Comments on "The Electroreduction of Acrylonitrile: A New Insight into the Mechanism" by Mertens et al.

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In 1982 (and not 1988 as mentioned in ref 2), Boiziau and Lécayon[1] mentioned that polyacrylonitrile (PAN) could be grafted on usual metals by cathodic electropolymerization in rigorously anhydrous acetonitrile. When the synthesis is performed under voltammetric conditions, the $i = f(E)$ voltammograms exhibit two peaks. Viel[3] described the two reduction peaks as stemming from a passivation of the surface (less cathodic peak, potential E_1, referred to as peak 1 from now on) and a diffusion-controlled peak (more cathodic peak, potential E_2, peak 2). Conversely, it was noted that the electroreduction of PAN gives two products of reaction: the so-called "grafted" polymer film, as well as a nongrafted film.[3] The latter can be removed by rinsing the electrode with a proper solvent of PAN (such as acetone or dimethylformamide (DMF)), while the former cannot.[3] The exact mechanism explaining the formation of both polymers was not established, but the key role of the reduction potential was alluded to.[3] In particular, Viel proposed that the grafting reaction probably occurred at potentials less cathodic than peak 2.

In their recent study of the electropolymerization of acrylonitrile at a nickel cathode,[2] Mertens et al. claim that the reduction of acrylonitrile (AN) occurs at the two distinct potentials according to two distinct mechanisms. More specifically, they propose that peak 1 is the result of a one-electron "partial"[2] reduction of AN, occurring at the metal surface and giving rise to the grafted portion, while peak 2 is the result of a one-electron traditional (faradaic[4]) reduction.

According to Mertens et al., "PAN is selectively electrografted onto Ni at the less cathodic of the two reduction potentials of AN..." as a result of "the formation of acrylonitrile radicals which are firmly linked to the cathode and propagate the radical polymerization of AN". This last proposal differs markedly from that of Lécayon et al.,[1] who proposed an anionic mechanism for the grafted growing chains. It is claimed by Mertens et al. that this anionic mechanism can be rejected on the basis of three new experimental results:

(i) the behavior of peak 1 as a function of scan rate identifies the process as a one-electron transfer;

(ii) the voltammetric characteristics of peak 1 (height etc.) are modified when one adds DPPH—a radical scavenger—to the electrolytic solution;

(iii) on the contrary, they are not modified when one adds ϵ-caprolactone (ϵ-CL), which is known to undergo selective ionic ring-opening reactions.

Let us first comment on point i above. As Mertens et al. mention, the use of their equation (2) linking the peak width with the number of electrons transferred is restricted to an irreversible electrochemical reaction, and no proof has been given for the moment that this is the case. The overall process {electron transfer + coupled polymerization} is definitely irreversible, but this may not be the case for the electron transfer step itself. If we nonetheless accept this hypothesis, we come—as Mertens et al. did—to the firm result that the electroreduction of AN is a one-electron process.

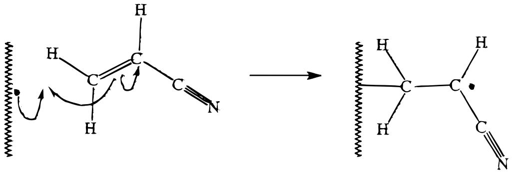

Figure 1. Picture of electronic rearrangements occurring in the electroreduction of acrylonitrile at peak 1, according to Mertens et al.[2]

One electron has been transferred from the surface to the molecule, and this is why a voltammetric current i is recorded at peak 1. In what follows, Mertens et al. indicate that such a hypothesis "requires that the oxidation at the anode does not create nor consume any charged species, since the transfer of one electron to AN and bonding of this monomer to the metal *must* form a radical species....[2] We cannot agree with this proposal: there is no element, neither theoretical nor experimental, indicating that one can impose the radical nature of the intermediate species. Let us recall that Mertens et al. admit that one electron has been transferred, accounting for the advent of the voltammetric current at peak 1.[2] We now wish to show that the above constraint—as further translated by depicting the electroreduction of AN as in Figure 1, which reproduces Scheme 2 of Mertens et al.[2]—is not compatible with the advent of a voltammetric current. In other words, the Lewis structure depicted in Figure 1 is not that of a reduced acrylonitrile molecule.

