Influence of the intra- and intermolecular hydrogen bonds on the redox properties of aminoanthraquinone derivatives

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Non-covalent interactions play a critical role in mediating a range of biological electron-transfer (ET) processes. While subject to considerable theoretical and experimental scrutiny, the fundamental principles of how such interactions might serve to modulate ET reactions remain recondite. Quinones are very important redox species that have played an important role in organic chemistry, electrochemistry, and other fields, including biochemistry where quinones take part in important processes such as respiration and photosynthesis. For this reason we have chosen to study simple model systems that would allow the underlying chemical and electrochemical events to be probed with precision. In this context, particular attention has been focused on chemical systems exhibiting intramolecular and intermolecular hydrogen bonding.

The molecules studied in this work, viz. 1-aminoanthraquinone (1-AAQ), 1,4-aminoanthraquinone (1,4-DAAQ), 1,5-diaminoanthraquinone (1,5-DAAQ) and 1,4,5,8-tetraaminoanthraquinone (1,4,5,8-TAAQ), belong to the anthraquinone family. These compounds exhibit intramolecular hydrogen bonds. In this work we will present the results of a full investigation of the mechanism of the electrochemical reduction of these anthraquinone derivatives in acetonitrile. In aprotic media the reduction of quinones occurs in two well-resolved steps forming first the radical anion, Q^{-}, and, at more negative potentials, the dianion,Q^{2-}. The introduction of amine as substituants on the anthraquinone system causes a shift in the reduction potential to a more negative value compared to that of the parent molecule. This behaviour can be explained by considering two separate electronic effects of the amino substituants. First, the inductive electron-withdrawing effect of the nitrogen atom which renders (if operate alone) reduction of aminoanthraquinone easier that reduction of anthraquinone itself. Second, the resonance effect is generally predominant and results in delocalisation of the lone pair of electrons of the nitrogen atom over the enone system of the quinone nucleus. This delocalisation requires that the amino substituents can adopt a specific conformation. In the presence of the intentionally added hydrogen donor, methanol, it is shown that the interaction of the basic anion and dianion of these quinone, leads to the formation of a hydrogen-bonded complex. This is manifested by positive shifts in the reversible potentials for one or both of the reduction steps.