Do standard potential differences measure the 'communication' between identical redox centers separated by a conjugated chain? Application to carotenoids

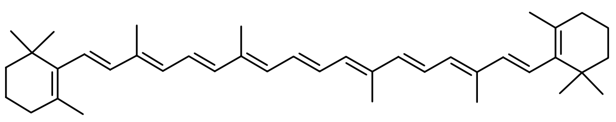
Valery Konovalov,[1] Philippe Hapiot,[2] Lowell Kispert,[3] and Jean-Michel Savéant [2]
[1] University of Alabama at Birmingham
Department of Physics, Box 1170
Birmingham, AL 35294, USA.
[2] Université de Paris 7 - Denis Diderot
2, place Jussieu
75251 Paris Cedex 05, France.
[3] University of Alabama
Department of Chemistry, Box 870336
Tuscaloosa, AL 35486, USA.

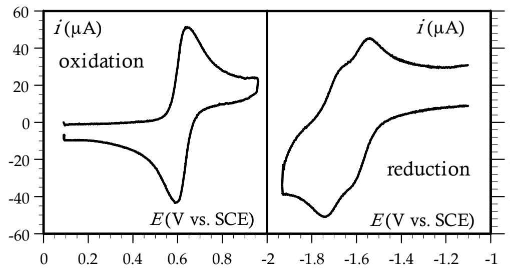
When two identical redox centers are separated by a saturated chain, the distance between their standard potential rapidly decreases as the chain length diminishes along with the decrease of the coulombic repulsion in the di-ion. When this has become negligible, the standard potential difference is:

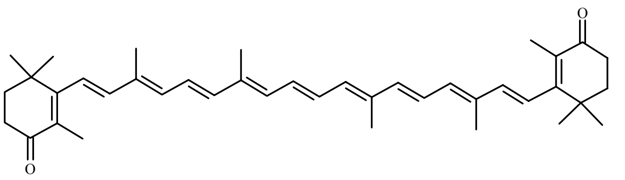
$$E_1^0 - E_2^0 = (RT/F)\ln 4$$

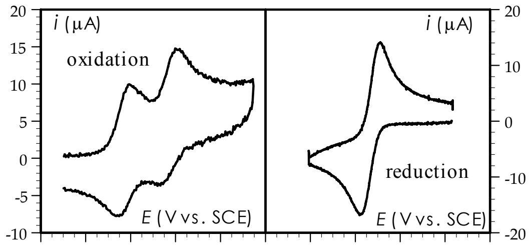
corresponding to a disproportionation equilibrium constant of the ion radical of 0.25. The cyclic voltammetric response is then exactly twice that of reversible one-electron system.

The replacement of the saturated chain by a conjugated chain of the same length is often considered to result in a separation of the two waves caused by the resonance stabilization of the intermediate ion radical, thus measuring the 'communication' between the two centers. This behavior is in fact not met in practice as typically exemplified by the cyclic voltammetric behavior of the carotenoids shown below. Carotene exhibits clear standard potential inversion upon oxidation whereas canthaxantin shows the same phenomenon upon reduction.

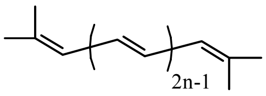


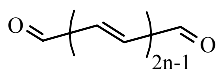






The factors that favor standard potential inversion are investigated by means of quantum chemical (*ab initio* and density functional) calculations on carotene and canthaxantin, and also, on model compounds, in which the various intervening factors are examined as a function of the length of the conjugated chain.





The main factors that control the standard potential inversion are as follows.

One is the weakening of the coulombic repulsion brought about by the localization of the two charges of the di-ion at the ends of the molecules, at a large distance from one another. Charge localization is favored by a good reducibility or oxidizability of the terminal groups in the case of reductions or oxidations, respectively. This is the reason that carotene shows potential inversion in oxidation and not in reduction whereas the behavior of canthaxantin is exactly the opposite (localization of the negative charges on the oxygens of the terminal carbonyls).

The same factor is also responsible for the effect of solvation playing in favor of potential inversion. Localization of the charges in the di-ion indeed contributes to its stabilization by interaction with the solvent. In addition, the delocalization of the charge over the whole molecular framework in the ion radical plays against its stabilization by interaction with the solvent. It is the combination of these two solvation effects that leads to potential inversion as opposed to the case where the two redox centers are linked by a saturated bridge where potential inversion cannot occur

A third, more minor factor is the structural change taking place upon electron transfer, particularly the fact that double bonds become single bonds and vice versa when going from the neutral species to the di-ion.