As is now well known from quantum chemistry, it is in general difficult (if at all meaningful) to say to which atom or to which part of a molecule an electron belongs when one considers the system at its equilibrium geometry. Quantum chemistry provides charge indices (Mulliken's, Löwdin's, etc.) which are well recognized as arbitrary but nevertheless conventional.[5] On the whole, the only serious way through which one can identify charge transfers is to examine how the resulting structure correlates at infinite separation when remaining on the same electronic state. In the present case, let us start with the {molecule + surface} system depicted in Figure 1 and perform an imaginary dissociation into the two {molecule} + {surface} subsystems. In the course of this formal dissociation, one has to keep in mind that we are reasoning at constant overall number of electrons. In that sense, the electrode surface is no longer a reservoir along the interaction potential *vs* distance curve, and the interest in considering such a process is to describe how the electrons are distributed. It is as if we could—for a moment—stop the flow of electrons, examine electron redistributions by studying the whole {potential energy} *vs* {separation distance} curves, and then let the current flow again. One can note that such a procedure is equivalent to the determination of major mesomeric forms (or configurations in a multiconfigurational or CI expansion in a post-Hartree−Fock calculation[5]) involving excitations from the molecular orbitals describing the interface bond. Mesomeric forms (or configurations) stemming from electronic rearrangements inside the organic itself or inside the metal itself are not considered, as we are mainly interested in the description of the interface

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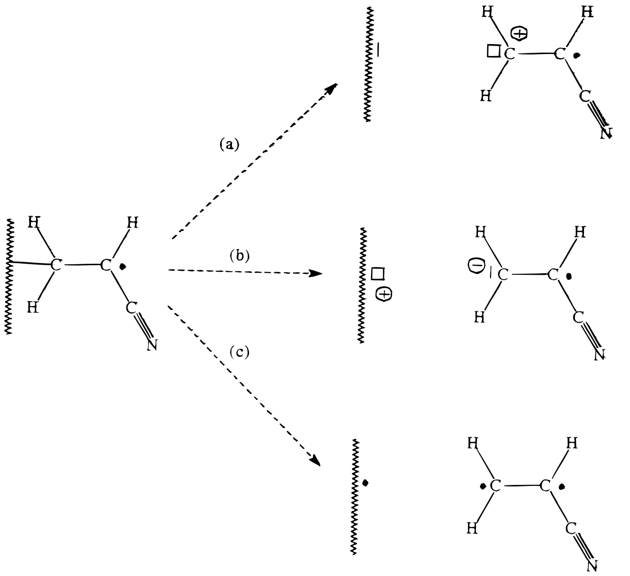

Figure 2. Picture of the Lewis structures of the electronic configurations which correlate to the surface radical of acrylonitrile proposed by Mertens et al.[2] (Figure 1) at infinite organics/surface separation (see text).

region and more particularly in the charge transfer.

We first note that the {molecule + surface} system depicted in Figure 1 is a spin doublet ($S = 1/2$). Several alternatives can be considered and are presented in Figure 2:

(a) The interface bond is dissociated so that the two electrons of the single C/surface bond are kept on the surface: the resulting organic moiety is a spin doublet, but constitutes a radical cation. There has been no net electronic transfer from the surface to the molecule, but rather from the molecule to the surface. In other words, configuration a alone would correspond to an electron counted in an anodic current and to a highly excited situation where the charge transfer is forced to be opposite to what electronegativities would impose;[6]

(b) The interface bond is dissociated so that the two electrons of the single C/surface bond are kept on the molecule. The electron transfer does give rise to a cathodic current, and the resulting fragments at infinite separation are an organic radical anion and a (locally) cationic site on the surface (Figure 2b). As mentioned above, this "hole" is not filled by electrons coming from the potentiostat, as we are performing our formal dissociation at constant overall number of electrons. An electron vacancy is thus created in the metal. Moreover, the radical anion then has a charge distribution which is opposite to that expected for its ground state,[7] and thus also corresponds to a highly excited state. In addition, if this structure were to give rise to the adduct shown in Figure 1, this would mean that it is the anionic end of the molecule which has chemisorbed on the surface: one can imagine that the electrostatic interaction between this anionic end and the (local) cationic site present on the surface upon formal dissociation is favorable. However, the rest of the (cathodically polarized) surface is negatively charged all around, and elementary electrostatics shows that the resulting anion/surface interaction is overwhelmingly repulsive, far more than the attraction of the local cationic charge. In other words, the overall potential energy is uniformly repulsive;

