

A combined theoretical and experimental study of the electrochemically induced chemisorption of acrylonitrile on nickel, copper, and zinc

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Abstract

We report a combined theoretical and experimental study of the interaction between a series of transition metals (Ni, Cu, Zn) and acrylonitrile. We demonstrate experimentally that the transition metal has a selective role in the grafting of electropolymerized acrylonitrile. Nickel and copper substrates support the formation of a polyacrylonitrile film, while zinc does not. Quantum chemical calculations indicate that acrylonitrile molecules form π -d bonds with Ni and Cu atoms, but do not react chemically with a Zn atom, in qualitative agreement with the experiment. Computational results also show that the electron affinity is significantly increased upon chemisorption, promoting radical anion species at the metal surface as initiators for polymerization.

1. Introduction

In the literature, there have been some promising reports on the possibility to electrochemically graft and grow polymer coatings on oxidizable metals, such as iron [1] or nickel [2]. This can be achieved by electropolymerization under cathodic polarization which, under certain conditions [3,4], results in chemisorption of the polymer on the metal surface.

Grafting of polymers on metal surfaces is of considerable interest for industrial applications involving coating or interface formation with molecular materials on metals. Prospective areas are, for example, corrosion protection or primers for top coatings, where the adhesion and stability properties of the interface are essential for the performance. One might also depict applications where biocompatibility of metal surfaces can be engineered by grafting of a suitable polymer film.

Polyacrylonitrile (PAN) is one of the most successful and thoroughly studied examples of such electrochemically grafted polymers. Both experimental and theoretical works have previously been performed in order to characterize the chemisorbed material and to study the conditions for effective chemisorption. Surface modifications of a nickel cathode due to polymer film formation have been observed using valence photoelectron spectroscopy (UPS) [5,6] and the chemisorbed polymer layer has been characterized by means of core-level photo-electron spectroscopy (XPS) [6], as well as infrared reflection absorption spectroscopy (IRRAS) [6] and metastable de-excitation spectroscopy (MDS) [5]. Theoretical studies have been performed at the ab initio Hartree-Fock/3-21G level to determine the structural and electronic properties of acrylonitrile and related monomers [7]. A model for the electrochemically induced chemisorption has also been proposed [2,8]: the polymerization is suggested to proceed via anionic species and the primary charge transfer between the electrode and the monomer leads to the formation of a single covalent bond between the metal surface and the organic molecule. In a recent theoretical study based on this model [9], the grafting of a related compound, poly-(methacrylonitrile) on nickel is investigated. With this approach, the final state of the electropolymerization, i.e., the grafted polymer is considered. These calculations are used to interpret chemical shifts observed in the C(1s) XPS core-level spectra.

In this work, we report a combined experimental and theoretical approach to study the interaction occurring at the molecular level between a series of transition metals (Ni, Cu, Zn) and an acrylonitrile monomer. The improved understanding of the chemisorption mechanism, which constitutes the initial step of the polymerization, is a prerequisite for further development of polymeric materials grafted by electrochemical methods. The grafting of electropolymerized acrylonitrile onto the transition metals is investigated experimentally with voltammetric methods. The experimental data is then interpreted with the aid of quantum chemical calculations. These results are used to propose a modified picture of the interaction of acrylonitrile and the metals with important implications for the chemisorption and for the

subsequent polymerization mechanism.

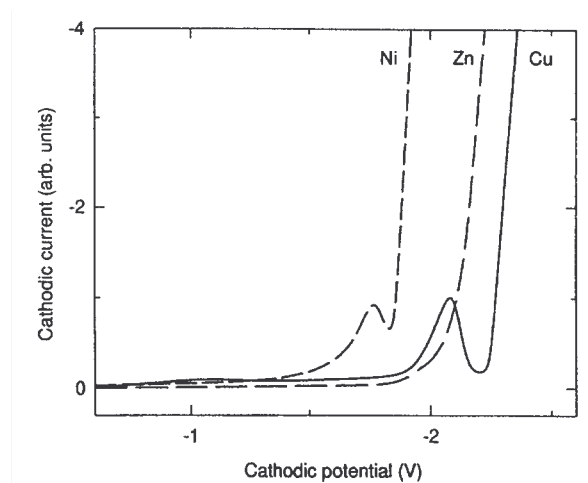


Fig. 1. Voltammograms obtained with acrylonitrile in CH_3CN with Et_4NClO_4 as support electrolyte and nickel, copper, and zinc as the cathode.

