

Simulation of the electron transfer process $\text{Cu}^{2+} + \text{Cu}^+ \rightleftharpoons \text{Cu}^+ + \text{Cu}^{2+}$ in aqueous solution

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Abstract

A Monte Carlo simulation is performed to investigate the role of solvent in the $\text{Cu}^{2+}/\text{Cu}^+$ electron exchange process in water. This study is based on the classical Marcus model using the energy gap between the reactant and product states as the reaction coordinate. Since the process has a rather high activation free energy, conventional simulations are not best suited to its complete description, and thus special sampling techniques are required. In this case, a mapping potential is used to drive the system from the reactants to the transition state, and free energies are computed by thermodynamic perturbation and thermodynamic integration methods. A comparison is made between the results obtained by both methods and conclusions are drawn concerning the applicability of the Marcus model to this kind of process.

Keywords: Aqueous solution; Electron transfer process; Marcus model; Monte Carlo simulation

1. Introduction

Electron transfer reactions are among the most fundamental chemical processes, playing a major role in many important chemical and biological phenomena. Electron transfer reactions occurring in aqueous solution are of special interest owing to the natural importance of this medium in chemical reactivity. Moreover, these processes consist essentially of a spatial rearrangement of electronic charge and are thus critically sensitive to an environment such as that provided by a polar solvent.

The current understanding of these reactions (for a review on this subject see Ref. [1]) is largely due to the pioneering theoretical work developed between the mid-1950s and the 1960s by Marcus [2–4],

Hush [5], Levich [6] and others. These theories aimed for both a qualitative and quantitative description of the aspects involved in this kind of reaction.

Two types of mechanism have to be distinguished. In one of them (the so-called inner-sphere mechanism), major internal rearrangement as well as chemical bond breaking and formation occur in the species, while in the other (the outer-sphere mechanism) only reorganization of the solvent is involved to adapt to the new charge distribution. In the latter case, the solvent plays a primordial role in the reaction kinetics due to the important energetics of electrostatic type between the changing charge distribution in the solutes and the polar solvent.

An outer-sphere mechanism was proposed consisting of four steps: a first step in which the reactants diffuse towards each other to form a precursor

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complex, a second one in which the solvent reorganizes to produce conditions appropriate for the transfer (this step being an activation step), a third one consisting of the actual electron jump from the reactants to the products to form a successor complex, and finally a fourth and last step where the products diffuse apart from each other.

This process can be understood in terms of a two-state diabatic formalism (one in which the states do not diagonalize the Born–Oppenheimer electronic Hamiltonian), where the two states represent the reactants and the products. Within a classical framework, the actual electron transition must occur at the intersection of the diabatic potential energy hypersurfaces of the reactants and products. Such a region is reached by non-equilibrium configurations of the solvent produced by thermal fluctuations. These fluctuations are the origin of the solvent reorganization in the above mechanism.

Marcus proposed that free energies should be used instead of the potential energy. Free energy curves can be defined as functions of a reaction coordinate that can be related to the evolution of solvent orientation. The determination of the activation free energy necessary for the calculation of the reaction rate constant is given, when the free energy curves are assumed to be of a harmonic form and of equal curvature, by the well-known Marcus relation:

$$\Delta A^\ddagger = (\Delta A^\circ + \alpha)^2 / 4\alpha \quad (1)$$

which relates the activation free energy ΔA^\ddagger to the reaction free energy ΔA° and the solvent reorganization energy α .

The development of these theories was based on a classical continuum picture of the solvent (Marcus' choice for the reaction coordinate was the solvent polarization). With the wide availability and use of computers in theoretical studies since the 1980s, which has been the powering force behind the many developments in condensed phase science achieved over the last few years, this subject has regained and even amplified its interest among researchers. With such new fast computational resources and consequent advances in the numerical simulations field, the latest theoretical studies have been directed towards the investigation of the aspects of the reactions at a discrete microscopic level.

