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A model for the effect of ion pairing on an outer sphere electron transfer

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Abstract

Ion pairing can strongly affect the rates of electron transfer reactions. To explain this effect we propose a model Hamiltonian which describes the interactions between the pairing ion and the reactant, solvent and inner sphere reorganization, and bond breaking. Explicit expressions for the energies of the initial and final states, and for the energy of activation are derived in the weak adiabatic limit. The model is applied to the reduction of Cu(II) in the presence of chloride ions. For this purpose the pertinent system parameters are obtained from density functional theory. Our model explains, why chloride enhances the rate of the first electron transfer in copper deposition.

1 Introduction

It is well known that ion pairing may effect both the rates and the thermodynamics of electron transfer reactions. In particular this is true for the deposition of multivalent metal ions, where the first step is often a one-electron transfer. Indeed, the plating industry uses various recipes for the baths from which metal ions are deposited, and ion pairing certainly plays a part in these processes [1]. For example, for copper deposition, baths containing both Cl⁻ ions and organic substances such as polyethylene glycol are commonly used [2].

Considering the importance of ion pairing, there are surprisingly few theoretical investigations of its effect on electron transfer. There are a considerable number of molecular dynamics studies of ion pairing in the bulk of the solution, and we shall discuss a few of them below, but they describe only the initial or final state of an electron transfer. A notable exception is the elegant work of Nagy et al. [3], which combines experimental work on the catalysis of copper deposition by chloride with an investigation of the electronic overlap of the reactant with a copper electrode. They conclude that the presence of chloride ions enhances the overlap and thereby catalyzes electron transfer. The effect is mainly attributed to the fact that chloride complexes can approach the electrode to shorter separations than the pure aquo-complexes.

In this work we want to approach the effects of ion pairing on electron transfer from a fundamental point of view. We start by proposing a model Hamiltonian for electron transfer in the presence of an ion which does not directly participate in the reaction. However, its interaction with the reactant changes during electron transfer, and its mere presence affects the accompanying solvent and inner sphere reorganization. From the Hamiltonian we derive an expression for the energy of activation for the reaction. We also consider the effect of bond breaking by including Saveant's model [4,5] in an extended version of the Hamiltonian.

As an application of our model we have considered the effect of chloride ions on copper deposition. For this purpose we have performed DFT (density functional theory) calculations for several Cu(I) and Cu(II) complexes with and without chloride. While these calculations are somewhat approximate they illustrate well how the model can be used, and they do explain why the presence of chloride accelerates the deposition process.

2 The model Hamiltonian

We consider an outer sphere electron exchange between a redox center labelled a and a metal electrode in the presence of an ion, which does not participate directly in the reaction, but forms an ion pair with the reactant. Our model is an extension of the theory of adiabatic electron transfer reactions proposed by one of us [6], and has also similarities with a model for combined electron and proton transfer [7].

The Hamiltonian consists of a number of terms, which we shall present in turn. Since we consider the transfer of one electron in the outer sphere, we can use the spinless version of the Anderson-Newns model [8,9] for the reactant and its interaction with a metal electrode:

$$H_{\text{el}} = \epsilon_a n_a + \sum_k \epsilon_k n_k + \sum_k [V_k c_k^+ c_a + V_k^* c_a^+ c_k] \quad (1)$$

The first two terms denote the reactant and the metal, the last term effects electron exchange between the metal and the reactant with amplitudes V_k . ϵ_k denotes the electronic energy of the metal states, n_k their number operator, and c_k^+ and c_k the creation and annihilation operators. The corresponding quantities for the state a are ϵ_a , n_a , c_a^+ and c_a . All energies ϵ_a and ϵ_k are measured with respect to the Fermi level of the metal.