2. Electrochemically induced grafting

The chemisorption of acrylonitrile on the different transition metal substrates is experimentally investigated by electrochemical methods.

A cathodic polarization is applied to the metal and the reaction is studied by voltammetry. The electrochemical bath consists of acrylonitrile (0.5 M) and tetraethyl-ammonium perchlorate (Et_4NClO_4 : 5×10^{-2} M) dissolved in either acetonitrile (a non solvent of polyacrylonitrile) or dimethylformamide (a solvent of polyacrylonitrile).

As illustrated in Fig. 1, the voltammograms show two typical responses. For the cases of nickel and copper as the cathode, a distinct peak is observed in the low negative voltage regime of the diagram. This peak corresponds to the transfer of electrons, which we associate with the grafting of acrylonitrile molecules onto the metal surface. Regardless of whether acetonitrile or dimethylformamide is used as the solvent, a resulting polyacrylonitrile film is firmly attached to the cathode. In the case of a zinc cathode, no such peak is observed and grafting of the polymer film is not achieved. A second peak, occurring when higher negative voltage is applied to the cathode, is observed for all three metals. This peak corresponds to a transfer of electrons to the monomer in solution without associated chemisorption, since the resulting polymer proves to be soluble in dimethylformamide. From these measurements, it is clear that the character of the metal does influence the ability to obtain electrochemical grafting. Nickel and copper substrates support the formation of a polyacrylonitrile film, while zinc does not. A detailed experimental account of the grafting and electropolymerization process for these metals will be reported elsewhere [10].

3. The acrylonitrile monomer

In order to investigate the chemisorption process theoretically, we first establish the ground-state structures of the acrylonitrile monomer and its radical anion, which are the two species expected to be present in the vicinity of the cathode. Quantum chemical calculations are performed using density functional theory within the local spin density (LSD) approximation [11-13]. We have applied full geometry optimizations to the molecular model systems, i.e., optimization of all degrees of freedom, without fixed variables. Due to the well known intrinsic properties of the optimization method, we cannot fully guarantee that the obtained geometry corresponds to the global energy minimum. We have, however, tried several realistic starting geometries. The present results are based on the systems with the lowest total energy that we have been able to find. A high-quality numerical split-valence basis set augmented with p- and d-type polarization functions was used [11] and core orbitals were frozen during the computations. The geometries optimized with comparable basis sets at the LSD level and (from the literature [7]) Hartree-Fock level are given in Fig. 2.

We have chosen the lengths of the C=C, C-C, and C \equiv N bonds (Fig. 2) to serve as basis for the

discussion of the chemical structure of the acrylonitrile molecule. The LSD values are in reasonable agreement with the Hartree-Fock results [7]; the largest discrepancy is obtained for the C-C bond length, due to the well known overbinding for single bonds by the LSD method [12,13]. The triple bond is also slightly longer in the results obtained by the LSD method, as compared to Hartree-Fock results. There is no doubt, however, that the single, double and triple characters of the bonds are easily identified from the LSD values. Bond angles and dihedral angles are not discussed, since we are not interested in the chemical structure of the molecule as such. The angles nevertheless agree well with the data given in Ref. [7].

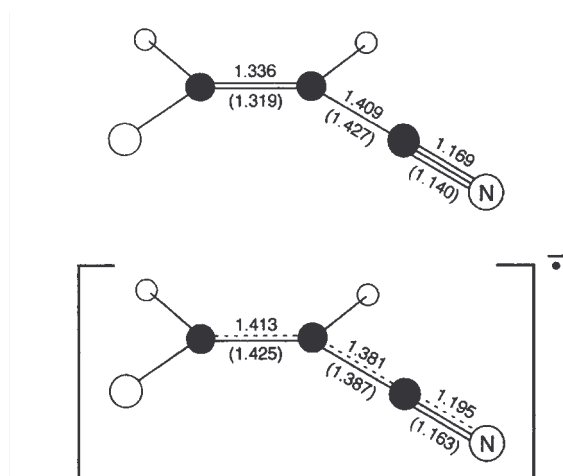


Fig. 2. Chemical structure of the acrylonitrile monomer (top) and its radical anion (bottom). LSD (this work) and between parentheses Hartree-Fock calculated bond lengths [7] are included in units of \AA

The highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) in the neutral molecule are delocalized over the four conjugated atoms. As expected, the HOMO has bonding character between the vinyl carbons and within the nitrile group, which is consistent with the presence of the double and triple bonds, respectively (accordingly, we observe antibonding character over the carbon-carbon single bond). The LUMO, in contrast, is antibonding over the double and triple bonds but bonding over the C-C bond. It is thus natural that the anion of the molecule displays reversed C-C and C=C bonds and that the C≡N bond length is elongated due to the occupation of the former LUMO. These results are in full agreement with previous Hartree-Fock calculations [7]. Since, in this study, we are primarily interested in the qualitative description of the metal/monomer interaction, we conclude that the LSD method provides an adequate picture of the geometric and electronic structure of the monomer.

In the chemisorption model originally proposed by Lecayon and coworkers [2,8] (hereafter referred to as the Lecayon model), the metal/acrylonitrile bonding is facilitated by the electric field present at the cathode. Because of the electronegativity of the nitrogen atom, there is a strong permanent dipole moment directed along the C≡N bond in the acrylonitrile molecule (experimentally determined to be 3.9 D [14]). This would orient the monomers near the cathode, which is assumed to be a necessity for electropolymerization to take place. As proposed by Lécayon et al. [2], the electric field would also transfer π -electrons towards the nitrile group, leading to the opening of the vinyl C=C bond (see Fig. 3). Subsequently the chemisorption of the monomer is suggested to occur through a metal-carbon bond formation leading to sp^3 -rehybridization of the CH₂ group on the unsubstituted side of the vinyl moiety. This involves the use of an electron pair from the metal to form the bond and is thus associated with a charge transfer of one electron to the acrylonitrile molecule. The active species would then be a carban-ion covalently linked to the Ni surface through a single carbon-metal bond.

To study the effects of a strong electric field on the monomer, a field strength of 2.1×10^{10} V/m was included in a full optimization of the monomer. This field is chosen to be identical to that considered in previous studies [7]; it is assumed to be intermediate to that in a typical electrical double layer ($\sim 10^9$ V/m) [14] and reactive atomic fields ($\sim 10^{11}$ V/m) [7]. Our results show that this causes a transfer of charge, mainly due to changes in the LCAO coefficients for the HOMO wavefunction. The electric field significantly increases the polarization of the C≡N bond, which expectedly orients with its dipole

moment parallel to the field, while the charge distribution at the C=C bond is less affected. We find that the vinylic C=C bond is not opened by a field of this strength; the bond length changes only from 1.336 to 1.355 Å, which is still clearly closer to a double than a single carbon-carbon bond. This result is not contradictory to that in the previous theoretical studies [7]. The low degree of π -charge polarization in the C=C bond indicates that the chemisorption mechanism is probably more complex than previously proposed, and that it needs to be more thoroughly studied.

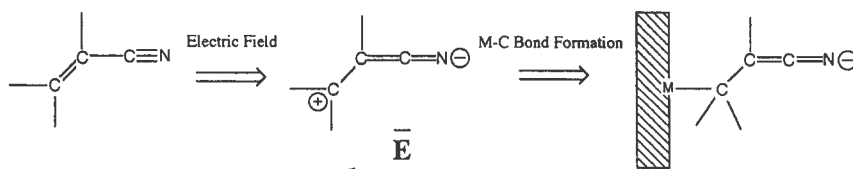


Fig. 3. Electric-field-induced chemisorption of the acrylonitrile monomer at the electrode surface, according to the Lécayon model.

4. The acrylonitrile-metal interaction

In order to obtain information about the theoretical conditions for interaction between the acrylonitrile monomer and the metal surface, we have studied complexes including a single metal atom. The calculations are again performed using density functional theory within the local spin density approximation (as described in the previous section), which should ensure that the properties of both the organic molecule and the transition metal atoms are adequately described. Although the complexes are indeed minimal cluster models, this approach has been successfully applied to similar situations, for instance, to describe chemisorption of ethylene on nickel [15-17]. As will be apparent below, the cluster models can account for important differences in the characteristics of the bonding between the acrylonitrile molecule and various transition metals.

