Solvent Effects on the Redox Potential of the Uranium(VI)–Uranium(V) Couple

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The solvent effect on the redox potential of the couple U^{VI}/U^{V} has been studied by multiregression analysis taking into account a wide range of solvent acidity, basicity, and polarity scales. The effectiveness of the method is discussed.

In a previous paper we reported the cathodic behaviour of uranyl(VI) ion in several non-aqueous solvents, correlating the trend of the formal electrode potentials for the U^{VI}–U^{V} couple with the so-called 'Gutmann's donor number.'[1] Although it is still common practice to study the solvent dependence of a physicochemical property on the basis of a single empirical parameter which accounts for the main solvent effect on the measured quantity, it becomes more and more evident that solvent effects should be rationalized on the basis of a multiparameter analysis.[2–5]

Here we re-examine the solvent effect on the redox potential of the couple UO_2^{2+}–UO_2^{+} in terms of multi-parameter equations. In the literature there are few examples of such an approach to the study of the influence of the solute–solvent interactions on redox potentials.

Results and Discussion

Table 1 reports the reversible half-wave potential values, which can be assumed as good estimates of the formal electrode potentials, for the couple UO_2^{2+}–UO_2^{+} in those solvents where this quantity can be reliably measured. Also reported are the empirical scales most frequently used in the study of solvent effects: $E_T(30)$ is the Dimroth–Reichardt parameter;[6] AN is Gutmann's acceptor number;[7] Z is the Kosower value;[8] χ_R and χ_B are the Brooker scales;[9] A_N is the Knauer–Napier parameter;[10] S is the Brownstein scale;[11] α, β, and π^* are the Kamlet–Taft solvatochromic parameters;[12] DN is Gutmann's donor number;[7] B is the Koppel–Palm parameter as refined by Shorter;[13] $\Delta\nu_D$ is the Kagiya solvent electron-donating power;[14] and PA is the solvent proton affinity.[5]

Table 2 reports the results of the correlation of $E_{\frac{1}{2}}^{r}$ with each single empirical parameter listed in Table 1, as well as with some common physical properties of the solvents.

Our effort has been directed towards an analysis of the available data through multiple regression which takes into account hydrogen-bonding-donor or Lewis-acidity parameters, hydrogen-bonding-acceptor or Lewis-basicity parameters, and polarity–polarizability parameters. $E_T(30)$, AN, Z, χ_R, χ_B, A_N, S, and α have been considered as acidity parameters, although, except for α, these scales are somewhat affected by polarity effects;[15,16] β, DN, B, $\Delta\nu_D$, and PA have been considered as basicity parameters; only the π^* scale has been considered in accounting for dielectric effects, because ε (dielectric constant), μ (dipole moment), and n (refractive index) are non-cybotactic parameters.[10]

The results of the multiregression analyses are reported in Table 3. All possible correlations with the parameters reported in Table 1 have been tested, but multiparameter equations are given only when the significance of each coefficient, as computed by the Student t-test, is higher than 90%. These data allow some interesting conclusions about the utility of the different empirical scales in explaining solvent effects on redox potentials, even if, of course, the small number of observations available reduces the importance of the statistical treatment.

It can be noted that, although DN *vs.* $E_{\frac{1}{2}}^{r}$ gives a fairly good linear correlation, a multiple regression which considers, together with DN, either acidity parameters or polarity effects leads to significantly better results in terms of correlation coefficients. Moreover, even if Table 2 shows that the B scale is quite satisfactory in explaining our redox data, suggesting that this parameter may include also polarity effects, the small

Table 1. Formal electrode potentials (*vs.* s.c.e., at 25 °C) for the couple U^{VI}–U^{V} in different solvents, together with available data for the most frequently used empirical solvent scales

	$E_{\frac{1}{2}}^{r}$	$E_T(30)$	AN	Z	χ_R	χ_B	A_N	S	$10^{-3}\alpha$	$10^{-3}\beta$	$10^{-3}\pi^*$	DN	B	$\Delta\nu_D$	PA
Solvent	V	kcal mol^{-1}	$(-\delta_{\infty}^{corr})$		kcal mol^{-1}		G			cm^{-1}		kcal mol^{-1}	cm^{-1}		eV
Acetic anhydride	+0.33[a]	43.9							0.000		0.756	10.5			
Water	−0.30[b]	63.1	54.8	94.6		68.9	17.175	+0.154	1.10	0.47	1.090	33			7.33
Propylene carbonate	−0.37[c]	46.6	18.3							0.38		15.1			
NN-Dimethylformamide	−0.40[a]	43.8	16.0	68.5	43.7	51.5	15.635	−0.142	0.000	0.69	0.875	26.6	166	107	
Dimethyl sulphoxide	−0.50[a]	45.0	19.3	71.1	42.0		15.692		0.000	0.76	1.000	29.8	192	141	
NN-Dimethylacetamide	−0.55[c]	43.7	13.6		43.0				0.000	0.76	0.882	27.8	178	113	
Pyridine	−0.78[a]	40.2	14.2	64.0	43.9	50.0	15.608	−0.197	0.000	0.64	0.867	33.1	260	168	9.71
Ethylenediamine	−0.94[a]									0.77		55.0			
Morpholine	−1.06[a]	41.0													

cal = 4.184 J, G = 10^{-4} T, eV ≈ 1.60 × 10^{-19} J. [a] From ref. 1. [b] M. Pourbaix, 'Atlas of Electrochemical Equilibria in Aqueous Solutions,' Pergamon Press, Oxford, 1966, p. 203. [c] H. Bildstein, H. Fleisher, and V. Gutmann, *Inorg. Chim. Acta*, 1968, **2**, 347.