Electron transfer is coupled to the reorganization of the solvent. Just like in Marcus [10] and Hush [11] theory, these modes are divided into a fast part, which is supposed to follow the electron transfer instantly, and a slow part. The former just renormalizes the electronic energy [12, 13], and will not be discussed further. The latter is modeled as a phonon bath, whose modes we label by ν :

$$H_{\text{sol}} = \frac{1}{2} \sum_{\nu} \hbar \omega_{\nu} (q_{\nu}^2 + p_{\nu}^2) \quad (2)$$

where q_{ν} and p_{ν} are dimensionless coordinates and momenta, and ω_{ν} the frequencies. These solvent modes interact with the charges of the reactant and of the ion which forms the pair. As usual, we take the interaction as linear and proportional to the charge. For simplicity we assume that the charge number of the reactant is unity when the valence orbital is empty. So we write the coupling terms as:

$$H_{\text{int}} = (1 - n_a) \sum_{\nu} \hbar \omega_{\nu} g_{\nu} q_{\nu} + \sum_{\nu} \hbar \omega_{\nu} f_{\nu} q_{\nu} \quad (3)$$

Here the g_{ν} denote the coupling constant of the reactant with the solvent modes, and the f_{ν} those of the ion. Since the latter does not change its charge state, we do not require its explicit value, it is contained in the coupling constant.

In addition, the interaction between the ion pair will change, and other inner sphere modes may be reorganized as well. We describe this by the term:

$$H_{\text{pair}} = (1 - n_a) U_1(x) + n_a U_2(x) \quad (4)$$

where x denotes a collection of variables. We assume that the two function $U_1(x)$ and $U_2(x)$ have the same minimum value; any difference can be incorporated in ϵ_a . The sum of the terms in eqs. (1) to (4) constitutes our model Hamiltonian.

In principle, electron transfer also involves a reorganization of the ionic atmosphere of the reactant. However, this effect is known to be weak and will not be discussed here. [14]

3 Weak adiabatic limit

Our model makes no assumption about the strength of the interactions between the reactant and the metal, and can be applied to catalytic reactions as well. Here,

however, we consider the outer sphere case. In the spirit of the Marcus theory [10] we assume that the interaction between the reactant and the metal is sufficiently strong to assure adiabaticity, but so small that it does not affect the energy. In addition, we assume that all the degrees of freedoms that are reorganized during the reaction are classical; other possibilities will be discussed below.

The energy of the system is a function of the coordinates q_ν and x . The stationary points on this surface are of particular importance; in the so-called normal region, where both the initial and the final point are stable, there are three such points corresponding to the initial, the transition, and the final states. Using the Hellman-Feynman theorem, the conditions for stationary points are:

$$\left\langle \frac{\partial H}{\partial q_\nu} \right\rangle = 0 \quad \text{and} \quad \left\langle \frac{\partial H}{\partial x_i} \right\rangle = 0 \quad (5)$$

In Marcus theory the inner sphere modes are treated by the same harmonic approximation as the solvent modes. In this case they can be included in the latter, i.e. the set q_ν then includes the x_i . In order to compare our results with Marcus theory we shall follow this approximation at first, and return to the more general case later.

Thus we consider only the first of the equations (5), which gives:

$$q_\nu = -(1 - \langle n_a \rangle) g_\nu - f_\nu \quad (6)$$

At this stage it is useful to define three energies of reorganization [7]:

$$\lambda_1 = \frac{1}{2} \sum_\nu \hbar \omega_\nu g_\nu^2, \quad \lambda_2 = \frac{1}{2} \sum_\nu \hbar \omega_\nu f_\nu^2, \quad \lambda_x = \frac{1}{2} \sum_\nu \hbar \omega_\nu g_\nu f_\nu \quad (7)$$

where λ_1 and λ_2 characterize the coupling of the redox couple and of the ion to the solvent, respectively, and λ_x indicates the interference.