The areas that have been explored recently include

quantum-mechanical studies focusing on the electronic jump step and on the evaluation of tunnelling effects [1–7], the study of solvent dynamical effects [8–10] by molecular dynamics simulations, among other techniques, the extension of the existing theories to the understanding of inner-sphere electron transfer reactions [11–13], and the investigation at a microscopic level of the validity of the assumptions made within Marcus' theory framework [14–17]. In particular, this last aspect has caused some controversy. A number of papers have been written concerning the verification of harmonicity and equal curvature assumptions and, therefore, the validity of Marcus' relation. The origin of the deviations from the relation in the so-called inverted region (where $|\Delta A^\circ| > \alpha$) has also been met with some interest.

The aim of this work is to investigate, for the $\text{Cu}^{2+}/\text{Cu}^+$ electron exchange reaction (which is assumed to occur by an outer-sphere mechanism), the role of the solvent when it is treated at a microscopic level by numerical simulation and to compare the results with Marcus' continuum solvent predictions. This work is the first step of an investigation to be carried out in our group. Particular current interest in this reaction is due to recently obtained experimental data [18]. For a long time, such information has not been available owing to the instability of the Cu^+ ion in aqueous solution. Such data will be compared with our results.

The study was performed by Monte Carlo simulations, using an umbrella sampling-like technique, where a mapping potential is used instead of a common potential. This approach is followed to account for the inefficiency of the conventional Monte Carlo sampling, because of the low probability of interesting configurations being near the transition state. The method is described in more detail in the next section. In Section 3, free energy curves are calculated by thermodynamic perturbation and thermodynamic integration, and compared with Marcus' predictions.

2. Model and methods

The Monte Carlo simulations were carried out in the *NVT* ensemble at a temperature of 298 K for a system of 200 water molecules surrounding the redox $\text{Cu}^{2+}/\text{Cu}^+$ pair. The two ions, separated from each other by 7 Å, were placed at the centre of a

rectangular box of dimensions 20 Å along the axis of separation of the ions and 18 × 18 Å in the other directions (these dimensions were chosen in order to obtain a density of unity for the 200 water molecules). In these simulations, the pair was held fixed, and periodic boundary conditions under the minimum image convention were applied. A total of 20 simulations were carried out according to the Metropolis algorithm and in each one 12 × 10⁴ steps (a Monte Carlo step consists of 200 single water random moves) were generated, but only the second half were used for averaging.

Pairwise additive potentials were used to model the interactions in the system. The SPC potential [19] was chosen to describe the water–water interactions. For the ion–water interactions, the ab initio analytical potentials employed were the Cu⁺/H₂O potential determined by Cordeiro et al. [20] and the Cu²⁺/H₂O potential of Curtiss et al. [21].

A coupling parameter, λ, is used to define a mapping potential of the form

$$U_m = (1 - \lambda_m)U_r + \lambda_m U_p \quad (2)$$

which is used as the effective ion–water potential in the simulations. λ is slowly varied in a way that converts the reference system (λ = 0) to the perturbed system (λ = 1). In this case, the reference system is taken as the reactants with potential energy U_r and the perturbed system consists of the products (U_p). It should be noted, however, that given the fact that the reaction is symmetric, λ needs only to be varied from 0 to 0.5.

The parameter λ has been incremented through the simulations according to the formula [22]:

$$\lambda_{i+1} = \frac{1}{2}\{1 + \tanh[(-N/2 + i)W]\} \quad i = 0, N - 1 \quad (3)$$

where N is the total number of simulations. The constant W was given a value of 0.02 which ensured that the free energy changes were very small on the first and last simulations.

The diabatic free energy curves for the reactants and products, ΔA_r and ΔA_p , can be defined as a function of the reaction coordinate x by the following expressions [13,14]:

$$\Delta A_r(x_i) = \Delta A_{r \rightarrow m} - \lambda_m x_i - kT \ln[(q_m^{(x_i)}/Q_m)/(q_r^{(x_i)}/Q_r)] \quad (4)$$

$$\Delta A_p(x_i) = \Delta A_{p \rightarrow m} + (1 - \lambda_m)x_i - kT \times \ln[(q_m^{(x_i)}/Q_m)/(q_p^{(x_i)}/Q_p)] \quad (5)$$

As mentioned before, the reaction coordinate x corresponds to the potential energy difference between products and reactants ($U_p - U_r$).

The last terms of Eqs. (4) and (5) are ratios of partition functions. For instance, the ratio $q_r^{(x_i)}/Q_r$ gives the probability that the configurations generated using the potential U_r belong to the set of reactants. For the reactions considered here, these ratios are approximately unity and thus the last terms containing them can be cancelled.

