# CALCULATION OF REDUCTION/OXIDATION POTENTIAL WITH COSMOTHERM

Whitepaper

Accurate reduction and oxidation potentials can be obtained by COSMOtherm by computation of the free energy of solvation in the respective solvent and the adiabatic ionization potentials or electron affinities in the gas phase. The workflow is similar to the usual COSMOtherm workflow for chemical reactions taking place in solution and may be computed with the help of the reaction panel.

INTRODUCTION

Redox potentials, i.e. oxidation and reduction potentials can be easily obtained by incorporation of solvation effects into the (adiabatic) ionization potential (AIP) and electron affinity (AEA), respectively. Taking furthermore into account the free energy of hydrogen reduction (-4.44 eV) versus the Normal Hydrogen Electrode (E vs. NHE):

$$H+_{(s)} + e^- \rightarrow 0.5\ H_{2(g)}\ \Delta G° = -4.44 eV$$
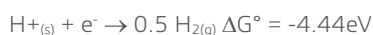
one obtains the oxiation potential for a compound M:

$$E°_{ox}(vs.\ NHE) = \Delta G(M \rightarrow M^{+*})_{(s)} -4.44 eV =$$
$$= \Delta G_{solv}^{ion} - \Delta G_{solv}^{neutral} + AIP - 4.44 eV$$

This is equivalent to using a thermodynamic cycle of the following kind, where the free energy $\Delta G(M \rightarrow M^{+*})_{(s)}$ is split up into a term due to adiabatic ionization and a solvation term $\Delta G_{solvation}$ (Scheme 1).
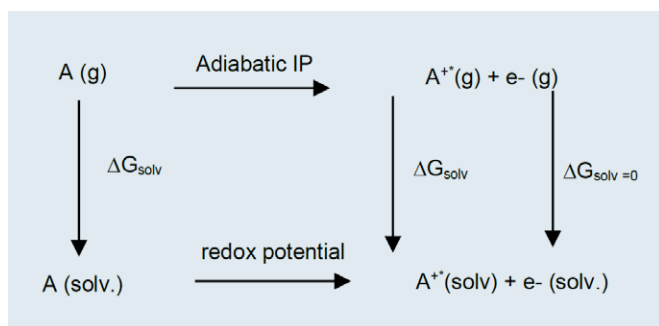
Scheme 1: Thermodynamic cycle for the oxidation potential in solution. The subsequent reduction of hydrogen gives an additional free energy term of -4.44 eV. [1]

The advantage of such an approach is that the gas phase ionization part and the solvation part can be obtained by different theoretical methods. The ionization energy can be calculated by density functional methods or highly correlated quantum mechanical approaches, depending on the system size. The solvation part can be obtained with high accuracy by COSMO-RS. The entropic change for the ionization step can usually be neglected. In order to obtain a good first estimate it is most often sufficient to use the TZVP level for solvation and gas phase, e.g.by simply using the reaction panel in COSMOtherm.

Of course, this simple approach cannot take into account a subsequent reaction or degradation reaction following the ionization process, which will significantly change the measured redox potential.

Computational Details

The screening charge densities for COSMOtherm calculations were generated by the Turbomole package V6.3 using the BP86 density functional with a TZVP basis set (BP-TZVP- COSMO level of theory). The Free energy of solvation at the molar framework [1 L gas over 1 L solvent] has been obtained using COSMOtherm, Release 1201 using the BPTZVP_C30_1201.ctd parameterization. The adiabatic ionization potential has been obtained from gas phase optimizations of the neutral and ionic compound at the BP-TZVP level of theory. Those structures can be used also for the computation of the free energy of solvation, i.e. it is not recommended to use the COSMOtherm-estimate for the gas phase energies of the

Oxidation and Reduction Potentials of Fluorescent Organic Dyes

For a set of several organic dyes the oxidation and the reduction potentials in the solvent acetonitrile have been computed with COSMOtherm, according to the steps outlined above. For each structure, i.e. neutral compound, cation and anion the gasphase and COSMO files have to be computed. The experimental data has been taken from Crespo et al.[5] The overall RMSE for the oxidation potentials amounts to RMSE = 0.17 V (3.93 kcal/mol). For the reduction potentials one obtains RMSE= 0.09 V (2.15 kcal/mol).
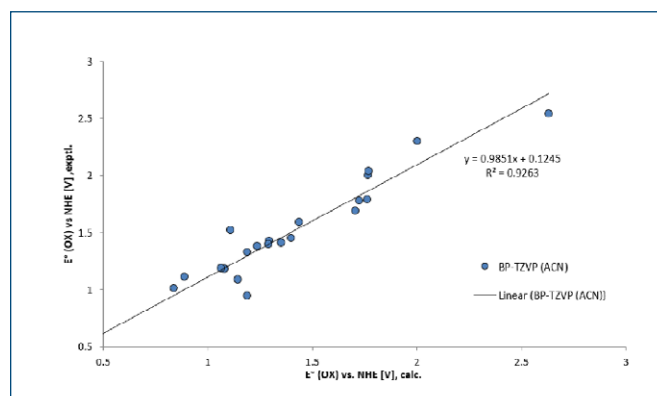