Considering electron transfer from the redox couple to the electrode, the initial state has $\langle n_a \rangle = 1$, and the corresponding energy is:

$$E_i = \epsilon_a - \lambda_2 \quad (8)$$

Conversely, in the final state we have $\langle n_a \rangle = 0$, and the energy is:

$$E_f = -\lambda_1 - \lambda_2 - 2\lambda_x \quad (9)$$

The energy ϵ_a , taken with respect to the Fermi level, shifts with the applied electrode potential. At equilibrium:

$$E_i = E_f \quad \text{and hence} \quad \epsilon_a = -\lambda_1 - 2\lambda_x \quad (10)$$

In the absence of the complexing ion, $\epsilon_a = -\lambda_1$, so ion pairing has an effect on the equilibrium potential for the reaction. Of course, this does not come unexpectedly, but the advantage of our formalism is that it gives a quantitative expression.

Electron transfer happens at the saddle point; an easy way to determine the latter is to note, that there the electronic level of the reactant is at the Fermi level. For this purpose we collect the terms in n_a and write:

$$\tilde{\epsilon}_a n_a = \left(\epsilon_a - \sum_{\nu} \hbar\omega_{\nu} g_{\nu} q_{\nu} + U_2(x) - U_1(x) \right) n_a \quad (11)$$

where we have included the terms in $U_1(x)$ and $U_2(x)$ for further reference; they will be used in the next section. Setting $\tilde{\epsilon}_a = 0$ and using eqs. (5) gives:

$$\text{saddle point: } \langle n_a \rangle = \frac{\epsilon_a + 2\lambda_x + 2\lambda_1}{2\lambda_1}, \quad \text{at equilibrium: } \langle n_a \rangle = \frac{1}{2} \quad (12)$$

Calculating the energy of activation is straightforward:

$$E_{\text{act}} = \frac{(\epsilon_a + 2\lambda_x)^2}{4\lambda_1} = \frac{(\lambda_1 - e_0\eta)^2}{4\lambda_1} \quad (13)$$

where we have introduced the overpotential through $\epsilon_a = -\lambda_1 - 2\lambda_x + e_0\eta$. This is the same expression as in normal Marcus theory without the complexing ion. Thus, the latter does not affect the expression for the energy of activation; of course it does affect the energy of reorganisation λ_1 by its presence.

4 Bond breaking electron transfer

So far we have not paid much attention to the term H_{pair} of eq. (4). If this denotes an inner sphere mode, it can be treated in the harmonic approximation, or if the exact curves are known they can be incorporated into the formalism without difficulties. In particular, they will not affect the formal expression for the energy of activation.

A more interesting case arises when it refers to bond breaking or formation. Then it is not a priori clear how this will be affected by the pair formation. To investigate this case we adopt the model of Saveant [4,5] and introduce the potentials:

$$H_{\text{pair}} = (1 - n_a)D \left[e^{-2\alpha x} - 2e^{-\alpha x} \right] + n_a D e^{-2\alpha x} \quad (14)$$

as proposed by Koper and Voth [15], and later adopted by our own group [16,17]. The first term describes a Morse potential with binding energy D , and the second term contains only the repulsive part. These potentials contain the essentials of

bond breaking, and permit analytical calculations. It is convenient to introduce: $y = e^{-\alpha x}$. Then the second part of eq. (5) for stationary points can be written in the compact form:

$$y = (1 - \langle n_a \rangle) \quad (15)$$

In the weak adiabatic limit the energy of the occupied state with $\langle n_a \rangle = 1$ remains unchanged:

$$E_i = \epsilon_a - \lambda_2 \quad (16)$$

while that for the empty state:

$$E_f = -\lambda_1 - \lambda_2 - 2\lambda_x - D \quad (17)$$

has been lowered by the binding energy. The calculation of the activation energy proceeds as before. Again the formal result is not affected by the solvation of the ion:

$$E_{\text{act}} = \frac{(\lambda_1 + D - e_0\eta)^2}{4(\lambda_1 + D)} \quad (18)$$

In particular, at equilibrium we have:

$$E_{\text{act}}^{\text{equi}} = \frac{\lambda_1 + D}{4} \quad (19)$$

Again, the ion pairing does not affect the formal expression of the activation energy, but those for the initial and final states. Of course, as stated before, the presence of the pairing ion affects the energy of reorganization by an excluded volume effect.