In qualitative agreement with experiment, we observe that as a result of the geometry optimizations, the copper and nickel atoms form stable complexes with acrylonitrile; the complex has considerably lower total energy than the isolated partners and the metal-carbon distances are at typical bond lengths. The ground-state geometries of Ni-acrylonitrile and Cu-acrylonitrile are shown in Fig. 4. In contrast, the zinc atom does not appear to form a stable complex with the molecule, consistent with the absence of bonding deduced from experiment. It is interesting to note that chemisorption has also been observed experimentally with iron [1], which, as Ni, is a metal with partially filled 3d levels. Although no theoretical study has yet been made on complexes with iron atoms, this might indicate that chemical reaction is facilitated by metals possessing partially filled 3d levels, while zinc does not react due to its completely filled 3d and 4s orbitals.

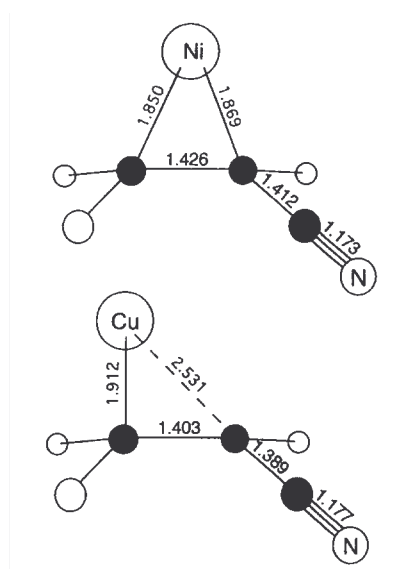


Fig. 4. Chemical structure of Ni-acrylonitrile and Cu-acrylonitrile complexes.

It is well known that many unsaturated hydrocarbons chemisorb to transition metal surfaces by π -d bonding (both π -d* and d- π * interactions) [18-20]. Detailed theoretical studies at the CASSCF (complete active space self-consistent-field) level show that this is also the case for a Ni/ethylene complex [16,17]. However, since acrylonitrile contains a reactive C \equiv N group, and since there are experimental indications of a possible reaction between the nitrogen lone pair and a nickel surface in the absence of an electric field [5], it is necessary to compare the reactivity of different sites of the monomer, at least for the case of nickel.

The LSD results indicate that the most stable conformation for a Ni/acrylonitrile complex, is by a π -d bond symmetric over the C=C bond (Fig. 4). An estimate of the binding energy associated with the chemisorption can be obtained by calculating the total energy difference between the complex and the Ni atom separated from the acrylonitrile. According to this scheme, the LSD binding energy for the π -d configuration is 72 kcal/mol, which is 8 kcal/mol more stable than Ni bonding to the C=N group and 9 kcal/mol more stable than bonding to the nitrogen lone pair. Although the LSD method is known to overestimate such binding energies significantly [12,13], we can conclude that there is a strong covalent interaction between the Ni atom and the monomer and that the formation of a π -d bond over the vinylene C=C bond leads to a more stable situation than reactions with the nitrile group. The ground state of the Ni/acrylonitrile complex is structurally very similar to that of the Ni/ethylene complex [16] and displays the same characteristic distortion of the H atoms out of the vinyl plane, indicating that the bonding mechanisms (π -d) are the same.

A significant charge transfer ($\approx 0.15|e|$) from the Ni atom to the organic molecule takes place; the transferred electron density appears to be equally distributed on the two carbon atoms of the vinyl unit. The highest occupied molecular orbitals of the complex have a strong Ni 3d character, along with some mixing with the C 2p_Z-N 2p_Z levels corresponding to the π and π^* levels of the molecule. In particular, one of those orbitals is built from the bonding combination of the LUMO of acrylonitrile, which possesses a node between the two vinyl carbons, and the 3d_{xz} orbital of the Ni atom; this interaction probably reflects the charge transfer from the metal atom to the molecule. We also observe a weak bonding interaction between the former HOMO of acrylonitrile and the 3d_{z²} orbital of the Ni atom, which suggests that backdonation also occurs to some extent in this system. Based on the analysis of the LCAO coefficients, both these π -d interactions are consistent with the fact that the charge transfer from the metal is equally distributed on the two carbon sites. In contrast to the π -d character of the highest occupied levels, the LUMO of the Ni/acrylonitrile complex originates from the combination of the Ni 4s orbital and the π -system of the molecule.

