta_R - \theta_P}$$  \hspace{1cm} (13)

where, $\mu_i = \mu_e + z_iF\phi_e = \mu_i^{(\text{red})} + z_iF\phi_e$. $\lambda_i$ and $z_i$ are the activity and charge number, respectively, of species $i$, and $\mu_i^{(\text{red})}$ and $\phi_e$ are the standard chemical potential and the Galvani potential in phase $\varphi$.

By dividing the two equations in 13 for species O and R, and taking into account that $(\mu_O - \mu_R)/RT = F(E - E^{0e})/RT$, with $E^{0e}$ being the formal potential of process (1), a potential–current relationship formally identical to the Nernst equation is obtained

$$E - E^{0e} = \frac{RT}{F} \ln\left(\frac{\theta_O}{\theta_R}\right) = \frac{RT}{F} \ln\left(\frac{f_O}{f_R}\right) = \frac{RT}{F} \ln\left(\frac{1 - f_R}{f_R}\right)$$  \hspace{1cm} (14)

because mass conservation holds ($f_R + f_O = 1$).

Equation 14 corresponds to an equilibrium-type situation that, in practice, is reached only when the charge-transfer reaction is very fast. If the rate constants $k_\text{ad}$ and $k_\text{red}$ are assumed as finite, an equation analogous to that of solution–soluble species is obtained:\textsuperscript{16,48}

$$\frac{I}{Q_F} = \frac{k_\text{red}}{\theta} \left(\theta_e^e - \theta_O\right) = k_\text{red}(f_e^e - f_O)$$  \hspace{1cm} (15)

with

$$\eta = \frac{F}{RT}(E - E^{0e})$$  \hspace{1cm} (16)

The particular expression for the rate constant $k_\text{red}$ depends on the kinetic formalism,\textsuperscript{39,40} and two of them will be considered here, the Butler–Volmer and the asymmetric Marcus–Hush one, for which $k_\text{red}$ is given as (see ref 36)

$$k_\text{red} = k^{0e}_\text{red} \eta$$

with $g(\eta)$

$$g^{BV}(\eta) = e^{-\eta}$$

$$g^{MH}(\eta) = F(\eta, \Lambda) \frac{F(0, \Lambda)}{F(0, \Lambda)} = \frac{\int_{-\infty}^{-\eta} e^{-\eta + \eta^2/(1 + \eta)} \, d\eta}{\int_{-\infty}^{-\infty} e^{-\eta + \eta^2/(1 + \eta)} \, d\eta}$$  \hspace{1cm} (17)

In eq 17, $k^{0e}_\text{red}$ is the conditional rate constant, $\alpha$ is the charge-transfer coefficient, and

$$\Delta G_\text{red}^\text{fi}(\eta, \Lambda, \gamma) = \frac{\Lambda}{4} \left(1 + \frac{\eta + \epsilon}{\Lambda}\right) + \gamma \left(\frac{\eta + \epsilon}{4}\right)$$

$$\left(1 + \left(\frac{\eta + \epsilon}{\Lambda}\right)^2\right) + \gamma \frac{\Lambda}{16}$$  \hspace{1cm} (18)

$\Lambda$ is the dimensionless reorganization energy given by

$$\Lambda = \frac{\lambda}{RT}$$  \hspace{1cm} (19)

where $\lambda$ is the molar reorganization energy,\textsuperscript{36,38,49} and $\gamma$ is the asymmetry parameter that accounts for differences between the inner-shell force constants of the oxidized and the reduced species (a positive $\gamma$ value is associated with greater force constants for the oxidized species and the opposite for negative $\gamma$ values). The case $\gamma = 0$ (equal force constants for both reduced and oxidized states) corresponds to the simpler symmetrical Marcus–Hush model. Note that for both MH and BV kinetics formalisms, the following is fulfilled

$$\frac{k_\text{ad}}{k_\text{red}} = \frac{e^\eta}{e^{\eta^2}}$$  \hspace{1cm} (20)

5.2. Nonideal Behavior and the Presence of Intermolecular Interactions: Laviron–Tokuda Fully Randomized Monolayer Model, LT-FR, with the Presence of the Electroinactive Coadsorbate. The presence of intermolecular interactions between redox species confined at the electrode surface give rises to the appearance of "nonidealities" in the electrochemical response of these systems. Typical deviations of the ideal behavior in CV are the shift of the peak potentials as the number of redox moieties at the electrode surface increases, as well as half peak width values below or above 90 mV.\textsuperscript{17,19}

