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On the Nature of Solvent Effects on Redox Properties

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The one-electron reduction potentials of six radical cations, four cations, and four neutral radicals in tetrahydrofuran, dichloromethane, dimethyl sulfoxide, *N*-methyl-2-pyrrolidinone, *N*,*N*-dimethylformamide, acetonitrile, methanol, ethanol, 2-propanol, acetone, formamide, and 1,1,1,3,3,3-hexafluoropropan-2-ol have been measured by cyclic voltammetry. For 10 of the redox couples, the redox process was reversible in all solvents. These results have been used to evaluate solvent effects by means of the Kamlet−Taft relationship. The relative importance of the solvent parameters α, β, π^*, and δ_H is 54.9, 9.6, 15.5 and 20.0%, respectively, for the radical cation displaying the strongest solvent dependence. In addition, we have studied the entropy contribution to some of the observed solvent effects by measuring the redox potentials as a function of temperature. The absolute value of the entropy appears to increase with increasing hydrogen bond donor ability of the solvent. The variation in entropy indicates that specific solvation is of main importance when considering solvent effects on redox properties.

Introduction

Solvent effects on reaction kinetics and mechanisms have been a subject of interest for a number of years.[1] More recently, studies of solvent effects on redox properties of radicals and radical ions have occurred in the literature.[2,3] Quantitative descriptions as well as fundamental understanding of the nature of solvent effects on redox properties are very important for scientists trying to understand the chemistry of more complex systems where direct measurements are difficult or even impossible. In addition, improved understanding of solvent effects is useful when making quantitative comparison of redox data from different solvents. Solvent effects on one-electron reduction potentials (eq 1) are a measure of the solvent dependence on the difference in free energy of solvation for a given redox couple O/R (eq 2).[4]

$$\mathrm{O} + \mathrm{e}^- \rightleftharpoons \mathrm{R} \qquad (1)$$

$$\mathrm{IP} \approx C + E° + \frac{\Delta G^\circ_{\mathrm{solv}}(\mathrm{R}) - \Delta G^\circ_{\mathrm{solv}}(\mathrm{O})}{F} \qquad (2)$$

This can be understood from the above approximate relation between $E°$ and the corresponding gas-phase ionization potential, *IP*, where the constant C is the absolute potential of the reference electrode in a given solvent (e.g., 4.44 (±0.02) eV[5] for the hydrogen electrode in water), $\Delta G^\circ_{\mathrm{solv}}$ (R) and $\Delta G^\circ_{\mathrm{solv}}$ (O) are the free energies of solvation of species R and O, respectively, and F is the Faraday constant.[6] It should be noted that the ionization potential is the enthalpy of ionization at 0 K; thus, the ionization entropy and temperature correction are neglected in eq 2. However, these corrections are assumed to be fairly small.

In practice, solvent effects on redox properties are usually quantified by one-electron reduction potentials measured against a reference redox couple for which the solvent sensitivity is assumed to be very small. Ferrocene is one possible candidate. Interestingly, a recent study on the redox properties of substituted ferrocenes indicates that the solvent effects are substantial.[7] However, the potentials were determined directly against the reference electrode without taking differences in liquid junction potential into account. Other studies display a weaker solvent dependence on the redox properties of ferrocene.[8]

Properties in solution, e.g., solubility, rates of reactions and free energy, and enthalpy of equilibria, can often be described by so-called linear free energy relationships (LFER) or linear solvation energy relationships (LSER).[9] One of the most successful relationships has been found to be the Kamlet−Taft expression (eq 3), where *XYZ* is the property of interest, XYZ_0, a, b, s, and h are solvent independent coefficients characteristic of the process, α is the hydrogen bond donor (HBD) ability of the solvent, β is the hydrogen bond acceptor (HBA) or electron pair donor ability to form a coordinative bond, π^* is its dipolarity/polarizability parameter, and δ_H is the Hildebrand solubility parameter which is a measure of the solvent−solvent interactions that are interrupted in creating a cavity for the solute.[9,10]

$$XYZ = XYZ_0 + a\alpha + b\beta + s\pi^* + h\delta_{\mathrm{H}} \qquad (3)$$

For some processes, any of the coefficients XYZ_0, a, b, s, and/or h may be negligibly small, so that the corresponding terms do not play a role in the characterization of the solvent effects for these processes. This approach has been criticized for not separating specific and nonspecific effects.[11] Alternative approaches which separate specific and nonspecific effects have also been elaborated, e.g., by Koppel and Palm[1,11,12] and more recently by Drago and co-workers.[13,14]

The Kamlet−Taft expression has been found to describe solvent effects on one-electron reduction potentials of dications,

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TABLE 1: Reduction Potentials (V vs Fc^+/Fc) for Substances 1−14 Measured by Ordinary Cyclic Voltammetry in Different Solvents Containing 0.1 M Bu_4NBF_4 Unless Otherwise Noted[a]

