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Two Parameter Donor—Acceptor Approach to Solvent Effects on the Electrode Kinetics of Cations

Short Communication

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A two parameter approach to solvent variations in the electroreduction rate constants of cobalt complexes and europium cations is presented and discussed in terms of solvent—solute and solvent—solvent interactions.

(Keywords: Cobalt complexes; Electrochemistry; Electrode kinetics; Europium cation; Solvent effects)

Ein Zwei-Parameter Donor—Acceptor-Ansatz für Lösungsmitteleffekte bei der Elektrodenkinetik von Kationen (Kurze Mitteilung)

Es wird eine Zwei-Parameter-Annäherung der Lösungsmitteleinflüsse auf die Geschwindigkeitskonstanten der Elektroreduktion von Kobalt-Komplexen und Europium-Kationen präsentiert und auf der Basis von Lösungsmittel—gelöster Stoff- und Lösungsmittel—Lösungsmittel-Wechselwirkung diskutiert.

The modern theory of heterogeneous electron transfer[1] predicts that the rate of such a process should depend on the nature of the solvent which is treated as a uniform dielectric continuum. However, no agreement with the experimental results has been observed[2,3]. On the other hand the importance of the short range donor-acceptor interactions in the solvent effects was realized in the last years[4], especially for solvents with a higher dielectric constant[5,6]. The application of the simple equation—similar to the one proposed by *Krygowski* and *Fawcett*[7] but using the *Gutmann* donor number *DN*[8] (from Refs.[4,9]) and the *Mayer* et al.[10] acceptor number *AN*—to the literature data of the electrode kinetics is given in this communication.

The full equation:

$$G = a_D DN + b_A AN + c \tag{1}$$

was used if the addition of the second parameter is statistically significant at $\alpha = 0.05$ (c.f. the values of the F_{imp} test, according to Ref.[11], given in Table 1).

The application of eqn. (1) to the double-layer corrected rate constants $\ln k_{corr}$ (extracted from Ref.[2]) for the electroreduction via the outer-sphere mechanism of the three cobalt complexes is given in Table 1. The observed solvent effect is reproduced quite well (94–98%) and depends on both *DN* and *AN*. The constants a_D are negative as can be predicted from the fact that higher donicity means a greater increase in the stabilization of the form *Ox* compared to *Red*. The contribution from *AN* is slightly greater and the constants b_A are positive. In order to understand this observation the entropy changes will be considered. *Sahami* and *Weaver*[12] measured the reaction entropy ΔS°_{rc} (i.e. the entropic contribution to the formal potentials) for $Co\,(en)_3^{3+}$ in different solvents and found[2] that these values correlate with the variations in the intrinsic free energy of activation. The changes in ΔS°_{rc} can explain 83% of the variations in $\ln k_{corr}$. Moreover, the *Criss* and *Salomon* parameter a[13,14] was choosen as a measure of the reaction entropies[12]. But there are no significant correlations between $\ln k_{corr}$ and the *Criss* parameter. Moreover, the two parameter correlations with *DN* added are much weaker [$R = 0.899$, 0.939 and 0.803 for $Co\,(en)_3^{3+}$, $Co\,(NH_3)_6^{3+}$ and $Co(NH_3)_5F^{3+}$, respectively].

It was suggested[7] that the entropy change may be approximately linear to the acidity function, particularly for the highly structured H-bonded solvents. And indeed the application of eqn. (1) to the reaction entropies from Ref.[12], presented in Table 1, gives in all cases better results than obtainable by use of the *Criss* parameter. This indicates that the donor—acceptor approach is satisfactory at least for the considered solvents which are most usual in electrochemistry. The reaction entropy should depend on two factors (in analogy to the ionic entropy[13,14]): the first one is determined by the reorientation of the solvent in the field of a complex and could be represented by the solvent—solute interactions and the second is described by the disruption of the original solvent structure. Since not the absolute value of entropy but its change between the *Ox* and *Red* states is considered, the strength of the solvent—solvent interactions determining the easyness of disrupture of the solvent structure should be taken into account and not the *Criss* parameter expressing the degree of internal order. The observed correlations of ΔS°_{rc} indicate that the short range specific interactions can express the change not only in the solvent—solute but also in the