To incorporate the influence of intermolecular interactions to the ideal situation (eqs 14 and 15), from a theoretical point of view, usually assumed the so-called “mean-field approximation”, which considers that all adsorbates on the surface lattice are randomly mixed and uncorrelated.\textsuperscript{50} As a result, the average interaction energy that an adsorbate feels from the others is proportional to the coverage $f$. If we restrict to the nearest-neighbor interactions, an additional energy term should be added to the electrochemical potential, thus giving rise to the Frumkin isotherm, which for two adsorbates O and R and an electroinactive coadsorbate P takes the following expression\textsuperscript{31}

$$\exp\left(\frac{\mu_e}{RT}\right) \exp\left(2a_{00}^\text{fi}\theta_O + 2a_{0R}^\text{fi}\theta_R + 2a_{0P}^\text{fi}\theta_P\right)$$

$$= \frac{\theta_O}{1 - \theta_O - \theta_R - \theta_P}$$

$$\exp\left(\frac{\mu_R}{RT}\right) \exp\left(2a_{RR}^\text{fi}\theta_R + 2a_{OR}^\text{fi}\theta_O + 2a_{RP}^\text{fi}\theta_P\right)$$

$$= \frac{\theta_R}{1 - \theta_O - \theta_R - \theta_P}$$  \hspace{1cm} (21)

with $a_{00}^\text{fi}$, $a_{0R}^\text{fi}$, $a_{OR}^\text{fi}$, $a_{RP}^\text{fi}$ and $a_{RR}^\text{fi}$ being the interaction coefficients for couples O–O, R–R, O–R/R–O, OP, and RP, respectively (with $a_q$ being positive for attractions and
negative for repulsions\(^30\)). As in the ideal case described in section 2.1, eq 21 corresponds to an equilibrium-like situation.

To consider finite electron transfer kinetics, the treatment followed in ref 30 will be employed where intermolecular interactions are assumed to cause a linear increase of the activation free energy of the anodic and cathodic charge-transfer processes. Within a transition-state kinetic formalism, initial and final "equilibrium" states O and R also interact with a transition state denoted as \( \ne \)

\[
R \ne \ne \ne O + e^- \tag{II}
\]

and thus, new interaction coefficients \( a_{\ne O} \) and \( a_{\ne R} \) would appear. Under these conditions, the activation free energy for species O, R, and \( \ne \) are given by

\[
\frac{\Delta G_{\ne}}{RT} = -2a_{\ne O} \theta_O - 2a_{\ne R} \theta_R - 2a_{\ne \ne} \theta_{\ne}
\]

\[
\frac{\Delta G_{R}}{RT} = -2a_{R \ne} \theta_R - 2a_{OR} \theta_O - 2a_{RP} \theta_P
\]

\[
\frac{\Delta G_{\ne}}{RT} = -2a_{\ne R} \theta_R - 2a_{\ne \ne} \theta_{\ne} - 2a_{\ne P} \theta_P
\]

and the free energy of anodic and cathodic reactions are

\[
\frac{\Delta G_{R}}{RT} = \frac{\Delta G_{O} + \Delta G_{\ne}}{RT} = -2 \mu \theta_O - 2 \lambda \theta_R - 2 \xi_{\ne \ne} \theta_{\ne}
\]

\[
\frac{\Delta G_{\ne}}{RT} = \frac{\Delta G_{R} + \Delta G_{\ne}}{RT} = -2 \nu \theta_R - 2 \theta_{\ne} - 2 \xi_{\ne \ne} \theta_{\ne}
\]

where

\[
\mu = a_{\ne O} + a_{\ne \ne}
\]

\[
\nu = a_{R \ne} + a_{\ne \ne}
\]

\[
\lambda = a_{R R} + a_{\ne \ne}
\]

\[
\xi_{\ne \ne} = a_{\ne \ne} + a_{\ne P} + a_{R \ne} + a_{\ne \ne}
\]

The linear contributions to the activation free energy due to the interactions are translated into the appearance of activity coefficients for species O and R, \( \nu_O \) and \( \nu_R \), which depend on the coverages of the three species present in the monolayer, O, R, and P (see, e.g., refs 8, 30, and 37)

\[
\nu_O = e^{\Delta G_{O}/RT} = e^{-2 \delta (\theta_O + \nu_R + \xi_{\ne \ne})}
\]

\[
\nu_R = e^{\Delta G_{R}/RT} = e^{-2 \delta (\theta_R + \nu_O + \xi_{\ne \ne})}
\]

The current–potential relationship under these conditions is given in terms of the activities of species O and R, defined as the products \( \nu f_i \) (i = O, R)

\[
\frac{I}{Q_F} = k_{red}(\nu_R f_R) e^\theta - \nu_O f_O
\]

\[
= k_{red}(f_R) e^{-2 \delta (\theta_O + \nu_R + \xi_{\ne \ne})} - f_O
\]

\[
e^{-2 \delta (\theta_R + \nu_O + \xi_{\ne \ne})}
\]

