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Review

Electrostatic interactions within mixed-valent compounds

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ABSTRACT

The electrochemical properties of bi- and multi-metallic compounds are a convolution of several factors, among which through-bond electron transfer and through-space electrostatic features are the most prominent. Whereas optical and vibrational properties, and to a growing extent computational studies, are able to probe the 'electronic coupling' aspects of the interactions, determining the extent of electrostatic interaction requires careful experimental and comparative studies. This review highlights the methods that can be used to identify and assess, at least qualitatively, the nature of the often less well explored electrostatic contributions to the electrochemical behavior of such multiredox systems. Therefore, advances in finding reliable models for intramolecular electrostatic interactions are recapitulated. In addition, inter- and intra-molecular influences on the electrostatic properties as well as the exploitation of different ion-pairing capabilities of various electrolytes in order to gain information on electrostatic repulsion energies are discussed.

Contents

1. Introduction

According to the classification system introduced by Robin and Day, mixed-valent species may be grouped into one of three broad classes, depending on the extent of charge transfer or delocalization [1,2]. The strength of electronic interaction between the oxidized and reduced sites ranges from essentially zero (class I) to weak or moderate (localized valence, class II) to very strong electronic coupling (delocalized valence, class III) [1–9]. For a moderately coupled class II bimetallic compound, the mixed-valence situation is described by the equilibrium between two ground states involving valence-trapped systems in which an electron transfer from M to M′ and vice versa occurs (Scheme 1). The accessibility of the charge delocalized excited state allows the occurrence of the intervalence charge transfer (IVCT), *i. e.* a metal-to-metal charge transfer (MMCT) [9].

For a delocalized, class III bimetallic system there is no thermal barrier to the electron transfer and the two metal ions hold formally an averaged oxidation state in the ground state, that is, for example, “2.5” for a mono-oxidized bis-iron complex [1–9]. Therefore, the situation is to be described as resonance between two mesomeric structures (Scheme 2).

In order to classify the strength of electron transfer within mixed-valent species, several spectroscopic and electrochemical techniques have been used including cyclic voltammetry [10,11], polarography [12,13], X-ray structure analysis [14], ^{57}Fe Mössbauer- [15,16], ESR- [17,18] and VT-NMR-spectroscopy

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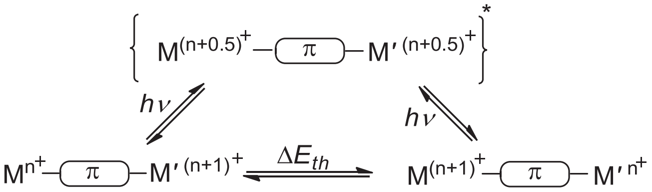
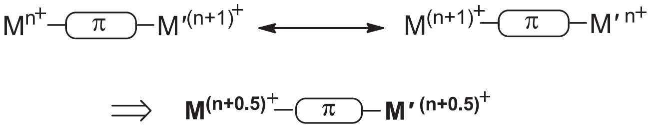


Scheme 1. Class II electron transfer is induced thermally (ΔE_{th}) or photochemically ($h\nu$); M and M′ represent the redox-active units (foremost metals) with M = M′ or M ≠ M′, which are connected by a π-conjugated bridging system [9].



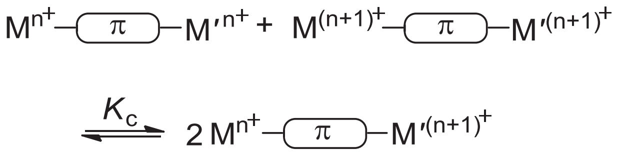
Scheme 2. Class III equals a full resonanz description [9]. M and M′ represent the redox-active units (foremost metals) with M = M′ or M ≠ M′, which are connected by a π-conjugated bridging system.

[19,20], photoelectron spectroscopy, [21] and IR- [22] as well as UV–Vis/NIR spectroscopy [23–26]. Most of these analytical methods aim to detect physical differences for the redox sites being in different oxidation states and/ or electron transfer rates by determining dynamic changes of the respective properties [14–22,27,28]. The photophysically induced electron transfer between the redox-active sites is detectable as a broad weak band (for class II systems) in the Vis/NIR region of the electromagnetic spectrum and hence the spectroscopic characterization of IVCT bands, or more broadly the low energy optical transitions emerges as one of the most powerful tools in mixed-valence chemistry.