(c) The interface bond is dissociated so that one electron of the single C/surface bond is kept on the molecule, and one on the surface. By comparing the surface to what it was before interaction, as depicted in Figure 1, one sees that there has been no net electronic transfer and that this process does not give rise to any voltammetric current. In addition, the resulting organic fragment is a mixing of spin doublet and quartet and thus constitutes an excited configuration ($\pi-\pi^*$). In other words, it is merely a mesomeric form corresponding to the adsorption of an excited ($\pi-\pi^*$) state of the neutral parent molecule.

The structure of lowest energy being probably c, Figure 1 describes the adsorption of an excited ($\pi-\pi^*$) acrylonitrile molecule which has been adsorbed on the surface, with possible (weak) contributions from mesomeric forms (or configurations) a and b. In particular, no net charge transfer has occurred to reach such a final state. This final state cannot possibly correspond to the experimental results obtained by Mertens et al., since these authors describe voltammetric peak 1 as corresponding to the grafting reaction. An essential incoherence appears in the interpretation of the results of Mertens et al. In addition, these authors mention that this process "...requires that the oxidation at the anode does not create nor consume any charged species, since the transfer of one electron to AN and bonding of this monomer to the metal must form a radical species...". This restriction is capable of accounting for the global electroneutrality, which has to be fulfilled over the whole electrochemical cell, but we are not aware of any electrochemical reduction nor oxidation which would give rise to a current and "...not create nor consume any charged species...".

Let us now examine points ii and iii. At the beginning of their paper, Mertens et al. say that "...Lécayon et al. propose a unique mechanism although two reduction reactions are observed...".[2] Examples of the advent of several polarographic waves or voltammetric peaks in cases where a unique electrochemical reaction is involved have been known for more than 50 years[8,9] and theoretically understood for more than 30 years.[10] The fundamental reason why such multiple peaks may appear in voltammograms is that a single organic molecule may be involved in adsorption phenomena on the electrode surface, and it is the dynamic interplay of adsorption *vs* electrochemistry which gives rise to such behavior.

Such a hypothesis has been alluded to by Lécayon et al.[11] in order to explain the existence of peak 1 at a potential lower than that of the diffusion peak in the case of methacrylonitrile at a nickel cathode, but it appears that Mertens et al. were unaware of this work. As has been shown by Wopshall and Shain[10] for adsorption phenomena and by Savéant et al.[12] for chemical reactions following the charge transfer, the information carried out by the voltammetric current is kinetic in nature, which means that it lets one have information on the rate-limiting step only. In the case of several competing steps, it may be that the nature of the rate-limiting step varies with the applied electrode potential. In particular, the existence of these various pre- and postpeaks (which correspond to cases where the product or the reactant of the electrochemical reduction is adsorbed, respectively) is merely the result of a competition between the kinetics of adsorption *vs* that of diffusion. Alternatively, when coupled chemical reactions are involved, the kinetic control may be achieved either by the charge transfer step or by the coupled reaction.[12] The existence of domains of electrode potentials, concentrations, and scan rates where the coupled chemistry is rate-limiting has been a very efficient tool to determine the order of very fast coupled reactions as well as the value of their kinetic constants. One famous example is that of the electrohydrodimerization of acrylonitrile.[13] Hence, the above sentence cited by Mertens et al.[2] gives the impression that these authors have ruled out the possibility of a unique mechanism bearing several elementary steps, the competition between which is driven (in particular) by the electrode potential, although such a reading of the electrochemical literature is quite standard.