For the Cu/acrylonitrile complex, we also find that the C=C bond is the most favorable bonding site, which leads to a geometric structure close to that determined above in the case of nickel. However, since the Cu/acrylonitrile complex has one more partially occupied electron level, the HOMO of this complex corresponds to the LUMO of Ni/acrylonitrile; it therefore displays an antibonding character between the dominating Cu 4s orbital and the p_Z orbital of the substituted side of the vinyl unit.

This results in a strongly distorted complex, where the near symmetrical position of the metal atom over the C=C bond is lost (Fig. 4). Consequently, the 0.13|e| charge transfer from the copper atom only affects the terminal carbon of the acrylonitrile molecule.

Upon adding one extra negative charge, we observe that the geometry of the complex with Ni shows a tendency towards distortion, giving rise to a structure similar to that of Fig. 4. This is consistent with the fact that this anion is isoelectronic to the neutral Cu/acrylonitrile complex. The HOMO of the negatively charged Ni complex thus shows a strong Ni 4s character; accordingly, the major part of the charge ($> -0.6|e|$) is located on the metal atom. In the molecule, the changes in the electron density relative to the neutral complex, remain small, except on the nitrogen atom ($\Delta q = -0.13|e|$). In the case of the Cu/acrylonitrile anion, the extra electron fills up the previously half-filled HOMO. As a consequence, the geometry of the complex remains almost unaffected. Due to the marked 4s character of this level, the copper accommodates the major part of the charge ($\approx -0.55|e|$), with a minor contribution from the cyano group ($\approx -0.2|e|$).

We also observe that the bonding of a metal atom to the acrylonitrile molecule strongly modifies the electron affinity of the molecule. By performing full geometry optimizations on the singly charged anions and comparing the total energy of the anions with that of the neutral species, we find that the electron affinity increases by 0.7 and 1.8 eV for the acrylonitrile compound after reaction with a Ni and a Cu atom, respectively. The larger increase in the electron affinity of the complex with Cu might be due to the fact that, since the extra charge goes mostly to the metal atom as described above, adding one electron to the Cu/acrylonitrile complex result in a configuration closer to 4d¹⁰4s² for the copper

atom. The higher electron affinity of the complexes significantly favors the formation of a radical anion, which according to our calculations should be the initiator of the polymerization. This is in contrast to the Lécayon model, which proposes anions as the origin of polymerization. The details of the polymerization mechanism are presently being investigated.

Our results provide a different picture from that suggested in the model proposed by Lécayon. Upon trying to simulate absorption according to the Lécayon model, we are unable to locate a stable minimum for a Ni-acrylonitrile complex in the sp^3 conformation (as suggested by Lécayon), with or without the presence of a strong (2.1×10^{10} V/m) electric field. Instead, we find that by applying a strong electric field, the basic character of the Ni-acrylonitrile (or Cu/acrylonitrile) π -d bonding previously described does not change significantly. There are, however, minor structural distortions to the nitrile group due to the field.

5. Conclusions

Experimentally, we have found that the transition metal cathode (Ni, Cu, or Zn) has a selective role in the grafting of electropolymerized acrylonitrile. Nickel and copper substrates support the formation of a polyacrylonitrile film, while zinc does not. Results from quantum chemical calculations, performed at the local spin density level, show that acrylonitrile molecules form π -d bonds with Ni and Cu atoms, but does not react chemically with a Zn atom, in qualitative agreement with experiment.

Based on our results, we propose a modified picture of the interaction between acrylonitrile and the metals, with important implications for the chemisorption and subsequent polymerization mechanism. In agreement with previous studies, we find it reasonable that neutral acrylonitrile monomers are oriented with the strong dipole moment of the $C \equiv N$ group parallel to the electric field, i.e., perpendicular to the cathode surface if the field is homogeneous. We also find it plausible that the electropolymerization starts off by chemisorption of a monolayer on the cathode. However, our calculations suggest that a neutral monomer chemisorbs by a π -d bonding to Ni or Cu surfaces, rather than by sp^3 -hybridization, even in the presence of a strong electric field. Furthermore, our results show that the electron affinity is significantly increased upon the chemisorption, promoting radical anion species at the metal surface, rather than anions as proposed in previous models.

Further investigations are needed to study the effects of the electric field on the charged molecule chemisorbed to the cathode and also to study, in greater detail, the polymerization mechanism following the initial chemisorption. The exact role of the nitrile group in the electropolymerization properties of acrylonitrile is another topic of prime interest for future investigations.

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