The free energies $\Delta A_{r \rightarrow m}$ (or $\Delta A_{p \rightarrow m}$) can be calculated by the common thermodynamic perturbation method:

$$\begin{aligned} \Delta A_{r \rightarrow m} &= \Delta A(\lambda_r \rightarrow \lambda_m) = \sum_{i=r}^{N-1} \Delta A(\lambda_i \rightarrow \lambda_{i+1}) \\ &= -kT \sum_{i=r}^{N-1} \ln \left\langle \exp - \left(\frac{U_{i+1} - U_i}{kT} \right) \right\rangle_{\lambda_i} \end{aligned} \quad (6)$$

or the thermodynamic integration method:

$$\Delta A_{r \rightarrow m} = \int_{\lambda_r}^{\lambda_m} \langle U_p - U_r \rangle_{\lambda} d\lambda \quad (7)$$

where $\langle \dots \rangle_{\lambda_i}$ are canonical averages based on the potential U for a particular λ_i .

The averages in each simulation were calculated by the block means method as proposed by Bishop and Frinks [23], with a block size of 600 steps. The statistical errors in the free energy calculations were assumed to have a normal distribution in the simulations. In the thermodynamic perturbation method, these errors were estimated according to Straatsma and McCammon [24]. In the thermodynamic integration method, the trapezoidal integration method was used, for which the statistical errors are estimated as proposed by Pearlman [25].

Although a better estimate of the statistical errors and of hysteresis could have been found with independent forward ($\lambda = 0 \rightarrow \lambda = 1$) and backward ($\lambda = 1 \rightarrow \lambda = 0$) processes, only the forward process was performed. However, in the case of the thermodynamic perturbation method it was possible to obtain simultaneously the free energy change for $\lambda_i \rightarrow \lambda_{i+1}$ and $\lambda_i \rightarrow \lambda_{i-1}$ using the double-wide sampling [26].

The values reported for this method are thus an average of the results of the double-wide sampling for the forward process.

3. Results and discussion

In each simulation corresponding to a definite value of λ , monitoring of the fluctuations of x has been

performed. Fig. 1 displays the distributions of such fluctuations for $\lambda = 0$ and $\lambda = 0.5$.

It is clear from the observation of Fig. 1 that for $\lambda = 0$ the transition state region has an extremely low probability of being reached. Significant probabilities for those configurations appear only for higher values of λ . Therefore, these distributions very clearly illustrate the inefficiency of the conventional sampling and the need for a scheme such as that used in this work.

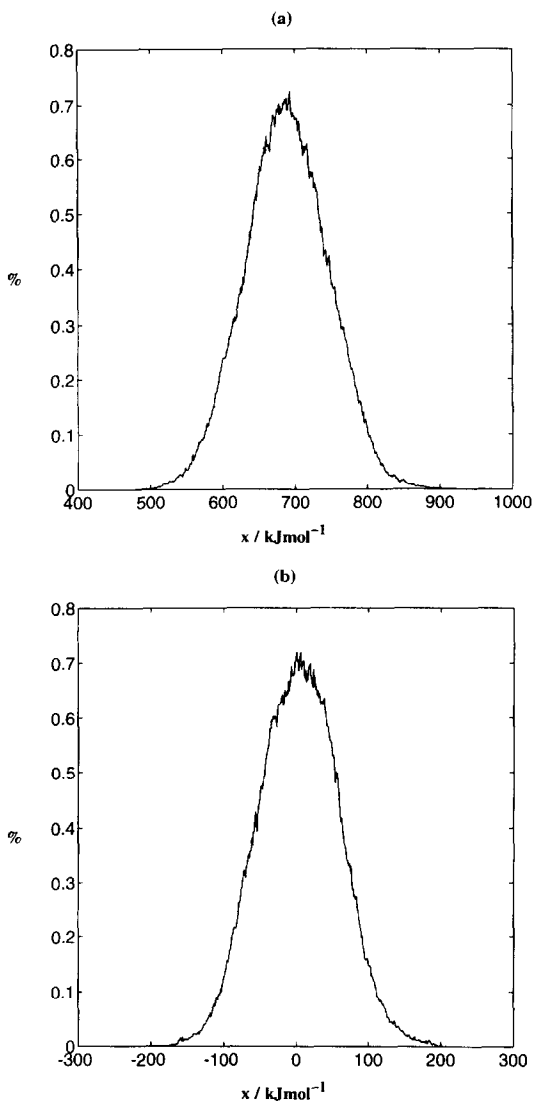


Fig. 1. Distributions of values of $x = U_p - U_r$, obtained during the simulations. (a) refers to the simulation with $\lambda = 0$ and (b) refers to $\lambda = 0.5$.