Electrochemical methods on the other hand serve to determine the thermodynamic stability of the mixed-valent oxidation state towards disproportionation to the respective neighboring homovalent states (Scheme 3). The comproportionation constant K_c can directly be determined from the difference of the 1st and 2nd oxidation process (henceforth, redox splitting $\Delta E^{o\prime}$) in a bimetallic compound (Eq. (1)).

$$\ln K_c = \ln\left\{\frac{\left[M_2^{(2n+1)^+}\right]^2}{\left[M_2^{(2n)^+}\right]\left[M_2^{(2n+2)^+}\right]}\right\} = -\frac{\Delta G_c^o}{RT} = \frac{\Delta E^{o\prime}\cdot F}{RT} \tag{1}$$

The free energy of comproportionation ΔG_c° consist of five main contributors: (i) the statistical term ΔG_s° = –RT/F·ln4 ≈ 36 mV at 25 °C, (ii) the inductive factor ΔG_i° due to metal–ligand back bonding interactions, (iii) the magnetic exchange energy ΔG_m°, (iv) the free energy of resonance stabilization ΔG_r°, which can be calculated from the physical parameter of the IVCT band, and (v) the electrostatic factor ΔG_e° arising from the repulsion of the two similarly charged metal ions linked by the bridging ligand (Eq. (2)) [9]. The magnetic exchange term and the inductive factor are in general discussed to be very small (<10 mV), while ΔG_r° and ΔG_e° dominate the electrochemical properties of mixed bi- or multimetallic complexes [9,10,28,29].



Scheme 3. Comproportionation equilibrium of two homovalent compounds $M_2^{(2n)+}$ and $M_2^{(2n+2)+}$ to the appropriate mixed-valent species ($M_2^{(2n+1)+}$) with M = M′ or M ≠ M′, which are connected by a π-conjugated bridging system.

$$\Delta E^{o\prime} = -\Delta G_c^o/F = -(\Delta G_s^o + \Delta G_i^o + \Delta G_m^o + \Delta G_r^o + \Delta G_e^o)/F \tag{2}$$

In recent years, the electron transfer interactions (as reflected by ΔG_r°) of redox-active centers within mixed-valent species have been thoroughly discussed [30–40]. While the analysis of mixed valent compounds *via* electrochemical measurements is wide spread and often the redox sepatation $\Delta E^{o\prime}$ is used as an indication for electronic coupling, it has been pointed out that the electrochemical results not always correlate with the electron transfer strength [10,41]. One of the reasons for non-correlated electrochemical behavior, especially in small, weakly to moderately coupled mixed valent systems, is that the electrostatic features have a considerably large impact on the electrochemical measurements [10,29,42]. Hence, this review aims to discuss electrostatic features within mixed-valent compounds, to show different approaches in electrostatic modelling and to demonstrate how inter- and intramolecular influences modify the electrostatic properties of analytes. It also highlights how to assess electrochemical interactions experimentally.

2. Electrostatic modeling

The first attempt to calculate the repulsive electrostatic stabilization energy for mixed-valent compounds, in order to determine their contribution to the overall wave splitting within electrochemical measurements, was made by Henry Taube, James Sutton and Patrick Sutton in 1979 [43]. They calculated the energy of bringing two point charges in a continuous dielectric medium to a distance equivalent to the metal–metal proximity within the bimetallic complex [μ-(4,4′-bipyridyl)-bis(pentaammineruthenium)]$^{5+}$ ([**1**]$^{5+}$). The energy they approximated was calculated by using an equation which was derived from Coulomb repulsion (Eq. 3), whereas Z_1 and Z_2 represent the charge at each of the ruthenium ions; e is the elementary charge, ε_0 the vacuum permittivity, ε_r the relative permittivity of the medium (water = 80), r the distance between the metal ions (10.8 Å), N_A Avogadro's number, I the ionic strength (0.1 mol/L), k_B the Boltzmann constant and T the temperature.

$$\Delta G_e^o = \frac{1}{4\pi\varepsilon_0\varepsilon_r}\frac{Z_1Z_2e^2}{r(1+\kappa r)} \tag{3.1}$$

$$\kappa = \sqrt{2000\frac{N_Ae^2I}{\varepsilon_0\varepsilon_rk_BT}} \tag{3.2}$$

For water as a solvent with a high dielectric permittivity Taube and Sutton estimated the contribution of the electrostatic repulsion to the overall redox splitting to be approx. 23 mV [43], however, using the same equation the contribution in dichloromethane solutions amounts to ≈100 mV (Fig. 1).

In order to refine their estimates and account for the low permitivity of the 4,4′-bipyridyl bridging unit in [**1**]$^{5+}$, Taube and Sutton adopted the ellipsoidal cavity field effect model as formulated by Ehrenson a few years earlier [44]. Working on estimates for the p*K*a values of diprotonic organic acids, Ehrenson studied the influence of electrostatic interactions within these systems on the acidity. He modified the early work on spherical field effect models of Kirkwood [45–47], Bjerrum [48], Eucken [49] and generalized it in order to account for actual molecule geometries. Within this model the reactive species was put in an ellipsoid with the molecular volume defining the volume of the ellipsoid cavity. Within the cavity a low dielectric constant is used to account for the unpolar organic nature of the molecules, while outside the cavity a medium of a higher dielectric constant was chosen in accordance to the surrounding electrolyte. On the example of a series of diprotonic acides (HO_2C-$(CH_2)_n$-CO_2H, n = 2–12) Ehrenson demonstrated that