5 Effect of Cl^- on the first step in copper deposition

The deposition of copper is known to be strongly affected by the presence of Cl^- ions, so we shall apply our formalism to this example, focusing on the transfer of the first electron in aqueous solutions. Chloride ions can replace water molecules as ligands from the nearest coordination sheath of d-metals. Therefore we shall compare two different cases: electron transfer without Cl^- : $\text{Cu}^{++}/\text{Cu}^+$, and with two Cl^- ; $[\text{CuCl}_2]/[\text{CuCl}_2]^-$. For the complex with one chloride, $\text{CuCl}^+/\text{CuCl}$ the reduced form has a very low solubility and forms an isolating deposit on the electrode surface. Therefore it is generally avoided in praxis, and we shall not discuss it further.

In order to estimate both the changes in the thermodynamics and in the energy of activation caused by the presence of the chloride ions, we have performed DFT calculations for various complexes of copper with water and with Cl^- . Solvation effects were treated in the framework of a mixed molecular-continuum model;

the technical details of the calculations are given in the appendix. These calculations were performed statically, without thermal average. However, because of the firm binding of water in the first and second solvation shell this is not a severe limitation. In any case, we want to show how the formalism can be applied, and to understand trends rather than obtain absolute values.

Quantum-chemical calculations for aqueous copper complexes have been performed by several other groups before [18–22]. Our calculations complement these previous works by focusing on the energetics of the electron transfer.

5.1 $\text{Cu}^{++} \cdot \text{aq} / \text{Cu}^+ \cdot \text{aq}$

To investigate this reaction we have considered copper complexes with 18 explicit water molecules. The rest of the solvent was described by an implicit solvation model (see appendix). For the Cu^{++} complex we found two locally stable configurations with slightly different Jahn-Teller distortion [23]. The most stable sixfold

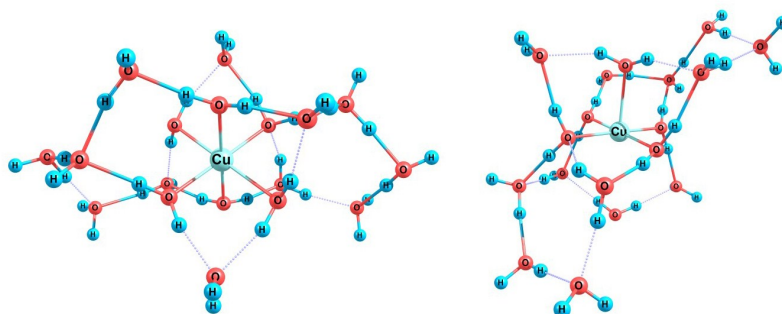


Figure 1: Optimized geometry of $[\text{Cu}(\text{H}_2\text{O})_{18}]^{2+}$ (oxidized state) Left: sixfold, right: fivefold coordinated complex.

coordinated Cu^{++} complex is shown at the left of Fig. 1; it has an axial Jahn-Teller distortion: $r(\text{Cu} - \text{O}_{\text{eq}}) = 1.99 - 2.14 \text{ \AA}$; $r(\text{Cu} - \text{O}_{\text{ax}}) = 2.29 \text{ \AA}$. The subscripts 'eq' and 'ax' stand for equatorial and axial, respectively.

Experimentally, a five-fold coordinated Cu^{++} has also been observed by neutron diffraction [24] and X-ray absorption spectroscopy [23, 25–27]. Further evidence in favor of this structure also follows from Car-Parrinello MD [28] and ab initio molecular dynamics [29, 31] simulations. Therefore we have also performed calculations for a five-fold coordinated complex (pyramidal structure) - see Fig. 2 right; according to our calculations within DFT error the Gibbs energies for both

