



The partial charge transfer

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ABSTRACT

In this review, we will examine the problems related to the chemisorption of molecules on electrodes, where the adsorbate may possibly share its electrons with the metal. The “partial charge transfer” between adsorbate and electrode cannot be measured, since the division of the bonding electrons into parts pertaining to the adsorbate and to the electrode is arbitrary; at most, it can be tentatively estimated on the basis of modelistic considerations. This point will be clearly demonstrated on the basis of simple thermodynamic considerations. A thermodynamically significant and experimentally measurable quantity that has often been conceptually related to partial charge transfer is the “electrosorption valency”. We will discuss methods by which it can be measured, both when only a single species is adsorbed and when its adsorption is accompanied by coadsorption or competitive adsorption with other species. A simple unified modelistic picture will be adopted to illustrate the extra-thermodynamic partial charge transfer coefficient for low surface coverages of ionic and neutral adsorbates and for compact chemisorbed monolayers both in solution and in vacuum. The relation between partial charge transfer coefficient and the dipole moment of the chemisorption bond will be clarified and the estimate of this bond in vacuum by work function or outer potential measurements will be described.

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Contents

1. Preamble	489
2. Introduction	490
3. Thermodynamic considerations	491
4. A modelistic picture of the partial charge transfer coefficient	492
5. The electrosorption valency and the partial charge transfer	493
5.1. Relation between dipole moment and electrosorption valency	496
6. The partial charge transfer at compact chemisorbed monolayers	496
6.1. Adsorbed monolayers involving coadsorption or competitive adsorption with other species	499
7. The partial charge transfer at adsorbed monolayers in vacuum	501
8. Theoretical quantum chemistry and partial charge transfer	502
9. Conclusions	503
Acknowledgements	503
References	503

1. Preamble

Electrochemical reactions involve charge transfer across a metal/solution interface and their kinetics belongs to the heart of

electrochemistry. Therefore, the charge flowing in the elementary act is an important characteristic of an electrode process. For a simple electron- or ion-transfer reaction, this charge is always a multiple of the unit charge: in the former case it is simply the number of electrons exchanged between the reactant and the electrode, in the latter case it is the valence of the ion that is embedded into the electrode. Nonetheless, in an adsorption reaction the adsorbate need not exchange an integral number of electrons with the electrode. Since it resides on the surface, it can share electrons with the electrode, forming a polar or a covalent bond, a phenomenon

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called chemisorption. However, the partial charge transferred by the adsorbate to the electrode is not clearly defined, since the division of the bonding electrons into parts pertaining to the adsorbate and to the electrode is arbitrary to some extent. In spite of this, the amount of charge flowing at constant electric potential can be directly measured, and this quantity is used to define the so-called “electrosorption valency”, in analogy to the valence of a metal ion deposited on an electrode. Two different attitudes towards the electro-sorption valency are normally taken. On the one hand, one can be satisfied with characterizing chemisorption solely by the measurable electro-sorption valency. On the other hand, one can try to relate electro-sorption valency to the charge exchanged between electrode and adsorbate, namely to a “partial charge transfer coefficient”. Unfortunately, the latter cannot be measured and is only defined within a particular model. One can only confine himself to regarding as worthwhile any efforts aiming at estimating partial charge transfer (pct) on the basis of simple modelistic or quantum chemical interpretations of electro-sorption valency and of other more or less directly measurable quantities. A quantity related to pct is the dipole moment associated with an adsorbate. Its definition is based on other concepts than the pct, but the two quantities are related, and one can be expressed through the other.

2. Introduction

When a species S^z is adsorbed at an electrode surface, it may form a purely physical bond (physisorption) or a much stronger chemical bond (chemisorption). Consider an electrode that is initially free of adsorbates and held at the potential of zero charge (pzc), and imagine bringing an adsorbing ion of charge ze to its surface, where e is the absolute value of the electron charge. This will cause a flow of a charge $-ze$ to the electrode surface along the external circuit, to maintain the electroneutrality of the whole interface. The two charges generate a dipole moment m , which can be regarded as a metal-ion purely ionic bond. Note that, both before and after the experiment, the sum of the charges on the metal surface and in the adsorbed species is zero, and hence there is no excess charge in the diffuse part of the double layer. However, after the adsorption has occurred, the electrode surface is no longer at the pzc, since it has taken up a charge in this thought experiment. In an electrolytic solution, the dipole moment of the adsorbed ion tends to align the dipole moments of neighboring solvent molecules in the opposite direction, thereby reducing its magnitude. Therefore, the dipole moment of an ionic species adsorbed from solution tends to be smaller than that for the same species in vacuum. One may envisage this situation as though the adsorbed ion were carrying a charge $(z + \lambda)e$, where λ is a fraction of $-z$, called “partial charge transfer coefficient”. In this case, thanks to the screening by solvent molecules, λ is different from zero even though the bond is purely ionic.