Figure 1: Predicted versus experimental oxidation potentials in acetontrile (E° (OX) vs. NHE [V] in AcN)

system	ΔG_{solv} [eV]	ΔG_{solv}^{ion} [eV]	AIP [eV]	E°/V	E°/V, exp
acenaphthene	-0.3338	-1.9056	7.41	1.40	1.45
benzene	-0.1767	-2.2907	9.19	2.63	2.54
anthracene	-0.4218	-1.9006	7.11	1.19	1.33
azulene	-0.3099	-2.0109	7.33	1.19	0.95
benzo(a)pyrene	-0.5853	-1.8621	6.80	1.08	1.18
fluoranthene	-0.4774	-1.8817	7.55	1.70	1.69
chrysene	-0.5495	-1.8785	7.21	1.44	1.59
anisole (methoxy-benzene)	-0.2634	-2.0909	8.03	1.77	2
dibenz_a_h_anthracene	-0.6715	-1.8742	6.94	1.30	1.43
Benzaldehyde	-0.3007	-2.2788	9.13	2.71	-
napthalene	-0.3003	-2.0250	7.89	1.73	1.78
Perylene	-0.5995	-1.6697	6.65	1.14	1.09
Pyrene	-0.4606	-1.8880	7.16	1.29	1.4
Tetracene	-0.5426	-1.8472	6.58	0.84	1.01
Triphenylene	-0.5527	-1.8888	7.54	1.76	1.79
4,4-dimethoxy-Benzophenone	-0.6830	-1.8935	7.48	1.83	-
4,4-dimethyl-Benzophenone	-0.5257	-1.8456	7.96	2.20	-
Carbostyryl-124	-0.7566	-2.4890	7.24	1.06	1.19
Coumarin-102	-0.6767	-2.0907	6.74	0.89	1.11
Coumarin-120	-0.6951	-2.4949	7.48	1.24	1.38
Coumarin-307	-0.5947	-2.2568	7.45	1.35	1.41
3-Cyano-7-methoxy-Coumarin	-0.7286	-2.5337	8.25	2.00	2.3
7-methoxy-Coumarin	-0.5413	-2.2579	7.93	1.77	2.04
1,5-dimethoxy-Naphthalene	-0.4658	-1.8156	6.90	1.11	1.52
2,4-dimethoxy-N,N-dimethylaniline	-0.4132	-1.7737	6.27	0.47	0.51
3,4-dimethoxy-N,N-dimethylaniline	-0.4575	-1.8370	6.20	0.38	0.44

Table 1: Predicted versus experimental oxidation potentials in acetonitrile. Computed free energies of solvation for neutral compounds and cations and adiabatic ionization potentials.
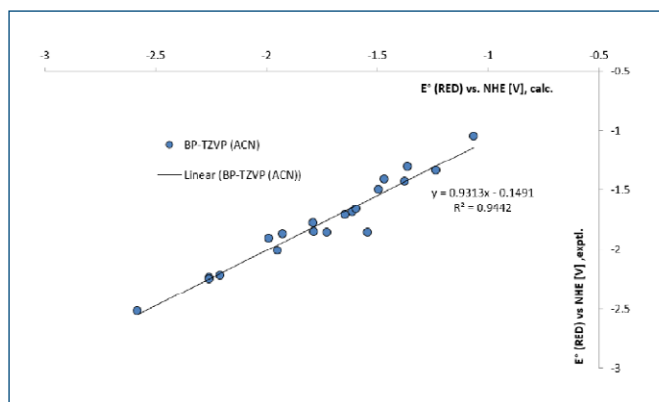