Table 1. *Application of eqn. (1) to electroreduction data*

Ox[a]	n[b]	a_D	b_A	c	R[c]	% *DN*[d]	% *AN*[d]	$1-R^2$	F_{calc}[e]	F_{imp}^{calc}	F_{imp}^{tab}
Corrected rate constant $\ln k_{corr}$ from Ref.[2]											
$Co(en)_3^{3+}$	7	−0.254	0.150	−6.59	0.968	39.6	54.1	6.3	29.6	17.7	7.71
$Co(NH_3)_6^{3+}$	6	−0.613	0.198	1.13	0.993	45.4	53.1	1.5	101.8	30.0	10.1
$Co(NH_3)_5F^{3+}$	6	−0.523	0.208	−1.46	0.980	40.1	57.8	2.1	70.7	25.7	10.1
Reaction entropy ΔS_{rc}° from Ref.[12]											
$Co(en)_3^{3+}$	8	0.206	−0.346	51.7	0.984	26.8	70.0	3.2	72.2	10.4	6.61
$Co(sep)^{3+}$	5	—	−0.727	60.9	0.978	—	95.6	4.4	64.6	—	—
$Co(bpy)_3^{3+}$	6	—	−0.771	64.4	0.908	—	82.5	17.5	18.8	—	—
$Co(phen)_3^{3+}$	8	—	−0.750	60.9	0.885	—	78.3	21.7	21.6	—	—
$Cr(bpy)_3^{3+}$	6	—	−0.740	43.9	0.980	—	96.0	4.0	119.8	—	—
$Fe(bpy)_3^{3+}$	5	—	−0.846	48.4	0.842	—	70.8	29.2	7.28	—	—
$Ru(NH_3)_6^{3+}$	6	—	−0.634	53.7	0.990	—	98.0	2.0	192.3	—	—
Corrected formal rate constant $\ln k_{corr}$ from Ref.[15]											
Eu^{3+}	5	−0.248	−0.128	1.05	0.994	51.1	47.7	1.2	84.4	60.7	18.5

[a] Abbreviations of ligands the same as in Refs.[2,12].

[b] Number of solvents.

[c] Correlation coefficient of the planar or linear correlation.

[d] Percentage contributions from *DN* and *AN* to the observed solvent effect according to eqn. (1), calculated after normalization as in Ref.[7].

[e] Calculated *Snedecor* *F*-value.

solvent—solvent interactions; however, the possibility of a dielectric contribution to the AN was noticed by *Mayer*[5].

With the exception of $Co(en)_3^{3+}$ only one parameter, AN, is statistically significant in the explanation of the observed solvent effect on ΔS°_{rc}. This may indicate the importance of aprotic solvents and indeed they fit better the correlation lines. An increase in the solvent—solvent interactions produces a decrease in the reorientation energy during the electrode process, which can explain the negative values of b_A. On the other hand the rate constant is reversely proportional to the entropy change and the constant b_A for the correlations of the $\ln k_{corr}$ is positive.

Eqn. (1) describes also the solvent effect on the double-layer corrected formal rate constants for the electroreduction of Eu (III/II) from recent results[15]. Differently to the complexes of cobalt stronger solvent—cation interactions and consequently a higher contribution from the solvent donicity may be expected (Table 1). The opposite sign of b_A compared to the case of the outer-sphere reduction also indicates that the energy of activation is determined mainly by the solvent—cation interactions in the inner layer, which became weaker with the increase of competitive solvent—solvent interactions.

The given approach is coherent with our results discussing the solvent effects on the electrode kinetics of radical anions in terms of the AN changes[3], although the possible contribution from the entropy was not considered there.

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