Hence, the fact that the voltammetric current is altered by the addition of DPPH and is not changed when one adds ϵ-CL merely indicates that DPPH is involved in the elementary step which is rate-limiting at the potential of peak 1 and that ϵ-CL is not involved in the *same* rate-limiting step. Mertens et al. find by SIMS that DPPH is present at the end of the synthesis and conclude that it was grafted on the polymer film (see Figure 11 in ref 2). This molecule, as well as many aromatic molecules, is known to adsorb quite readily on metallic surfaces (quinoline is used to poison Pd surfaces in catalysis), and the possibility of DPPH remaining adsorbed on the surface at the end of the synthesis has not even been considered. We note that their SIMS spectrum has been obtained on a film which is rinsed with acetonitrile, which is known to be a nonsolvent of the polymer. Hence, with the occurrence of a polymer film covering the surface,[11] it seems difficult to ascertain that the rinsing procedure is enough to fully remove DPPH possibly adsorbed on the surface under the polymer layer. As regards the effect of the adsorption of DPPH on the voltammetric current, one can propose that a fewer number of grafted chains are formed (due to surface occupation) and the arguments brought about by Mertens et al. are still valid. Now as regards ϵ-CL, a deeper uncertainty remains as neither the grafted polymer nor the electrolytic solution was analyzed after the synthesis. Again, the fact that the voltammetric current is not modified does not necessarily imply that ϵ-CL is not involved in the mechanism but merely that it is not involved in the rate-limiting step at the potential of peak 1. Assuming that this peak is an adsorption prepeak,[11] this means that the adsorption of the product of the electroreduction of AN is rate-limiting and that it is not influenced by ϵ-CL. In the case of reduction on a zinc surface, the oxide layer is too stable to be reduced during the process, and the very metallic surface is almost inaccessible. In that sense, the adsorption step is never rate-limiting, and this is why no adsorption prepeak is observed (the reduction is always diffusion-controlled, at least at the scan rates which have been studied). The same result is obtained with acrylonitrile on nickel in acetonitrile when one deliberately poisons the surface with thiourea.[14]

Mertens et al. also argue that the dianion formed at peak 2 is not grafted on the surface "...as evidenced by the absence of passivation...".[2] Again, we feel it necessary to stress that this is a misunderstanding of the very nature of electrochemical kinetics. As opposed to the above sentence, an observed peak in voltammetric experiments may originate from a passivation of the surface (a sort of cutoff in the current curve, due, e.g., to an occupation of the surface by some nonelectroactive materials, which is irreversible on the time scale of the electron transfer), from the exhaustive consumption of electroactive species (no more monomers to reduce), or from a change in the relative competition of kinetic steps.

In the case of an adsorption prepeak, the current starts at a lower potential thanks to adsorption stabilization (which lowers the activation energy of the electronic transfer).[10] When one imposes a yet more cathodic potential, one forces the number of reductions per second (i.e., the current) to increase, and the system follows this constraint as long as it can allow the reduced molecules to desorb, in order to free some metallic sites on the surface. There exists a potential limit above which the desorption is not fast enough, and molecules "waiting" to be reduced accumulate and thus the voltammetric current falls. For molecules having an infinite lifetime on the surface, this is a passivation in the strict sense that the surface is statically covered by nonelectroactive species. For noninfinite lifetimes, the adsorption/desorption process is active dynamically but may nonetheless lead to a decrease in the voltammetric current and to the formation of a current peak.

The above reasoning also indicates that the relative competition between adsorption and charge transfer phenomena may vary with the scan rate. Indeed, Savéant[12] et al. have shown that one had to consider the ($k_G v^{-1/2}$) and (kv^{-1}) ratios (where v is the scan rate, k_G is the electron transfer rate constant, and k is the kinetic constant of some first-order mechanism coupled, such as adsorption) as the dimensionless kinetic parameters of the charge transfer and any coupled first-order mechanism. In other words, these two new parameters do not decrease in the same way with increasing scan rate, and one may invert a competition and force one or the other to become rate-limiting. In an actual experiment, this amounts to enabling a prepeak to appear at high scan rates while a unique peak was obtained at low scan rates. As regards the very reason why one can indeed state that the dianion is not adsorbed on the surface, the answer can be found in the work of Baizer and Savéant[13] and involves a full kinetic study of all plausible mechanisms.