By dividing the two equations appearing in 21, or from eq 28, by inserting the condition \( k^0 \gg 1 \, s^{-1} \), it is possible to deduce the Nernstian limit which leads to a nonexplicit relationship between the potential and the surface coverage\(^29\)

\[
F \frac{RT}{2} (E - E_{ap}^0) = \ln \left( \frac{1 - f_R}{f_R} \right) + \theta_k G(2f_R - 1) + \frac{RT}{2} S P
\]

with

\[
E_{ap}^0 = E_{ap}^0 + \frac{RT}{F} \theta_k S + \frac{RT}{F} \theta_k f, S P
\]

\[
G = \lambda - \gamma + \mu = a_{\ne O} + a_{\ne R} - 2a_{OR}
\]

\[
S = \lambda - \gamma + \mu = \theta_{\ne} - a_{\ne O}
\]

\[
S_P = 2(\xi_{RP} - \xi_{\ne \ne}) = 2(\xi_{RP} - \xi_{\ne \ne})
\]

\( E_{ap}^0 \) is an “apparent” formal potential obtained by inserting conditions \( f_R = f_O = 1/2 \) and \( I = 0 \) in eq 28. \( G, S, \) and \( S_P \) are lineal combinations of the parameters defined in eq 26.

Note that \( G, S, \) and \( S_P \) do not contain \( a_{\ne \ne} \) terms (with \( i = O, \) R, and P), that is, they are related to states O, R, and P, and they do not inform about the transition state. It is usually assumed that the sign of parameter \( G \) defines the global character of interactions as attractive \( (G > 0) \) or repulsive \( (G < 0) \), whereas \( G = 0 \) would correspond to an ideal situation where positive and negative interactions cancel each other out (ideal behavior, see section 5.1).\(^17,20\) Note that the phenomenological character of the present model does not allow for giving a molecular insight to parameters \( G \) and \( S \), but it is clear that their values and sign are directly related to the “electrostatic landscape” of the redox probes. The latter is the result of the balance between Coulombic (long range) and van der Waals (short range) interactions that define the attractive/repulsive global character of the interactions. In this sense, and depending on the experimental conditions (redox probe, solvent, electrolyte), the increase of the coverage of the electroactive species could give rise to an increase or decrease of the values of parameters \( G \) and \( S \) because of a change in the dominant interaction from short range to long range or viceversa.\(^20,52\)

The model proposed in ref 30 was later refined in ref 32 by including the idea that interaction coefficients would affect both the rate constant and the formal potential such that only the apparent values could be obtained. This led Tokuda et al. to rewrite eq 28 in terms of \( E_{ap}^{0'} \) and \( E_{ap}^{0''} \) such that the I–E curve only depends on the interaction parameters \( G \) and \( S' \)

\[
\frac{I}{Q_F} = k_{ap}^{0'}(\nu_R f_R) e^{\theta_k \gamma/2((G+S')(1-2f_R))} - (1 - f_R)\]

\[
e^{-\theta_k \gamma/2((G-S')(1-2f_R))}
\]

where \( G \) is given by eq 31 and

\[
k_{ap}^{0'} = k^0 e^{\theta_k (S+S')+\theta_k (\gamma+\nu_R - 2 \delta (\nu_R+\xi_{\ne \ne}))}
\]

\[
k_{ap}^{0''} = k^0 e^{-\theta_k (\nu_R+\xi_{\ne \ne}) - 2 \delta (\nu_R+\xi_{\ne \ne})}
\]
\[ \eta_{ap} = \frac{F}{RT} (E - E_{ap}^0) = \eta - \theta_E (S + f_r S_P) \]  
(34)

\[ S' = \lambda - \mu - \beta + \gamma \]  
(35)

\[ g(\eta_{ap}) = \begin{cases} 
S^V(\eta_{ap}) = e^{-w_{ap}} \\
S^H(\eta_{ap}) = \frac{F(\eta_{ap}, \Lambda)}{F(0, \Lambda)} 
\end{cases} \]  
(36)

\[ E_{ap}' \]  
and \( S_P \) are given by eqs 30 and 31. Note that \( S' \) and \( S \) are not coincident (see eqs 31 and 35), and the relationship between them is

\[ S' = S + 2(\gamma - \mu) = S + 2(a_{OR} - a_{OR}) \]  
(37)

Equation 32 can be written in the following way

\[ \frac{I}{Q_{F}} = k_{ap,global}^0 e^{-\theta_S S'E}\left( f_{r} e^\theta_P e^{\theta G(1-f_r)} - (1 - f_r) \right) \]  
(38)

with

\[ k_{ap,global}^0 = k_{ap}^0 e^{\theta_S S'E}/ e^{0.5 G/2} \]  
\[ = k_{ap}^0 e^{-2\theta_S (a_{OR} + \varepsilon_{OR})} e^{-2\theta_P (a_{OR} + \varepsilon_{OR})} \]  
(39)