solvent	**1**[b]	**2**[c]	**3**[b]	**4**[c]	**5**[b]	**6**[b]	**7**[c]	**8**[c]	**9**[c]	**10**[c]	**11**[c]	**12**[c]	**13**[c]	**14**[c]
THF	0.549	0.236	0.933	−0.241	0.385	0.978	−1.190	−1.095	−1.403	−0.601	−2.044	−1.748	−1.904	−1.655
CH_2Cl_2	0.581[d]	0.317	0.904[e]	−0.278	0.338	0.983	−1.147	−1.021	−1.430	−0.653	−1.989	−1.693	−1.948	−1.677
DMSO	0.633	0.253	0.886	−0.275	0.376	0.880	−1.193	−1.091	−1.424	−0.652	−1.947	−1.720	−1.819	−1.568
NMP	0.605	0.222	0.883	−0.278	0.399	0.963	−1.190	−1.087	−1.428	−0.645	−2.039	−1.793	−1.868	−1.622
DMF	0.573	0.232	0.843	−0.277	0.371	0.872	−1.194	−1.081	−1.433	−0.650	−2.016	−1.760	−1.871	−1.623
MeCN	0.624	0.314	0.915	−0.279	0.367	1.005	−1.171	−1.051	−1.438	−0.648	−1.984	−1.697	−1.883	−1.623
MeOH	0.495	0.438	0.893	−0.279	0.353	0.939	−1.144	−0.992	−1.440	−0.661	−1.784[f]	−1.184[g]	−1.691	−1.556
EtOH	0.484	0.439	0.959	−0.275	0.379	0.963	−1.156	−0.997	−1.439	−0.648	−1.899[h]	−1.354[h]	−1.922[i]	
2-PrOH	0.500	0.388	1.105	−0.239	0.424	0.999	−1.179	−1.015	−1.423	−0.645		−1.494		
acetone	0.599	0.258	0.913	−0.290	0.355	0.999	−1.183	−1.079	−1.432	−0.642	−2.061	−1.718	−1.922	−1.668
FA	0.640	0.409	0.927	−0.266	0.403	0.913	−1.135	−0.969	−1.421	−0.651				

[a] The following abbreviations have been used: THF = tetrahydrofuran (with 0.3 M Bu_4NBF_4), DMSO = dimethyl sulfoxide, NMP = *N*-methyl-2-pyrrolidinone, DMF = *N*,*N*-dimethylformamide, MeCN = acetonitrile, MeOH = methanol, EtOH = ethanol, 2-PrOH = 2-propanol (with 0.2 M Bu_4NBF_4), and FA = formamide (with 0.2 M Bu_4NBF_4). The concentration of Bu_4NBF_4 in CH_2Cl_2 and acetone was 0.2 M. [b] Peak oxidation potentials measured at 0.5 V s^{-1} with a standard deviation of ±5 mV. [c] Standard potentials determined with an uncertainty of ±3 mV unless otherwise noted. [d] The standard potential was determined to be 0.549 V vs Fc^+/Fc. [e] The standard potential was determined to be 0.866 V vs Fc^+/Fc. [f] Determined by fast cyclic voltammetry with the switch potential set at the background reduction; uncertainty = 37 mV. [g] Determined by normal cyclic voltammetry with the switch potential set at the background reduction. [h] Determined by fast cyclic voltammetry with an uncertainty of 10 mV. [i] Determined by fast cyclic voltammetry with an uncertainty of 19 mV.

CHART 1

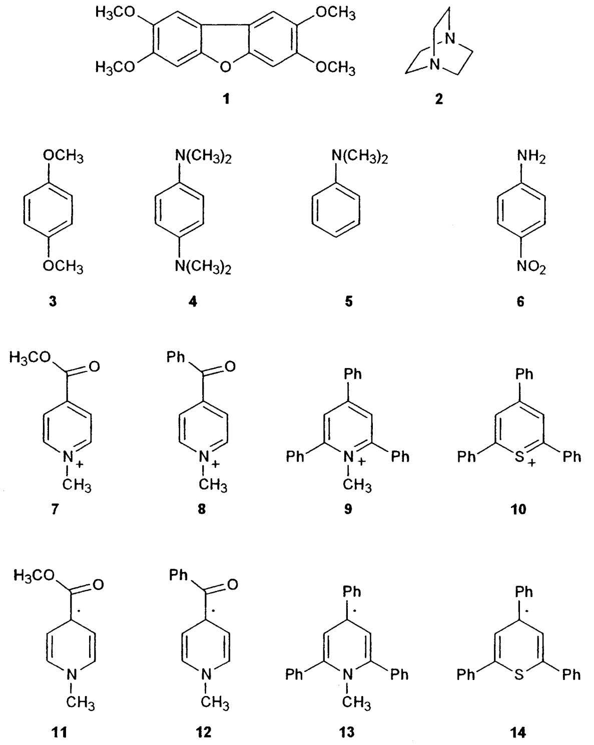

TABLE 2: Kamlet−Taft Solvent Parameters[10,23]

solvent	α	β	π*	δ_H
THF	0	0.55	0.58	9.1
DMSO	0	0.76	1	12
NMP	0	0.77	0.92	11.3
DMF	0	0.69	0.88	12.1
MeCN	0.19	0.40	0.75	11.9
MeOH	0.98	0.66	0.60	14.5
EtOH	0.86	0.75	0.54	12.7
2-PrOH	0.76	0.84	0.48	11.5
acetone	0.08	0.43	0.71	9.9
FA	0.71	0.48	0.97	19.2
HFP	1.96	0	0.65	9.72

radical cations, neutral molecules, and radical anions fairly well.[3] However, previous studies have included relatively few substances, and it has therefore been difficult to draw reliable general conclusions from the trends observed. Furthermore, some of the trends are based on irreversible peak potentials and may therefore not describe solvent effects on the thermodynamical potentials accurately. The magnitude of the solvent effects has been found to depend roughly on the charge localization reflected by the gas-phase ionization potential or electron affinity.[3] In addition, a series of studies by Svaan and Parker have shown that the entropy as well as the enthalpy contribution to the redox potential closely follow the charge localization.[15−21] This indicates that the relatively weak solvation of neutral molecules and radicals can be regarded as solvent independent and the main contribution to the solvent effect originates from differences in ion solvation. As the observed trend is quite rough, it is plausible that different families of compounds may follow slightly different trends due to differences in solvation of the neutral species. Solvents with more extreme properties (e.g., hexafluoro-2-propanol, which has very high hydrogen bond donor ability) can be expected to deviate from Kamlet−Taft expressions due to significantly stronger solvation of the neutral species.