Before ending this comment, we wish to point out that Mertens et al.[2] have put forth new experimental results which can all be interpreted on the basis of the mechanism proposed by Lécayon et al. As a first illustration, let us reconsider the anionic mechanism proposed by Lécayon et al.[3,6] with the same technique as that used to detail point i above. The formal dissociation procedure is applied to the adsorbed anionic species, and the three possible correlations at infinite molecule vs surface separation are depicted in Figure 3. In case a (the two electrons are kept on the surface), the system correlates with a mesomeric form of the neutral parent AN in its ground state plus a net negative charge on the surface. This configuration is higher than c by an amount ($-\mu$), where μ is the chemical potential of the polarized surface.[6] No net electron transfer has occurred, and this gives rise to no current. In case b the system correlates with a dianionic single monomer. The energy of this configuration is ($A_2 - I^{(-)}{}_1 - \mu$) above that of configuration c, where A_2 is the second electronic affinity of acrylonitrile, $I^{(-)}{}_1$ is the first ionization potential of the acrylonitrile radical anion, and μ is the chemical potential of the polarized electrode.[6] In case c, the system correlates with the radical anion (with the expected ground-state electron distribution) plus the surface in the same electronic situation as before the transfer occurred (it is thus in equilibrium with the potentiostat),

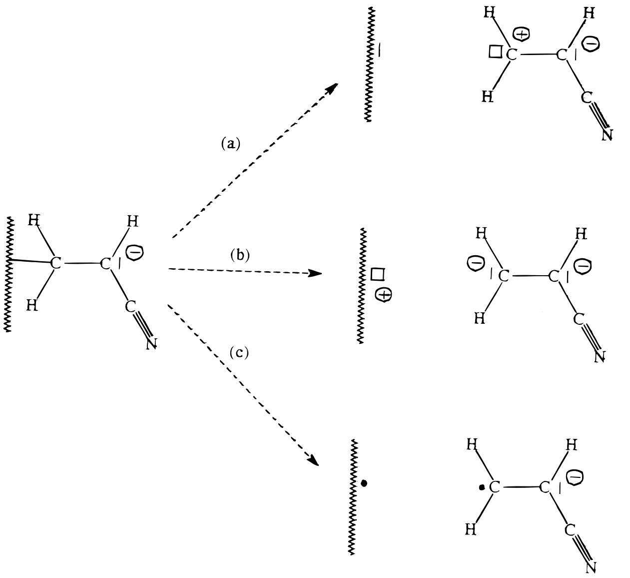

Figure 3. Picture of the Lewis structures of the electronic configurations which correlate to the surface anion of acrylonitrile proposed by Lécayon et al.[6] at infinite organics/surface separation (see text).

and one electron is counted in the current. From this analysis, we see that the chemisorbed anion depicted in Figure 3 describes an adsorbed radical anion of AN, plus residual (if relevant) contributions stemming from a and b. Thus, it actually describes a reduction of AN and is in agreement with the presence of a voltammetric current.

To us, this last case is not only fully compatible with the experimental results of Mertens et al. but also the most plausible of all cases examined herein. It is evident that this anionic species adsorbed on the surface involves a one-electron transfer and gives rise to a cathodic voltammetric current. The arrow indicated earlier by Lécayon et al.[1,3,6] and going from the surface to the molecule may have given the impression of a two-electron transfer, and these last authors may have wrongly considered this point up until now.

As regards the involvement of DPPH and ϵ-CL, we have already stressed that the adsorption nature lying under our proposed mechanism for peak 1 is sufficient to still consider the anionic mechanism as a candidate. Now, our above demonstration shows that the anionic mechanism is the only one to be able to account for all other experimental findings (e.g., the advent of a voltammetric current). We have shown recently that a diagnosis of adsorption phenomena could be obtained with the use of semi-integral voltammetry (SIV).[16] Our results show that adsorption phenomena are involved even at low AN concentrations ($<10^{-3}$ mol/L) for scan rates ranging from 20 to 2000 mV/s, even when one has only one peak which looks essentially like a pure diffusion peak.[16] In this last case, neither the precipitation of the polymer nor any kind of passivation may be invoked, as there is no apparent prepeak.[15] More work is needed to elucidate more thoroughly the localization and precise role of these compounds, as well as other types of inhibitors and/or transfer agents.

The conclusion of the present comment is that unsolvable contradictions are raised when one tries to put forward a radical mechanism for the formation of the grafted film in the electroreduction of acrylonitrile at a nickel cathode, as proposed by Mertens et al.[2] Contrary to what Mertens et al. conclude in ref 2, these contradictions are absent if one assumes an anionic mechanism.

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