5.3. Presence of Intermolecular Interactions: Simplified Laviron–Tokuda Fully Randomized Monolayer Model, s-LT-FR, with the Presence of the Electroinactivator Coadsorbate. An additional simplification of the LT-FR model can be introduced by assuming that the interaction parameters related to the transition state, \( a_{OR}, a_{OR} \) and \( a_{OR} \) are much smaller than the corresponding coefficients for \( O, R, \) and \( P, a_{OR}, a_{OR}, a_{OR}, a_{OR}, \) and \( a_{OR} \) (i.e., \( a_{OR} \ll a_{OR} \) with \( i, j = O, R, \) and \( P \)). Under these conditions (see eq 26)

\[ \beta = a_{OR} \]  
\[ \gamma = a_{OR} \]  
\[ \lambda = a_{OR} \]  
\[ \varepsilon_{OP} = a_{OR} \]  
\[ \varepsilon_{RP} = a_{OR} \]  
(40)

From eqs 31 and 35, it is clear that the expressions of \( G \) and \( S_P \) do not change and \( S' = S \). By following an analogous discussion to that shown in the previous section, it is possible to deduce the following expression for the current–potential relationship

\[ \frac{I}{Q_{F}} = k_{ap,global}^0 e^{-\theta_S S'E}\left( f_{r} e^\theta_P e^{\theta G(1-f_r)} - (1 - f_r) \right) \]  
(41)

with \( E_{ap}' \) given by eq 30 and

\[ k_{ap,global}^0 = k^0 e^{-2\theta_S (5-G - 2z_{ca})} e^{-2\theta_P a_{ca}} \]  
(42)

On the basis of eqs 38 and 41, it can be concluded that both the complete and simplified models have a formally identical current–potential relationship, although the global apparent rate constant for the LT-FR model depends on the interaction parameters in a more complex way. Moreover, the terms related to the transition state do not appear in the simplified model (see eq 42).

5.3.1. Limit Behaviors. 5.3.1.1. Homogeneous Interactions. If we assume that the interaction coefficients of the different pairs are approximately equal (homogeneous interactions, \( a_{OR} = a_{OR} = a_{OR} = a_{OR} = a_{OR} = a_{OR} = a_{OR} = a_{OR} \)), then \( G = S = S_P = \) 0 such that the current–potential relationship is formally identical to that corresponding to the ideal case (see eq 15), but there is a remaining influence of intermolecular interactions on the kinetics through coefficient \( a \) because (see, e.g., 53)

\[ k_{ap,global}^0 = k^0 e^{-2\theta_P (1+f_r)} \]  
(43)

5.3.1.2. Absence of the Electroinactivator Coadsorbate. It is evident that the above formalisms can also be applied to a monolayer without the presence of an electroinactivator coadsorbate by simply inserting the condition \( f_r = 0 \) in eqs 30, 41, and 42 for the general case and in eq 43 for homogeneous interactions.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsomega.7b01995.

Additional theoretical results, expressions for the dimensionless current corresponding to high overpotentials, influence of the double layer current on the chronoamperometric response of monolayers, and additional experimental results (PDF)

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Notes

The authors declare no competing financial interest.

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ADDITIONAL NOTES

“This situation is different from the case of CV where the potential dependence of the rate constants, that is, in particular, the kinetic formalisms, needs to be established in an explicit way for obtaining a solution of the problem.

This different behavior at small or high values of \( T \) will have a strong influence on the current response (e.g., in the case of CV curves as compared with chronoamperometric ones).

This is in line with a more sophisticated model by Matsuda et al., in which the FR assumption was changed by a “quasichemical approximation,” and a coordination number \( z \) for the redox probe was introduced in ref 41. In this paper, the authors claim that for a number of neighbors \( z \geq 10 \), the behavior observed for the current–potential response coincides...
with that obtained for a disordered monolayer. Thus, the “average” overall character of the current would reflect a combination of different coordination numbers, being equivalent under these conditions to a randomized monolayer.

In ref 45, two different values for the reorganization energy, \( \lambda_{\text{an}} \) and \( \lambda_{\text{cat}} \), were considered for the cathodic and anodic branches of the Chidsey–Tafel plots, with \( \lambda_{\text{an}} > \lambda_{\text{cat}} \) for gold and \( \lambda_{\text{cat}} \approx \lambda_{\text{an}} \) for platinum. This assumption is not compatible with the Nernst limit and can be avoided by considering the asymmetry coefficient \( \gamma \).

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