To fully understand solvent effects on redox properties, the nature of the solvent effects, i.e., the enthalpic and entropic contributions to the variation in solvation free energies between different solvents must be known. This has to our knowledge never been studied explicitly, although Svaan and Parker have studied the entropy contribution to redox potentials in a few aprotic solvents.[20] In many cases, where free energies expressed by redox potentials have been used to calculate enthalpies (e.g., bond dissociation enthalpies) via thermochemical cycles, the entropy contribution to the redox potential has been assumed to be negligible.[22] Yet, other studies have shown that the entropy changes for electron-transfer processes are directly related to the solvation energy changes.[15−21]

In this work, we have studied the solvent effects on the one-electron reduction potentials of the six radical cations, four cations, and four neutral radicals depicted in Chart 1. In addition, we have made an attempt to elucidate the entropy contribution to some of the observed solvent effects by measuring the redox potentials as a function of temperature.

Results and Discussion

The measured potentials and the Kamlet−Taft parameters for the solvents used in this study are collected in Tables 1 and 2, respectively.

TABLE 3: Kamlet−Taft Coefficients for Substances 2, 4, and 7−10

substance	XYZ_0	a (α)	b (β)	s (π*)	h (δ_H)	R^2	F^a
2	0.37 ± 0.07	0.49 ± 0.02	−0.22 ± 0.06	0.47 ± 0.08	−0.04 ± 0.005	0.99	247
4	−0.20 ± 0.06	0.12 ± 0.02	−0.06 ± 0.05	0.16 ± 0.07	−0.02 ± 0.004	0.92	17
7	−1.19 ± 0.01	0.05 ± 0.02	−0.05 ± 0.02	0.02 ± 0.03	0.001 ± 0.003	0.97	39
8	−1.13 ± 0.02	0.07 ± 0.03	−0.02 ± 0.02	−0.04 ± 0.05	0.008 ± 0.004	0.99	89
9	−1.45 ± 0.03	−0.09 ± 0.04	0.04 ± 0.03	−0.14 ± 0.07	0.01 ± 0.005	0.53	1.4
10	−0.62 ± 0.03	−0.11 ± 0.04	0.03 ± 0.03	−0.20 ± 0.07	0.01 ± 0.005	0.76	4

[a] The *F* statistic, or the *F*-observed value can be used to determine whether the observed relationship between the dependent and independent variables occurs by chance.

Solvent Effects on Electrode Potentials for Compounds 1—10. First of all it should be noted that the electrode process studied for the neutral compounds **1**−**6** is the oxidation to the pertinent radical cations while it for the cations **7**−**10** it is the reduction to the pertinent radicals. In the case of **2**, **4**, and **7**−**10** it was possible to attain reversibility in the cyclic voltammetry experiments for all solvents leading to the direct measurement of standard potentials. The solvent 1,1,1,3,3,3-hexafluoropropan-2-ol (HFP) was included in a few measurements where the standard oxidation potentials for **1** and **4** were determined to be 0.695 and −0.008 V vs Fc$^+$/Fc (abbreviation for ferrocenium/ferrocene), respectively, and the peak oxidation potential for **2** and **5** to be ca. 1.3 and 0.62 V vs Fc$^+$/Fc, respectively. In addition, the standard potential for **3** in HFP has been determined to be 1.48 V vs Fc$^+$/Fc by Eberson et al.[24,25]

As can be seen in Table 1, the one-electron oxidation potential for **1**, **2**, **3**, **5** and **6** vary significantly with solvent. Moreover, when including HFP we see that even the relatively solvent insensitive radical cation of **4** is strongly affected. The quite dramatic effect of HFP can only be attributed to its extremely high hydrogen bond donor ability (Table 2). In this context, however, it should be emphasized that the potentials listed for **1**, **3**, **5**, and **6** are irreversible, meaning that they are affected to an unknown extent by the presence of homogeneous kinetics and/or charge-transfer kinetics. Still, the results seem to be in accordance with the expectation that the radical cation of **4** as the most delocalized system is the one least influenced by solvent. As to the cations the standard potentials for **7**−**10** appear to be more or less solvent independent although measurements were not carried out in HFP in these cases. Thus, we can conclude that the solvation of these cations is relatively weak or at least similar to that of ferrocenium. This is attributed to the fact that the positive charge is shielded by the methyl and/or phenyl groups.

The redox data for compounds **2**, **4**, and **7**−**10** were all analyzed in terms of the Kamlet−Taft expression given in eq 3. The resulting coefficients are given in Table 3.