Figure 2: Predicted versus experimental reduction potentials in acetontrile (E° (RED) vs. NHE [V] in AcN)

system	ΔG_{solv} [eV]	ΔG_{solv}^{ion} [eV]	AEA [eV]	E°/V	E°/V, exp
acenapthene	-0.3338	-2.5437	-0.23	-2.46	n.d.
2,4-dimethoxy-N,N-dimethylaniline	-0.4132	-2.6675	-1.18	-3.37	n.d.
3,4-dimethoxy-N,N-dimethylaniline	-0.4575	-2.6607	-1.17	-3.40	n.d.
anthracene	-0.4218	-2.4817	0.74	-1.64	-1.71
azuelene	-0.3099	-2.5739	0.71	-1.47	-1.41
benzaldehyde	-0.3007	-2.5911	0.54	-1.61	-1.69
benzene	-0.1767	-2.7207	-1.28	-3.18	n.d.
methoxy-benzene (anisole)	-0.2634	-2.7453	-1.20	-3.16	n.d.
benzo[a]pyrene	-0.5853	-2.4893	0.99	-1.54	-1.86
4,4-dimethoxy-Benzophenone	-0.6826	-2.7634	0.57	-1.79	-1.78
4,4-dimethyl-Benzophenone	-0.5256	-2.6002	0.77	-1.60	-1.66
Carbostyryl-124	-0.7566	-2.7466	0.19	-2.26	-2.24
chrysene	-0.5495	-2.4876	0.55	-1.95	-2.01
Coumarin-102	-0.6767	-2.7045	0.42	-1.99	-1.91
Coumarin-120	-0.6951	-2.7356	0.47	-1.93	-1.87
Coumarin-307	-0.5947	-2.5869	1.08	-1.36	-1.31
3-Cyano-7-methoxy-Coumarin	-0.7286	-2.5745	1.53	-1.07	-1.05
dibenz__a_h_anthracene	-0.6715	-2.5091	0.87	-1.73	-1.86
fluoranthene	-0.4774	-2.5125	0.91	-1.49	-1.5
napthalene	-0.3003	-2.5608	-0.08	-2.26	-2.25
1,5-dimethoxy-Naphthalene	-0.4658	-2.7179	-0.39	-2.58	-2.52
Perylene	-0.5995	-2.5016	1.16	-1.38	-1.43
Pyrene	-0.4606	-2.4939	0.62	-1.79	-1.85
Tetracene	-0.5426	-2.4532	1.29	-1.24	-1.34
Triphenylene	-0.5527	-2.5218	0.26	-2.21	-2.22

Table 2: Predicted versus experimental reduction potentials in acetonitrile. Computed free energies of solvation for neutral compounds and anions and adiabatic electron affinities.

OXIDATION POTENTIALS FOR RUTHENIUM BASED DYES USED IN DYE SENSITIZED SOLAR CELLS

For a set of ruthenium complexes that have been tested or used in dye sensitized solar cells (Grätzel cells) the oxidation potentials have been computed according to the protocol outlined above. The overall root mean squared error amounts to RMSE = 0.2 V (4.62 kcal/mol).
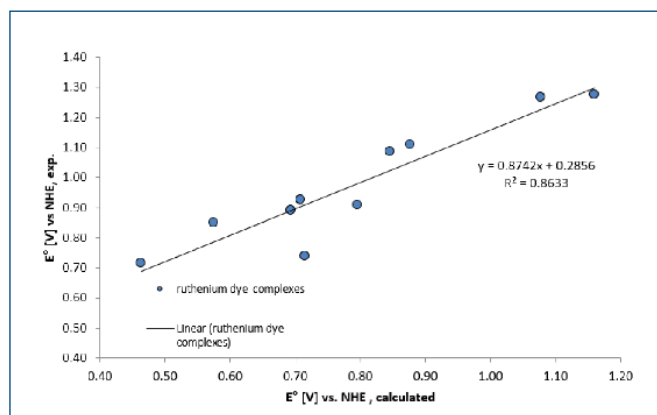

Figure 3: Computed versus experimental oxidation potentials for some ruthenium complexes used in dye sensitized solar cells.