Table 2. Correlation results between the redox potential of the couple U^{VI}–U^{V} in different solvents and the solvent empirical parameters. l = Number of available data; r = correlation coefficient

Correlation	l	r	Correlation	l	r
$E_{1/2}^{r}$ *vs.* $E_T(30)$	8	0.299	$E_{1/2}^{r}$ *vs.* B	4	−0.953
$E_{1/2}^{r}$ *vs.* AN	6	0.590	$E_{1/2}^{r}$ *vs.* $\Delta\nu_D$	4	−0.854
$E_{1/2}^{r}$ *vs.* Z	4	0.749	$E_{1/2}^{r}$ *vs.* ε	9	0.396
$E_{1/2}^{r}$ *vs.* χ_R	4	−0.356	$E_{1/2}^{r}$ *vs.* $\left(\frac{\varepsilon - 1}{2\varepsilon + 1}\right)^{a}$	9	0.583
$E_{1/2}^{r}$ *vs.* A_N	4	0.647	$E_{1/2}^{r}$ *vs.* μ	9	0.498
$E_{1/2}^{r}$ *vs.* β	7	−0.583	$E_{1/2}^{r}$ *vs.* n	8	−0.581
$E_{1/2}^{r}$ *vs.* π^*	6	−0.377	$E_{1/2}^{r}$ *vs.* $\left(\frac{n^2 - 1}{2n^2 + 1}\right)^{b}$	8	−0.445
$E_{1/2}^{r}$ *vs.* DN	8	−0.821			

[a] Dielectric constant function (see R. W. Taft, J.-L. M. Abboud, and M. J. Kamlet, *J. Am. Chem. Soc.*, 1981, **103**, 1080). [b] Refractive index function (see reference in footnote *a*).

Table 3. Multiregression analyses

Independent variables						
Acidity parameter	Basicity parameter	Polarity parameter	r	l	Parametric equation ($E_{1/2}^{r}$ in V)	Standard error of estimate[a]
$E_T(30)$	DN	π^*	0.995	6		
$E_T(30)$	DN		0.995	6	$E_{1/2}^{r} = -0.132 + 0.021\ E_T(30) - 0.046$ DN	0.050
$E_T(30)$		π^*	0.819	6	$E_{1/2}^{r} = 0.899 + 0.052\ E_T(30) - 4.053\ \pi^*$	0.279
	DN	π^*	0.977	6	$E_{1/2}^{r} = -0.533 - 0.060$ DN $+ 1.935\ \pi^*$	0.103
AN	DN	π^*	0.990	5		
AN	DN		0.857	6	$E_{1/2}^{r} = -0.214 + 0.009$ AN $- 0.017$ DN	0.113
AN		π^*	0.688	5		
$E_T(30)$	β	π^*	0.877	5		
$E_T(30)$	β		0.720	6		
	β	π^*	0.657	5		
AN	β	π^*	0.860	5		
AN	β		0.635	6		
$E_T(30)$	B		0.957	4		
$E_T(30)$	$\Delta\nu_D$		0.944	4		
A_N	DN		0.988	4	$E_{1/2}^{r} = -3.394 + 0.291\ A_N - 0.058$ DN	0.054
A_N	β		0.796	4		
χ_R	DN		0.942	4		
χ_R	β		0.598	4		
χ_R	B		0.953	4		
χ_R	$\Delta\nu_D$		0.902	4		
χ_R		π^*	0.368	4		
A_N		π^*	0.679	4		
Z	DN		0.999	4	$E_{1/2}^{r} = -0.180 + 0.016\ Z - 0.048$ DN	0.010
Z	β		0.847	4		
Z		π^*	0.750	4		
	B	π^*	0.960	4		
	$\Delta\nu_D$	π^*	0.947	4		

[a] Computed as $\sqrt{\Sigma R_i^2/m}$, where R_i are the residuals and m the degrees of freedom.

number of values available prevents a definite choice of such a scale to account for solvent effects on redox potentials, and a search for even better results through multiple regression involving this parameter. Finally, although the significance of the relevant coefficients is not as high as 90%, based on the correlation coefficients, several other couples of parameters could be regarded as effective models.

It must be said that in many cases it was impossible to test multiple correlations because the paucity of data caused the degrees of freedom to be equal to zero. A similar drawback must be *a priori* taken into account in the case of electrochemical studies, due to both the relatively small number of suitable solvents and the need for reversible responses which are only of thermodynamic significance.

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