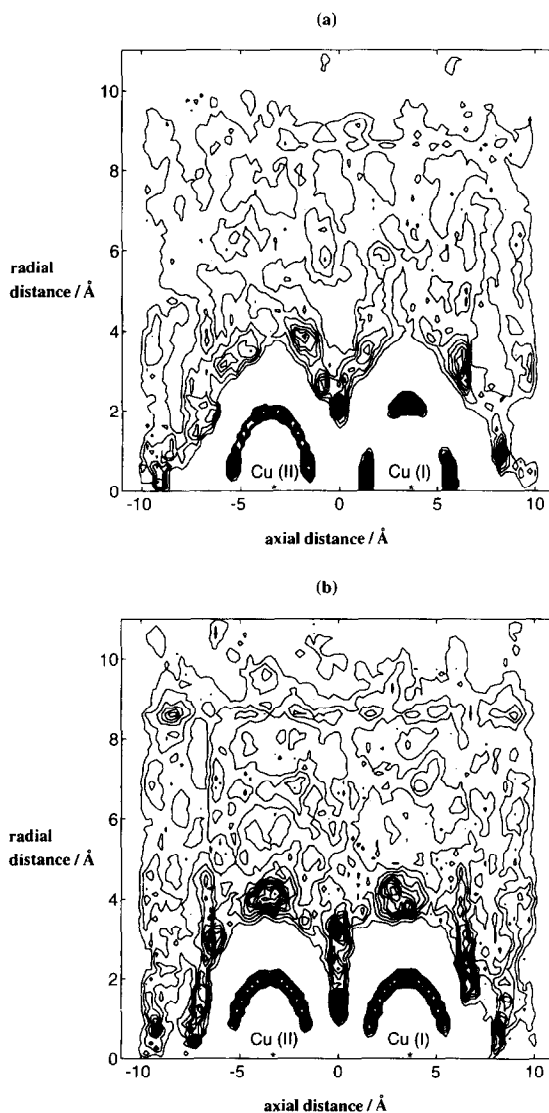


Fig. 2. Contour map of the distribution of the ion-oxygen separation distances during the simulations. (a) refers to the simulation with $\lambda = 0$ and (b) refers to $\lambda = 0.5$.

The evolution along the reaction coordinate x enforces a modification of the solvation geometry. A clear measure of the changes in the solvation structure can be taken from the contour maps of the oxygen distributions at different stages of the simulations ($\lambda = 0$ and $\lambda = 0.5$) as depicted in Fig. 2. These distributions were computed over two distances x and r according to the procedure already used by Clementi et al. [27]. The former is an axial distance identified by the longer axis of the simulation box, and the latter is a radial distance ($r^2 = y^2 + z^2$).

Noticeable features are the shifts in the copper–oxygen distances and the changes in orientation of the first solvation shell on going from the reactants to the transition state. The $\text{Cu}^+ - \text{O}$ distance undergoes a contraction from 2.10 Å ($\lambda = 0$) to 2.00 Å ($\lambda = 0.5$) and the $\text{Cu}^{2+} - \text{O}$ distance experiences an expansion from 1.95 Å ($\lambda = 0$) to 2.00 Å ($\lambda = 0.5$). Also, the solvent shells evolve from a well-defined orientation to a more random one.

In Fig. 3, the free energies $\Delta A_{r \rightarrow m}$ are presented as calculated from eqn (6) by the thermodynamic perturbation method and averaging of the double-wide sampling results. It should be noted that the hysteresis effect was verified as acceptable (in the order of $\approx 10\%$ in the worst cases). From the values reported in Fig. 3, the diabatic free energy curves $\Delta A_r(x)$ and $\Delta A_p(x)$ were computed using Eqs. (4) and (5). These curves are shown in Fig. 4.