The relative importance of the different solvent properties can be evaluated from so-called beta coefficients derived according to eq 4−7 where a', b', s', and h' are the partial regression coefficients (or "β coefficients"),$|a|$, $|b|$, $|s|$, and $|h|$ are the absolute values of the regression coefficients, α_i, β_i, $\pi^*{}_i$, and δ_{H_i} are the Kamlet−Taft parameters of a given solvent (i), $\bar{\alpha}$, $\bar{\beta}$, $\bar{\pi}^*$, and $\bar{\delta}_H$ are the average values of these quantities in a given set of solvents, E_i^0 is the potential measured in a given solvent and $\bar{E}^{\circ}$ is the average value of the potentials in a given set of solvents.[26]

$$a' = |a| \sqrt{\frac{\sum_{i=1}^{n} (\alpha_i - \bar{\alpha})^2}{\sum_{i=1}^{n} (E_i^{\,0} - \bar{E}^0)^2}} \tag{4}$$

$$b' = |b| \sqrt{\frac{\sum_{i=1}^{n} (\beta_i - \bar{\beta})^2}{\sum_{i=1}^{n} (E_i^{\,0} - \bar{E}^0)^2}} \tag{5}$$

$$s' = |s| \sqrt{\frac{\sum_{i=1}^{n} (\pi^*{}_i - \bar{\pi}^*)^2}{\sum_{i=1}^{n} (E_i^{\,0} - \bar{E}^0)^2}} \tag{6}$$

$$h' = |h| \sqrt{\frac{\sum_{i=1}^{n} (\delta_{H_i} - \bar{\delta}_H)^2}{\sum_{i=1}^{n} (E_i^{\,0} - \bar{E}^0)^2}} \tag{7}$$

The relative importance of a given parameter can be calculated from the beta coefficients using eq 8.

$$\bar{a} = \frac{a'}{a' + b' + s' + h'} \tag{8}$$

This equation gives the relative importance of α, the hydrogen bond donor ability of the solvent. For compound **2** (displaying the strongest solvent dependence) the relative importances of α, β, π*, and δ_H are 54.9, 9.6, 15.5, and 20.0%, respectively, when HFP is included and 52.9, 8.9, 22.2, and 16.0%, respectively, when HFP is excluded. Hence, the most important solvent parameter is α while β appears to be of minor importance.

This trend is similar to that previously found for the reduction potentials of neutral species but it clearly deviates from that found for the oxidation of a compound such as **2** (DABCO).[3] In this context, it is important to note that the previous set of oxidation potentials of **2** was based on irreversible measurements in a limited set of solvents.[3] However, the Kamlet−Taft relationship based on the reversible potentials obtained herein becomes similar to the previous one, if the solvent effects are only quantified in the solvent set used in ref 3. Thus, we can conclude that the main reason for the discrepancy observed for **2** is the different sets of solvents considered. Admittedly, the

TABLE 4: Ionization Potentials and Solvation Free Energies (Relative to Fc^+/Fc) for Substances 2−5 and Fc

		$\Delta\Delta G^\circ_{solv}$ (kJ mol^{-1})^a										
substance	IP (eV)[26]	THF	CH_2Cl_2	DMSO	NMP	DMF	MeCN	MeOH	EtOH	2-PrOH	acetone	FA
2	7.321	36.2	28.4	34.5	37.5	36.6	28.7	16.6	16.6	21.5	34.1	19.5
3	7.56	−8.0	−5.2	−3.5	−3.2	0.7	−6.3	−10.5	−10.5	−24.6	−6.1	−7.4
4	6.1	−35.6	−32.0	−32.2	−32.0	−32.1	−31.9	−32.3	−32.3	−35.8	−30.9	−33.2
5	7.12	2.4	6.9	3.3	1.1	3.8	4.1	3.0	3.0	−1.4	5.3	0.7
Fc	6.71	0	0	0	0	0	0	0	0	0	0	0

[a] $\Delta\Delta G^\circ_{solv} = \Delta G^\circ_{solv}(R) - \Delta G^\circ_{solv}(O)$.

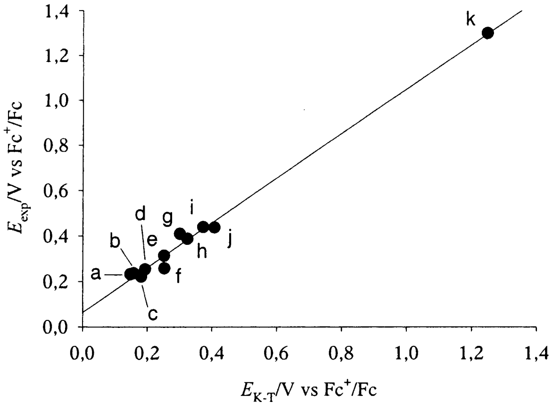

Figure 1. Experimentally determined oxidation potentials for DABCO (**2**) plotted against the corresponding values estimated using the Kamlet−Taft relationship given in Table 3: (a) DMF, (b) THF; (c) NMP, (d) DMSO, (e) MeCN, (f) acetone, (g) FA, (h) 2-PrOH, (i) EtOH, (j) MeOH, and (k) HFP.

strong dependence on the hydrogen bond donor ability originates from the high potentials determined in HFP, but even when the Kamlet−Taft relationship for DABCO is determined without including the value in HFP, the strong dependence on α is present. Furthermore, the relative importance of α does not change significantly when excluding the value in HFP. It is quite plausible that bases like DABCO may be protonated in HFP. Measurements of the conductivity of HFP and MeCN containing DABCO show that DABCO increases the conductivity of HFP significantly while the conductivity of MeCN remains virtually unchanged. This indicates that DABCO is protonated to some extent in HFP. However, this does not appear to cause any significant deviation from the Kamlet−Taft correlation. In Figure 1, the experimentally determined oxidation potentials of **2** are plotted against the corresponding values estimated using the Kamlet−Taft relationship. As can be seen, the Kamlet−Taft relationship successfully describes the solvent dependence on the one-electron oxidation potential of **2**.

The reason for mainly focusing on the oxidation of **2** in the above discussion is that this radical cation shows the most pronounced solvent dependence and that the potentials are reversible. The potentials for **4** (TMPD) as well as **7**−**10** are also reversible but the solvent dependence is relatively weak with the notable exception of the value for **4** determined in HFP. We also measured the peak oxidation potentials for **2** in the solvents given in Table 2, and it was found that the irreversible potentials essentially showed the same solvent dependence as the reversible potentials although to a slightly larger extent. The irreversible potentials determined for **1**, **3**, and **5** could thus describe the solvent dependence for these substances at least qualitatively correctly.