compound solvent	solvent	ΔG/eV	E°/V	E°/V, exp	Lit. source
Ru(bpy)2(C2N2S2)[(1)]	DMF	4.90	0.46	0.72	McCall et al. Journal of Photochemistry and Photobiology A : Chemistry, 202(2-3). 196.
Ru(decbpy)2(C2N2S2)[(2)]	DMF	5.15	0.71	0.93	McCall et al. Journal of Photochemistry and Photobiology A : Chemistry, 202(2-3). 196.
Ru(dcbpy)2(C2N2S2)[(3)]	DMF	5.24	0.80	0.91	McCall et al. Journal of Photochemistry and Photobiology A : Chemistry, 202(2-3). 196.
Ru(bpy)2(S2COEt)+	DMF	5.29	0.85	1.09	McCall et al. Journal of Photochemistry and Photobiology A : Chemistry, 202(2-3). 196.
Ru(decbpy)2(S2COEt)+	DMF	5.52	1.08	1.27	McCall et al. Journal of Photochemistry and Photobiology A : Chemistry, 202(2-3). 196.
Ru(dcbpy)2(S2COEt)+	DMF	5.60	1.16	1.28	McCall et al. Journal of Photochemistry and Photobiology A : Chemistry, 202(2-3). 196.
N719	DMF	5.13	0.69	0.89	Lu et al. Inorg. Chem. 2011, 50, 4289.
Z907	DMF	5.16	0.72	0.74	Lu et al. Inorg. Chem. 2011, 50, 4289.
N3	ACN	5.32	0.876	1.11	McEvoy, Markart, Castaner, Practical Handbook of Photovoltaics: Fundamentals and Applications, academic press, waltham, USA, 2012.
Ru(bipy)3	ACN	5.01	0.575	0.85	Glazier et al., Macromolecules 2003, 36, 1272-1278

Table 3: . Computed and experimental oxidation potentials for some ruthenium complexes used in Grätzel cells.

OXIDATION POTENTIALS FOR THE DATA SET OF AREY AND CO-WORKERS

Arey and co-workers[2] report in their work on the prediction of oxidation potentials of organic compounds in water a somewhat wrong slope of the size ~0.62 (i.e. for the regression of predicted versus experimental data). This finding is quite similar to the "slope problem" found for predicted pKa-values versus experimental pKa-values with quantum chemical based solvation models.[3] For pKa-prediction the slope is somewhat closer to 1 if explicit solvent molecules are incorporated into the model (cluster-continuum approach).[4] The slope is also closer to the expected value of 1.0 in non-aqueous solvents, as for the predictions of the aromatic dyes reported above. In addition, the better predictions may be due to the stronger charge delocalization of the respective radical cations and ions and hence a somewhat better description of the ΔG_{solv} term for the ions.
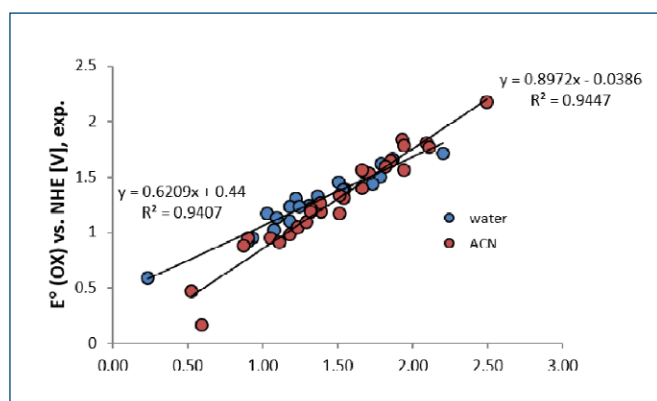

Figure 4: Predicted oxidation potentials for the dataset of Arey and co-workers in water and in acetontrile. The regression versus the experimental data shows a similar "slope problem" as it is known for the prediction of pKa-values, though the slope in acetonitrile being significantly closer to 1.0.
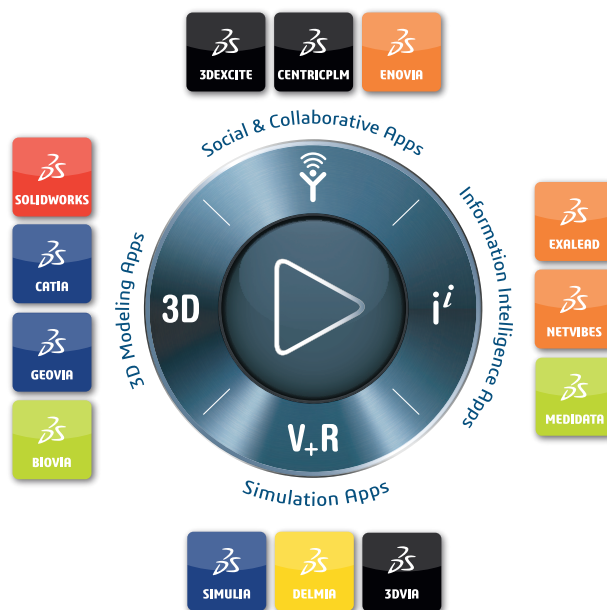
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