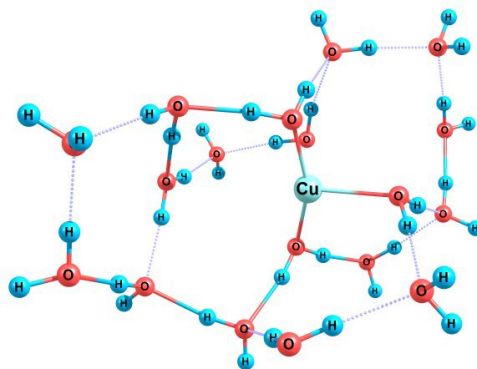


Figure 2: Optimized geometry of $[\text{Cu}(\text{H}_2\text{O})_{18}]^+$ (reduced state).

types of complexes are about the same (formally the five-coordinated structure was found to be 0.072 eV more favorable). In the following, we consider only the fivefold complex. The calculated Cu-O bond lengths are in good agreement with experimental data [25]; the difference amounts to 0.05 Å.

In qualitative accord with [30] we have found that the reduced form $[\text{Cu}(\text{H}_2\text{O})_{18}]^+$ is only threefold coordinated. Two water molecules reveal the shortest Cu-O bond lengths, ca. 2 Å, while the bond of the Cu atom with the third molecule is elongated (2.32 Å). Blumberger have reported a larger value (2.6 - 2.8 Å) for this bond length [29]; this difference might be attributed to the shortcomings of our model. Ab initio calculations by Lee et al. [17] point to a rather small difference of the hydration Gibbs energy between two- and threefold coordinated Cu^+ . Thus, the reduction can be considered to be accompanied by the breaking of at least two bonds. The calculated free energy of the reduction can be converted into the equilibrium potential by referring these values to the standard hydrogen electrode on the absolute scale. Unfortunately the value of the latter is somewhat uncertain, 4.5 ± 0.2 V is a good estimate. Using the medium value we obtain for the standard equilibrium potential a value of +0.22 V (fivefold Cu^{2+}). The actual experimental value is 0.16 V [32]. Considering the uncertainties of DFT and the approximate nature of the calculations the agreement is acceptable. Actually, we are less interested in obtaining the absolute value but in the changes caused by complexation with chloride. The energetics of the reorganization will be discussed below.

5.2 $\text{CuCl}_2 \cdot \text{aq} / \text{CuCl}_2^- \cdot \text{aq}$

For the CuCl_2 complex in aqueous solutions we found four different geometries with energy differences less than 0.2 eV. The optimum geometry is shown at the left of Fig. 3, it has the form of a $[\text{CuCl}_2\text{-trans}]$ (five-fold) complex with the shape

of a pyramid. The Gibbs energy of the process $\text{Cu}^{++}(\text{aq}) + 2 \text{Cl}^{-}(\text{aq}) = \text{CuCl}_2(\text{aq})$ is -0.55 eV , so that the addition of two chlorides is favorable.

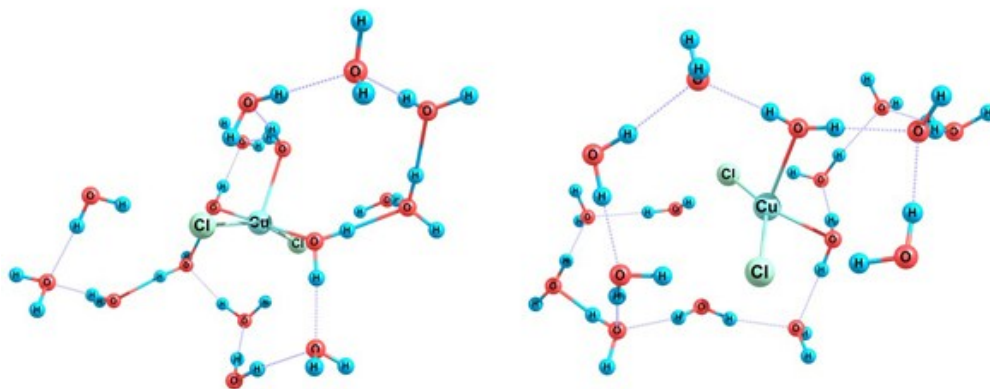


Figure 3: Left: Optimized geometry of $[\text{CuCl}_2(\text{H}_2\text{O})_{16}]$ (oxidized state), right: reduced state.