Qualitatively, it would be expected that the solvent effect increases with increasing charge localization of the corresponding cation. The only substances for which the ionization potentials (assumed to reflect the degree of charge localization) are known are **2**−**6** and therefore we can only base the analysis on these substances. However, the 4-nitroaniline radical cation **6** can undergo deprotonation and therefore it is excluded from the analysis. Using eq 2, we can calculate the difference in free energy of solvation, $\Delta\Delta G^\circ_{solv}$, between the neutral species and the corresponding cation. To avoid errors due to uncertainties in the absolute potential for the reference electrode in the different solvents, we have calculated $\Delta\Delta G^\circ_{solv}$ for substances **2-5** relative to $\Delta\Delta G^\circ_{solv}$ for Fc^+/Fc. These values are given in Table 4 along with the corresponding gas-phase ionization potentials.

When plotting $\Delta\Delta G^\circ_{solv}$ against the ionization potential we can make the general observation that $\Delta\Delta G^\circ_{solv}$ indeed increases with increasing ionization potential (i.e., charge localization) as shown for acetonitrile in Figure 2; similar correlations can be obtained for the other solvents used in this study. However, the compound **3** (i.e., 1,4-dimethoxybenzene) deviates significantly from the general trend. This deviation is much larger than the uncertainty introduced in the electrochemical determination due to the use of irreversible peak potentials. Moreover, we see no similar deviation for compound **5,** the measurements of which also were based on irreversible potentials. The deviation indicates that the suggested proportionality between the ionization potential and $\Delta\Delta G^\circ_{solv}$ cannot be taken for granted and that the presence of different heteroatoms may cause deviations from the general trend.

The suggested relationship between the solvent effect on E° and $\Delta\Delta G^\circ_{solv}$ cannot be verified from the present data, although it is obvious that the most strongly solvated cation **2** also displays the strongest solvent sensitivity (judging from the K−T relationships). It should be noted that compound **3**, which is considerably less solvated, also displays a significant solvent sensitivity. The difference between the highest and the lowest potential is in fact larger for compound **3** than for compound **2**. Again, this could suggest that the solvent dependence is strongly governed by the nature of the heteroatom. However, it should be noted that the potentials for compound **3** are irreversible and that the irreversible potentials for **2** were shown to be more solvent sensitive than the corresponding reversible potentials.

Solvent Effects on Electrode Potentials for Compounds 11—14. In these cases the electrode process studied is the reduction of the radicals to the pertinent anions. Table 5 comprises the Kamlet−Taft coefficients obtained for **11**−**14**.

As can be seen, the quality of the Kamlet−Taft relationships is relatively low and there is no significant dependence of E° on the Kamlet−Taft parameters within experimental error. As previously shown for reduction of neutral species, the hydrogen bond donor ability, α, and to some extent also the dipolarity/polarizability, π^*, of the solvent are of major importance. The small coefficients and the poor correlations found for substances **11**−**14** can probably be attributed to the structure of these compounds. They contain bulky substituents that could shield the charge and thereby weaken the solvation of the ion. This

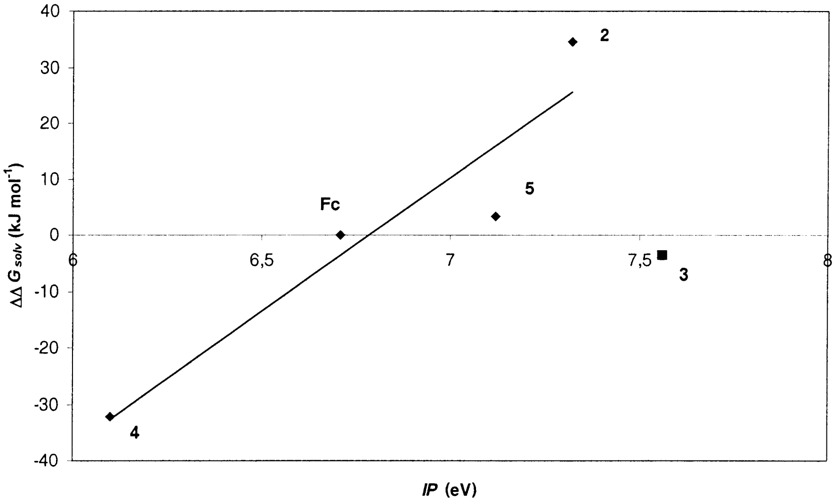

Figure 2. Solvation free energies ($\Delta\Delta G^\circ_{\text{solv}}$) for substances **2**−**5** and Fc relative to Fc^+/Fc plotted against the corresponding ionization potentials.

TABLE 5: Kamlet−Taft Coefficients for Substances 11−14

substance	XYZ_0	a (α)	b (β)	s (π^*)	h (δ_H)	R^2	F
11	−2.2 ± 0.4	0.2 ± 0.3	−0.07 ± 0.25	0.17 ± 0.57	0.009 ± 0.06	0.90	4.3
12	−2.3 ± 0.2	0.1 ± 0.2	0.02 ± 0.15	−0.02 ± 0.36	0.03 ± 0.04	0.90	6.8
13	−2.3 ± 0.3	−0.06 ± 0.36	−0.02 ± 0.26	−0.05 ± 0.62	0.04 ± 0.06	0.54	0.9
14	−1.8 ± 0.1	0.06 ± 0.14	0.07 ± 0.10	0.08 ± 0.22	0.01 ± 0.02	0.85	2.8

would also make the redox properties less solvent sensitive, which is exactly what we observe.