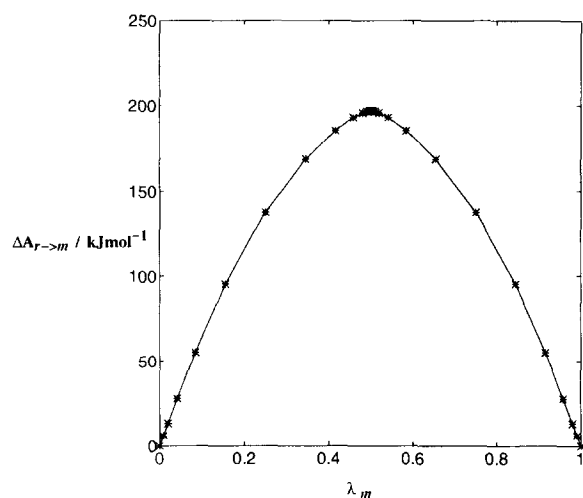


Fig. 3. Free energy as a function of the parameter λ which is varied in the simulations.

The curves appear to have a parabolic shape, as expected if the Marcus relation is obeyed. The activation free energy ΔA^\ddagger for this electron transfer process is $196.9 \pm 7.6 \text{ kJ mol}^{-1}$. A similar value ($196.8 \pm 4.8 \text{ kJ mol}^{-1}$) was obtained by resorting to the thermodynamic integration method. As the free energy of the process is 0 kJ mol^{-1} , the reorganization energy α is predicted by Marcus relationship to be four times bigger than the activation free energy. There is a slight disagreement between our calculations and this prediction (within a 15% margin). Nevertheless, there is room for improvement in the model used here, i.e. the performance of more and longer simulations with independent forward and reverse runs, the inclusion of contributions such as solvent polarization effects, more appropriate potentials which may include non-additive terms, a study of Jahn–Teller effects on inner-shell reorganization and a choice of better ion separation for the $\text{Cu}^{2+}/\text{Cu}^+$ couple. With respect to this last item, it should be emphasized that our choice seems to be reasonable considering the recent work presented by Nagy et al. [28]. Still, a more thorough investigation concerning this aspect could be carried out, for example, by computing the mean force potential between the two copper ions. Studies on these and other related questions are now in progress in our laboratory. Results obtained with improved models will then be

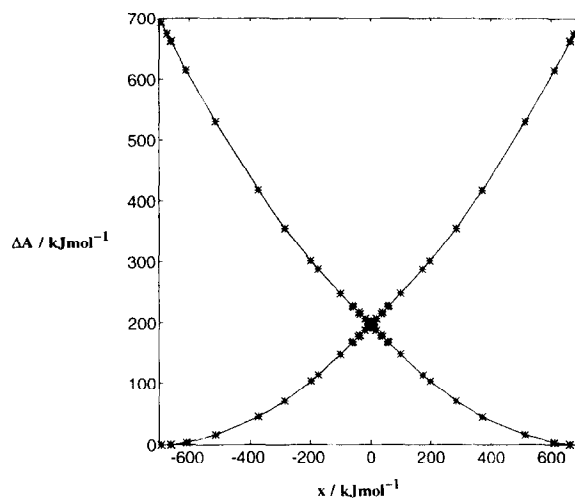


Fig. 4. Free energy curves for reactants and products. From these curves the activation free energy and reorganization energy can be obtained and compared with Marcus' predictions.

compared with the present results to evaluate the importance of the refinements introduced.

Finally, some experimental data available for this reaction should be mentioned here. Stepnik-Swiatek and Malyszko [18] have done some research on this reaction in the last years and have published experimental activation free energies. The comparison between this data and our results is poor (the experimental free energies are four times smaller). However, this fact is not surprising. As mentioned above, there is still some room for improvement of the present model. The most striking factor to be refined is probably the interionic distance, as the activation free energy is strongly dependent on this parameter. It should also be noted that the experimental conditions used, including highly concentrated background electrolytes to stabilize Cu^+ , have a severe influence on the experimental observations and lead to weaker ion–water interactions.

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