For the reduced form of this complex we found two different forms, (i) and (ii). The form (i) looks like an ionic associate, $[\text{Cu}(\text{H}_2\text{O})_2]^+ 2\text{Cl}^-$, where the ions are not separated by water molecules. In contrast, the form (ii) is a tetrahedral four-coordinated complex $[\text{CuCl}_2(\text{H}_2\text{O})_2]^-$ with the bond lengths $r(\text{Cu}-\text{Cl}) = 2.33 - 2.34 \text{ \AA}$ and $r(\text{Cu}-\text{O}) = 2.28 - 2.33 \text{ \AA}$. The form (ii) is more stable by a Gibbs energy of 0.22 eV . Thus, the reduction entails the breaking of one bond. As shown by our calculations, the reduced form (Fig.3, right) has no negative frequencies and can be considered as a local minimum of the multidimensional potential energy surface. We treat this form as a final state in the elementary act of electron transfer. This does not exclude, however further transformation of the complex in subsequent chemical steps. The equilibrium potential was estimated to be $+0.07 \text{ V}$, i.e. within DFT error, is nearly the same as for the pure aquo complex without chloride.

6 Energetics of reorganization

In the theoretical sections 1 - 4 we had concluded that ion pairing may affect the free energy of the reaction and hence the equilibrium potential. Here, by coincidence, the value for the $\text{CuCl}_2/\text{CuCl}_2^-$ couple is practically the same as for $\text{Cu}^+/\text{Cu}^{++}$ couple, for which we calculated a potential which is just a little higher than the experimental value.

The formal expression for the activation energy is not changed by ion pairing, but the values of the quantities which enter are affected. These are the energies of reorganization λ_{out} for the solvent in the outer sphere and λ_{in} for the complex, and the bond breaking energy D . In the two reactions we consider here the inner sphere reorganization plays no role; as all degrees of freedom were allowed to relax when calculating D , therefore the inner sphere reorganization is already contained in the bond breaking.

The outer-sphere solvent contribution was estimated from the Marcus formula:

$$\lambda_{\text{out}} = \frac{e_0^2}{8\pi\epsilon_0 r_{\text{eff}}} \left(\frac{1}{\epsilon_\infty} - \frac{1}{\epsilon_s} \right) \quad (20)$$

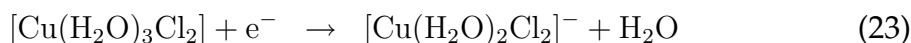
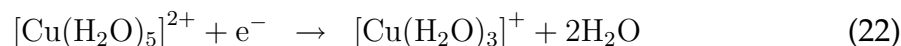
where ϵ_s and ϵ_∞ are the static and the optical dielectric constants of water, and r_{eff} is the effective radius of the complex; the other symbols have their usual meaning. In the literature there is some discussion about a possible effect of the image charge on the energy of solvated ions. According to recent simulations [39], in aqueous solutions the image interactions are strongly screened by the water molecules; therefore we have neglected them in this equation.

The effective radius r_{eff} was estimated as suggested in ref, [44]: According to the Born formula the free energy of solvation for a spherical ion is:

$$\Delta G_{\text{sol}} = -\frac{e_0^2}{8\pi\epsilon_0 r_{\text{eff}}} \left(1 - \frac{1}{\epsilon_s} \right) \quad (21)$$

We have calculated the solvation energies of the various reactants from PCM and then chosen r_{eff} in such a way, that the value obtained from formula (21) agreed with the former. The results are shown in Tab. 1.