As discussed for cations, general equations describing solvent effects on redox properties based on $\Delta\Delta G^\circ_{\text{solv}}$ or EA only, are not to be expected for the reduction of neutral species either. Equations describing the variation in the Kamlet−Taft coefficients as a function of $\Delta\Delta G^\circ_{\text{solv}}$ or EA has been derived for series of structurally similar substances, e.g., nitrobenzenes.[3]

Differences in Solvation between Anions and Cations. The standard potentials for substances **7**−**14** constitute an interesting set of data since we here have the possibility of elucidating the solvent effects on both the reduction and the oxidation potentials for four different neutral radicals. In addition, this set of data, in principle, also allows the evaluation of the difference in solvation between cations and anions with identical structure as a function of solvent and completely independent of the radicals. From the above treatment of reduction potentials for cations and neutral species, we can see that the main contribution to the solvent effects on substances **7**−**14** originates from the reduction of neutral species. It should be noted that the absence of solvent effects on the reduction potentials of the cations does not imply that the solvation energies are solvent independent. Formally, the only conclusion that can be drawn from this is that solvation of these cations follows that of ferrocene. From the two sets of potentials it is also possible to derive the disproportionation equilibrium constants for the radicals, but as it seems to present no obvious correlation with the solvent parameters, we did not consider it further.

The Thermodynamic Nature of Solvent Effects. To assess the entropy and enthalpy contribution to the observed solvent effects on redox properties (relative to ferrocene) we measured the standard potential for a number of substances in a few solvents with different properties as a function of temperature ($\partial G/\partial T = -S \Rightarrow \Delta S^\circ = F\, dE^\circ/dT$).[28] The temperature intervals were 5−80 °C for MeCN, 20−60 °C for DMSO, and 5−60 °C for MeOH. The resulting temperature effects on the reversible potentials and the calculated entropies are given in Table 6.

As expected the entropy for reduction of neutral species is negative while for the reduction of cations it is positive.[15−21] Interestingly, the absolute value of the entropy appears to increase with increasing hydrogen bond donor ability of the solvent going from dimethyl sulfoxide and acetonitrile to methanol. For a series of structurally similar substances in a given solvent, Svaan and Parker have shown that the enthalpic contribution to the potential is proportional to the entropic contribution.[16] Thus, strong solvation of an ion is accompanied by a large decrease in entropy as also seen herein for the delocalized ions of nitrobenzene 4-nitrobenzonitrile, 2,5-dimethylbenzoquinone, and 3,5-di-*tert*-butyl-1,2-benzoquinone. This is also what we would expect from Born's model for ion solvation. In Born's model for solvation of small ions the free energy of solvation as well as the entropy of solvation are proportional to z^2/r where z is the charge and r is the ionic radius. It should be noted that this purely electrostatic model does not describe solvent effects on one-electron reduction potentials of organic substances successfully. Furthermore, the entropy for compound **3** is relatively small, which is well in line with the low free energy of solvation observed in this work.

When analyzing the data in Table 6, it is obvious that the difference in entropy between two solvents is larger than the apparent difference in solvation free energy for a given solute. Hence, the change in entropy is to some extent compensated by a change in enthalpy. Consequently, the main contribution to the observed solvent effects is a change in the relative importance of the entropic and the enthalpic contribution to the free energy of solvation. This, in turn, is strongly governed by the hydrogen bond donating ability of the solvent. The variation in entropy indicates that specific solvation is of main importance when considering solvent effects on redox properties.

Experimental Section

Reagents. The supporting electrolyte tetrabutylammonium tetrafluoroborate (Bu_4NBF_4) was prepared by standard procedures. Ferrocene (98%) was purchased at Aldrich and used as received. Tetrahydrofuran (Lab-Scan) was distilled over sodium and benzophenone under a nitrogen atmosphere. Dichloromethane (Gropa) and acetonitrile (Lab-Scan) were both

TABLE 6: Slopes of $\Delta E°/\Delta T$ and Entropies $\Delta S°$ for the Reduction of Different Substrates in MeOH, MeCN, and DMSO Relative to Fc$^+$/Fc