However, λ may also be different from zero if the adsorbing ion and the metal orbitals share electrons, giving rise to a polar or nonpolar covalent bond. The partial charge on an adsorbed species is ill defined, since one has to introduce a plane separating the electronic density into a part belonging to the adsorbed species and one belonging to the metal; obviously, this is not measurable. The notion of partial charge can be understood in terms of quantum-mechanical considerations. To be specific, let us consider the adsorption of a Cs^+ ion at an electrode from an aqueous solution, and assume that the electric potential is in the range where no reactions occur. When the ion is in the bulk of the solution, the valence orbital has a well-defined energy lying above the Fermi level of the electrode; hence the valence orbital is empty. When this ion is adsorbed on the electrode surface, its valence orbital overlaps with the metal orbitals. If we put an electron into the valence orbital

of the adsorbed Cs ion, it has only a finite lifetime τ in this state before it is transferred to the metal; the stronger the interaction, the shorter τ is. According to the Heisenberg uncertainty principle, a finite lifetime τ entails an energy uncertainty $\Delta = \hbar/\tau$. Hence, the valence orbital is broadened and acquires a density of states $\rho(\varepsilon)$ of width Δ , a phenomenon known as “lifetime broadening” and familiar from electronic spectroscopy. This density of states is filled up to the Fermi level of the metal, as shown in Fig. 1. For an adsorbed Cs atom the center of the density of states lies well above the Fermi level E_F , the occupancy n is generally quite small, and the partial charge $z + \lambda = 1 - n$ is close to unity. In contrast, halide ions typically carry a negative excess charge, and the center of the density of states of their valence orbitals lies below or near the Fermi level of the metal [1].

The above view gives rise to the idea of a partial charge transfer during adsorption, which can formally be written as an adsorption reaction:



Here λ is generally a positive or negative fractional number and e^- denotes the negative electronic charge. This process is called a “partial charge transfer” (pct) reaction. We will exclude the case in which a pct step is followed by one or more further pct steps, ultimately resulting in the overall transfer of a unitary charge $|e^-|$ with formation of a redox partner of S^z capable of existing in the bulk solution. The pct coefficient λ was first introduced by Lorenz and Salié [2] in connection with an experimental research on the Tl-amalgam/Tl⁺ ion electrode reaction. The authors recognized [3] that λ cannot be estimated without having recourse to some modelistic assumption [4].

In the framework of a traditional picture of a metal|solution interface, the chemisorption of a species, with or without pct, can be envisaged as follows. Imagine adding, say, a specifically adsorbing anion to a solution containing a strong excess of a nonspecifically adsorbed electrolyte and imagine following its adsorption at the metal/water interface, at constant applied potential. If the anion were itself nonspecifically adsorbed, and hence had not to be deprived of its solvation sheath on the metal side in its position of closest approach to the electrode surface, then it would be accompanied in this approach by a nonspecifically adsorbed cation, and hence no flow of electrons along the external circuit would be observed. This situation is depicted schematically in Fig. 2a, where x is the distance from the electrode surface, and $x = d$ is the distance of closest approach of the nonspecifically adsorbed ions to the electrode. The $x = d$ plane is called the “outer Helmholtz plane”. The potential-distance profile is represented schematically by curve 1.

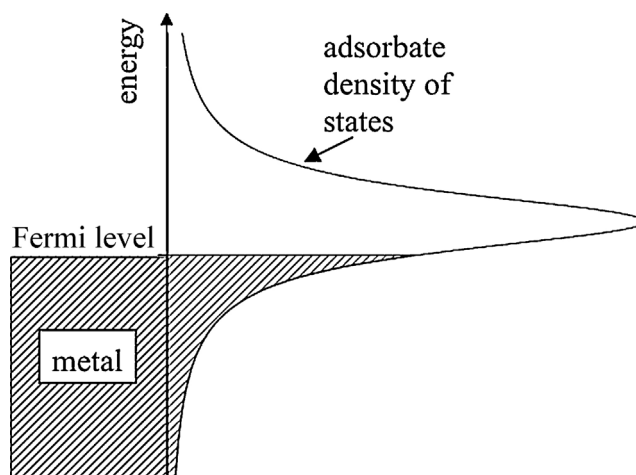


Fig. 1. Density of states of an adsorbed cation (schematic).

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