The bond breaking energies D have been estimated from the following reactions:



The two parameters D , λ_{out} characterize the reorganization of the reactants during electron transfer. In particular, they determine the energy of activation, which can be calculated from eqs. (19) and (18). The corresponding values have been collected in Tab. 1. Previously Blumberger [30] made an attempt to address the first step of reduction of $[\text{Cu}(\text{H}_2\text{O})_5]^{2+}$ in terms of asymmetric reorganization ($\lambda_{\text{Red}} \neq \lambda_{\text{Ox}}$), despite of the breaking of bonds between the central ion and water molecules in the first solvation shell. Using the data reported in work [30] and the formula from Ref. [44] to calculate the averaged reorganization energy, a value of 0.46 eV can be obtained for the activation barrier, which is close to our estimate (0.62 eV). Our value is somewhat lower than that of 0.77 eV obtained by Pinto

	$[\text{Cu}(\text{H}_2\text{O})_5]^{2+}$	$[\text{Cu}(\text{H}_2\text{O})_4\text{Cl}_2]^+$
$r_{\text{eff}} / \text{\AA}$	3.4	2.5
D	1.35	0.2
λ_{out}	1.14	1.56
ΔE_{act}	0.62	0.44

Table 1: Effective radius r_{eff} , the bond breaking energy D , the energy of reorganization λ_{out} of the outer sphere, and the activation energy ΔE_{act} at zero overpotential. All energies are in eV.

et al. [33] from classical molecular dynamics. The same group had obtained an activation energy of 0.68 eV for the second step, so that the first electron transfer would be slow and rate-determining.

Halley et al. [45] have measured an activation energy of $\Delta E_{\text{act}} = 0.33 \pm 0.05$ eV for the first electron transfer step of the pure aqua-complex, together with an unusually low pre-exponential factor of about 10^2 cm s^{-1} . Our theoretical value is substantially lower. The difference can be due to a compensation effect between the activation energy and the pre-exponential factor in the experiments because of the limited temperature range. Alternatively it could be caused by the neglect of quantum tunneling in our calculations, which would produce the same effect, or to other shortcomings in our model.

The complex with two Cl^- ions has the lower activation energy. Since its equilibrium potential is similar to that of the pure aquo-complex, it offers a favorable reaction path, which would explain the catalytic effect of chloride on copper deposition. Unless the deposition step $\text{Cu}^+ + \text{e}^- \rightarrow \text{Cu}$, which we have not investigated, is also catalyzed, this would make this deposition step rate-determining. As can be seen from Table 1, the solvent reorganization energy for $[\text{CuCl}_2]$ is larger compared with a pure Cu^{++} aqua complex, therefore the catalytic effect results from a smaller intramolecular reorganization for the aquachloro complex.

These findings are in line with the work of Nagy et al. [3]: These authors performed experimental work in perchloric acid. In the absence of chloride, the first electron transfer in the reduction of copper was found to be rate-determining. Even small amounts of chloride accelerated the first electron transfer, but had no effect on the second step, which became rate-determining as the chloride concentration was increased. They explained the catalysis of the first step through an increase of the overlap of the reactant with the copper electrode in the presence of chloride, while we explain it through the reduction of the energy of reorganization. These two explanations do not exclude each other. The work of Markovic et al. [34] further supports our conclusions: They noted, that the overpotential deposition of copper on platinum is slow in pure perchloric acid, but substantially enhanced by the presence of chloride. They suggested that chloride perturbs the

solvation sphere of the copper ions and thereby accelerates the reaction, which qualitatively agrees with our conclusions.

There is a plethora of articles on copper deposition, and an exhaustive citation, let alone discussion, is outside the scope of this article, in which copper deposition is treated as an example. Many studies have been conducted in sulphuric acid, e.g. [2, 35, 37, 46] which also enhances the deposition rate compared to perchloric acid [3]. Other studies focused on high chloride concentrations, where complexes with three or more chloride ions can be formed [36, 46], and where disproportionation of Cu^+ might also play a role. All studies agree that small and intermediate concentrations of chloride catalyze copper deposition. Most studies also agree that in the absence of chloride the deposition occurs in two steps, where the first electron transfer determines the rate. However, sometimes a direct two-electron transfer is proposed [46]. This would require an energy of reorganization four times larger than that for a single electron transfer, and is therefore unlikely [38].