	MeOH		MeCN		DMSO	
substance	slope (mV K^{-1})	$\Delta S°$ (J mol^{-1} K^{-1})	slope (mV K^{-1})	$\Delta S°$ (J mol^{-1} K^{-1})	slope (mV K^{-1})	$\Delta S°$ (J mol^{-1} K^{-1})
Fc$^+$		(12.6^{8})[a]		(48.1^{8})[a]		(52.3^{8})[a]
nitrobenzene	−4.0 ± 0.2	−386 ± 19 (−373)[b]	−1.25 ± 0.3	−120 ± 29 (−72)[b]	−1.12 ± 0.07	−108 ± 7 (−56)[b]
4-nitrobenzonitrile	−6 ± 1	−579 ± 96 (−566)[b]	−1.12 ± 0.3	−108 ± 29 (−60)[b]	−1.4 ± 0.2	−138 ± 19 (−86)[b]
2,5-dimethyl-benzoquinone	−6 ± 2	−579 ± 193 (−566)[b]	−1.4 ± 0.2	−133 ± 19 (−85)[b]	−0.3 ± 0.1	−29 ± 10 (23)[b]
3,5-di-*tert*-1,2-benzoquinone	−3 ± 1	−289 ± 96 (−276)[b]	−1.3 ± 0.1	−124 ± 10 (−76)[b]	−0.5 ± 0.3	−48 ± 29 (4)[b]
3[c]	0.5 ± 0.1	48 ± 10 (61)[b]	0.1 ± 0.1	10 ± 10 (58)[b]		
4	−0.56 ± 0.04	−54 ± 4 (−41)[b]	0.01 ± 0.03	1 ± 3 (49)[b]		
7	0.9 ± 0.2	87 ± 19 (100)[b]	1.1 ± 0.4	106 ± 39 (154)[b]	0.4 ± 0.2	39 ± 19 (91)[b]
8	0.8 ± 0.4	77 ± 38 (90)[b]	0.5 ± 0.1	48 ± 10 (96)[b]	0.2 ± 0.1	19 ± 10 (71)[b]
9	0.9 ± 0.3	87 ± 29 (100)[b]	0.1 ± 0.1	10 ± 10 (58)[b]	0.2 ± 0.1	19 ± 10 (71)[b]
10	0.8 ± 0.2	77 ± 19 (90)[b]	0.2 ± 0.3	19 ± 29 (67)[b]	0.4 ± 0.1	39 ± 10 (91)[b]
11	−1.1 ± 0.7	−106 ± 68 (−93)[b]	−0.9 ± 0.1	−87 ± 10 (−39)[b]	−0.5 ± 0.2	−48 ± 19 (4)[b]
12	−2.6 ± 1.0	−251 ± 96 (−238)[b]	−1.3 ± 0.2	−125 ± 19 (−77)[b]	−0.6 ± 0.1	−58 ± 10 (−6)[b]
13	−0.4 ± 0.2	−39 ± 19 (−26)[b]	−0.4 ± 0.1	−39 ± 10 (9)[b]	−0.6 ± 0.1	−58 ± 10 (−6)[b]
14	−1.3 ± 1.0	−125 ± 96 (−112)[b]	−0.5 ± 0.1	−48 ± 10 (0)[b]	−0.3 ± 0.1	−29 ± 10 (23)[b]

[a] From ref 8. [b] Absolute values calculated from the absolute entropy for Fc$^+$/Fc given in ref 8. [c] On the basis of reversible potentials measured at a sweep rate of 2 V s^{-1}.

distilled over CaH_2, followed in the case of acetonitrile by successive distillation over P_2O_5 and K_2CO_3. The solvent 1-methylpyrrolidin-2-one (Merck-Schuchardt) was distilled under a nitrogen atmosphere. Dimethyl sulfoxide (Aldrich, sure seal bottle) was stored under nitrogen. All solvents including *N*,*N*-dimethylformamide (Lab-scan), methanol (Merck), 99.9% ethanol (DDSF), and 1,1,1,3,3,3-hexafluoropropan-2-ol (Lancaster) were dried over activated alumina (ICN Alumina-I-Super) prior to use and handled with normal syringe techniques.

Tetramethoxydibenzofuran (**1**) was a generous gift from Dr. Jonas Hellberg (Stockholm); the synthesis procedure is described in ref 29. 1,4-Diazabicyclo[2.2.2]octane (DABCO) (**2**), 1,4-dimethoxybenzene (**3**), *N*,*N*,*N′*,*N′*-tetramethylphenylene-1,4-diamine (TMPD) (**4**), *N*,*N*-dimethylaniline (**5**), and 4-nitroaniline (**6**) were of the purest grade available (Lancaster and Aldrich) and used as supplied. The preparation of 4-methoxycarbonyl-1-methylpyridinium perchlorate (**7**) is described in ref 30. 4-Benzoyl-1-methylpyridinium perchlorate (**8**) was synthesized by reacting isonicotinophenone with dimethyl sulfate. The compounds 2,4,6-triphenylthiopyrylium perchlorate (**9**) and 2,4,6-triphenyl-1-methylpyridinium perchlorate (**10**) were both prepared from 2,4,6-triphenylpyrylium perchlorate as described in ref 31. To obtain **9**, 2,4,6-triphenylpyrylium perchlorate was treated with sodium sulfide,[32] while in the case of **10** it was allowed to react with glycine.[33] The neutral radicals **11**−**14** were generated electrochemically during the cyclic voltammetric scan from the pertinent cations **7**−**10**, i.e., the redox features of **11**−**14** could be characterized by studying the second redox waves of **7**−**10**. All other compounds were of commercial origin.

Instrumentation. In the normal cyclic voltammetric experiments (sweep rate $\nu < 30$ V s^{-1}) a three-electrode setup was employed with a glassy carbon (o.d. = 1 mm) or a gold electrode (o.d. = 1 mm) serving as working electrode. The reference electrode applied was Ag/AgI, I^- = 0.1 M, but all potentials measured were also referenced against the ferrocenium/ferrocene (Fc$^+$/Fc) redox couple. A platinum coil was used as counter electrode. The ohmic drop was compensated with a positive feedback system incorporated in the home-built potentiostat. In fast cyclic voltammetry (500 V s^{-1} < ν < 3 kV s^{-1}) the working electrode was a gold ultra-microelectrode (Ø = 25 μm).

Procedures. In normal cyclic voltammetry standard potentials were measured as the midpoint between the cathodic and anodic peak potentials against the Fc$^+$/Fc redox couple for three different sweep rates, typically 0.1, 1, and 10 V s^{-1}. All systems were well-behaved exhibiting a peak separation of less than 100 mV. The same procedure was employed in the fast cyclic voltammetric experiments using sweep rates until 3 kV s^{-1} but with a substantially larger uncertainty as the peak separation amounted to as much as 100−400 mV. The measurements were not influenced by the working electrode material. For instance, the value of the standard potential of **8** in methanol was found to be essentially the same at both glassy carbon ($E° = -1.000$ V vs Fc$^+$/Fc) and gold ($E° = -0.992$ V vs Fc$^+$/Fc). In THF, the corresponding numbers were −1.099 and −1.095 V vs Fc$^+$/Fc, respectively. For compounds **1**, **3** and **5** the voltammograms appeared irreversible at all accessible sweep rates and accordingly we have listed the peak potentials obtained at $\nu = 0.5$ V s^{-1} in these cases. The standard potentials of the radical species **11**−**14** were measured from the second waves recorded in the cyclic voltammograms of the corresponding cationic compounds **7**−**10**. The reduction wave pertaining to **12** was irreversible in methanol and ethanol unless the switch potential was adjusted at the background reduction. Apparently, the use of such a large overpotential increased the basicity of the solution at the vicinity of the electrode surface thereby preventing the protonation of the anion.

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References and Notes

(1) Reichardt, C. In *Solvents and Solvent Effects in Organic Chemistry*, 2nd ed.; VCH: Weinheim, Germany, 1988.

(2) Shalev, H.; Evans, D. H. *J. Am. Chem. Soc.* **1989**, *111*, 2667.

(3) Jonsson, M.; Houmam, A.; Jocys, G.; Wayner, D. D. M. *J. Chem. Soc., Perkin Trans. 2*, **1999**, 425.

(4) Pearson, R. G. *J. Am. Chem. Soc.* **1986**, *108*, 6109.

(5) Trasatti, S. *Pure Appl. Chem.* **1986**, *58*, 955.

(6) There are uncertainties with respect to liquid junction potentials and the standard state of the electron and therefore the term "absolute potential" is not strictly correct. However, to avoid confusion we have adopted the terminology as suggested by Pearson (ref 4).

(7) Baker, M. V.; Kraatz, H.-B.; Quail, J. W. *New. J. Chem.* **2001**, *25*, 427.

(8) Sahami, S.; Weaver, M. J. *J. Solution Chem.* **1981**, *10*, 199.

(9) Marcus, Y. *Chem. Soc. Rev.* **1993**, 409 and references therein.

(10) Kamlet, M. J.; Abboud, J.-L. M.; Abraham, M. H.; Taft, R. W. *J. Org. Chem.* **1983**, *48*, 2877.

(11) Fawcett, W. R. In *Quantitative Treatments of Solute/Solvent Interactions*; Politzer, P., Murray, J. S., Eds.; Elsevier, Amsterdam, 1994; pp 183−212.

(12) Koppel, I. A.; Palm, V. A. In *Advances in Linear Free Energy Relationships*; Chapman, N. B., Shorter, J. Eds.; Plenum: London, 1972; Chapter 5.

(13) Drago, R. S. *J. Chem. Soc., Perkin Trans. 2* **1992**, 1827.

(14) Drago, R. S.; Hirsch, M. S.; Ferris, D. C.; Chronister, C. W. *J. Chem. Soc., Perkin Trans. 2* **1994**, 219.

(15) Svaan, M.; Parker, V. D. *Acta Chem. Scand. B* **1981**, *35*, 559.

(16) Svaan, M.; Parker, V. D. *Acta Chem. Scand. B* **1982**, *36*, 351.

(17) Svaan, M.; Parker, V. D. *Acta Chem. Scand. B* **1982**, *36*, 357.

(18) Svaan, M.; Parker, V. D. *Acta Chem. Scand. B* **1982**, *36*, 365.

(19) Svaan, M.; Parker, V. D. *Acta Chem. Scand. B* **1984**, *38*, 751.

(20) Svaan, M.; Parker, V. D. *Acta Chem. Scand. B* **1984**, *38*, 759.

(21) Svaan, M.; Parker, V. D. *Acta Chem. Scand. B* **1984**, *38*, 767.

(22) Arnett, E. M.; Venimadhavan, S. *J. Am. Chem. Soc.* **1991**, *113*, 6967.

(23) Barton, A. F. M. *Chem. Rev.* **1975**, *75*, 731.

(24) Eberson, L.; Hartshorn, M. P.; Persson, O. *J. Chem. Soc., Perkin Trans. 2* **1997**, 195.

(25) Eberson, L.; Hartshorn, M. P.; Radner, F.; Persson, O. *J. Chem. Soc., Perkin Trans. 2* **1998**, 59.

(26) Krygowski, T. M.; Fawcett, W. R. *J. Am. Chem. Soc.* **1975**, *97*, 2143.

(27) NIST Standard Reference Database Number 69, July 2001 Release.

(28) Yee, E. L.; Cave, R. J.; Guyer, K. L.; Tyma, P. D.; Weaver, M. J. *J. Am. Chem. Soc.* **1979**, *101*, 1131.

(29) Söderholm, S.; Werner; H. P.; Krzystek, J.; von Schütz, J. U.; Hellberg, J.; Ahlgren, G. *Synth. Met.* **1987**, *20*, 15.

(30) Daasbjerg, K.; Pedersen, S. U.; Lund, H. *Acta Chem. Scand.* **1989**, *43*, 876.

(31) Wizinger, R.; Losinger, S.; Ulrich, P. *Helv. Chim. Acta* **1956**, *39*, 5.

(32) Wizinger, R.; Ulrich, P. *Helv. Chim. Acta* **1956**, *39*, 207.

(33) Katritzky, A. R.; Grzeskowiak, N. E.; Eweiss, N. F.; Elsherbini, E. A. *J. Chem. Soc., Perkin Trans. 1* **1983**, 497.