We tentatively conclude that our results explain the experiments in perchloric acid and chloride concentrations that are not so high that complexes with three or more chloride ions may form. A theoretical explanation of the majority of the experimental data would have to include the elucidation of the effect of sulphate on the reaction.

7 Conclusions

We have developed a model Hamiltonian for the effect of ion pairing on an outer sphere electron transfer reaction, which was solved in the weak adiabatic limit, i.e. on the Marcus and Hush level [10, 11]. The formal expression for the activation energy, including the effect of bond breaking, is not affected by ion pairing. However, the presence of the ion modifies the energy of reorganization.

As an application, we have investigated copper deposition from aqueous solutions, focusing on the transfer of the first electron. For this purpose, we have performed DFT calculations for various aqueous copper complexes with and without chloride. Our results suggest that the reaction: $\text{CuCl}_2 \cdot \text{aq} + \text{e}^- \rightarrow \text{CuCl}_2^- \cdot \text{aq}$ has a much lower activation energy than the reaction for the pure aquo-complex, and may be responsible for the experimentally observed catalysis of copper deposition by chloride.

In summary, we have developed a framework for investigating the effect of ion pairing on electron transfer, and a first application to copper deposition has given promising results.

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Appendix: Technical details of the DFT calculations

The quantum chemical calculations were performed at the DFT level with the hybrid exchange correlation functional B3LYP as implemented in the Gaussian 16 program suite [40]. The orbitals of the Cu, Cl, O and H atoms were described by the standard basis set of triple-zeta quality augmented by diffuse and polarization functions, 6-311++g(d, p). The initial geometry of the complex species was obtained at the same DFT level but using a smaller basis set. In these calculations a basis set of double-zeta quality was employed to describe the valence orbitals of the Cu atom, while the effect of inner electrons was included in the effective core potential developed by Hay and Wadt (LanL2) [40]. The standard basis set 6-31g(d, p) was used to describe the electrons in the Cl, O and H atoms. The open shell systems were treated in terms of the unrestricted formalism. The geometry of complex forms was fully optimized without symmetry restrictions. Water molecules were included directly into the first and second coordination spheres; the rest of aqueous medium was addressed by the PCM (Polarized Continuum Model) [40]. A value of 78 was used for the static dielectric constant of electrolyte solutions. Non-electrostatic (cavitation, dispersion and repulsion) contributions to the solvation free energy were calculated as well. The solvation effects were found to be important in further calculations. Zero-point energy correction and vibrational contributions to the free energy were neglected when estimating the equilibrium potentials. The stability of Kohn-Sham orbitals was checked with the help of a standard routine in the Gaussian 16 package. The program ChemCraft [42] was used for the visualization of geometry and orbitals. A similar model approach was employed earlier to investigate the reactivity of In(III) [41] and Fe(III) [43] aqua- and aquahydroxocomplexes

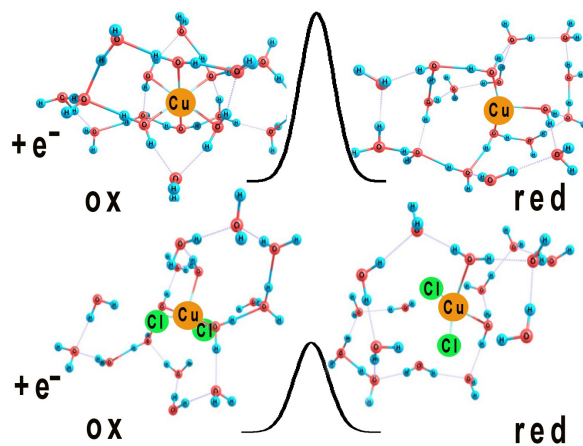
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Our theory for the effect of ion pairing on electron transfer explains why chloride catalyses copper deposition.