Solvent effects on redox properties of radical ions[1]

Mats Jonsson,*† Abdelaziz Houmam, Gloria Jocys and Danial D. M. Wayner

Steacie Institute for Molecular Sciences, National Research Council of Canada, Ottawa, Ontario, Canada K1A 0R6

Received (in Cambridge) 4th December 1998, Accepted 28th January 1999

The one-electron reduction potentials of the radical cations of 1,4-diazabicyclo[2.2.2]octane (DABCO) and *N*,*N*,*N*′,*N*′-tetramethylphenylene-1,4-diamine (TMPD) in propan-2-ol, ethanol, methanol, acetone, acetonitrile and dimethyl sulfoxide have been measured by cyclic voltammetry. Furthermore, the one-electron reduction potentials of 1,4-benzoquinone, 1,4-benzoquinone radical anion, methyl viologen dication and methyl viologen radical cation also have been measured in a number of solvents. The present results, together with previously published data on radical anions, have been used to evaluate solvent effects in view of the Kamlet–Taft relationship. The main factors affecting the magnitude of the solvent effects are the gas-phase redox properties of the corresponding neutral molecule (ionization potential and electron affinity) and the charge. In general, the magnitude of the solvent effects on solution redox properties of radical ions decreases with increasing redox stability of the radical ion, reflected by low ionization potential of the corresponding neutral molecule for radical cations and by high electron affinity of the corresponding molecule for radical anions.

Introduction

Solvent effects on reaction kinetics and mechanisms have been a subject of interest for a number of years.[2] In recent years, this has also become a topic of interest in the field of radical chemistry.[3,4] An understanding of the effects of the local environment (which includes solvation) on both reaction kinetics and thermodynamic properties of reactants, products and intermediates is of vital importance for the interpretation and prediction of data for complex chemical systems such as those found in heterogeneous and interfacial systems (*e.g.*, heterogeneous catalysts, enzymes, biological membranes). Furthermore, this knowledge provides a useful basis for the design or optimization of new chemical processes.

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).[5] One of the most successful relationships has been found to be the Kamlet–Taft expression [eqn. (1)], where XYZ is the property of interest,

$$XYZ = XYZ_0 + a\alpha + b\beta + s\pi^* + h\delta_H \qquad (1)$$

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, *i.e.*, its ability to donate a proton in a solvent-to-solute hydrogen bond, 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.[5,6] 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 non-specific effects.[7] Alternative approaches which separate specific and non-specific effects have also been elaborated, *e.g.*, by Koppel and Palm[2,7,8] and more recently by Drago and co-workers.[9,10]

In a recent study we found that the one-electron reduction potentials of some aromatic amine radical cations appear to vary with the dipolarity/polarizability of the solvent (as given by the π^* scale).[11] Studies on the redox properties of other radical cations have revealed similar trends.[12–14] Unfortunately, all these observations are based on measurements in only a few solvents where the difference in dipolarity/polarizability is rather small. In order to explore the generality of these effects and other possible effects we have extended the solvent dipolarity/polarizability range used in previous studies and have measured the reduction potentials of the radical cations of 1,4-diazabicyclo[2.2.2]octane (DABCO) and *N*,*N*,*N*′,*N*′-tetramethylphenylene-1,4-diamine (TMPD) in propan-2-ol, ethanol, methanol, acetone, acetonitrile and dimethyl sulfoxide by cyclic voltammetry.

In general, one-electron oxidation of organic molecules initially results in the formation of radical cations that are often very reactive. The relative stability of a radical cation in solution (which often parallels its reactivity) is reflected by its one-electron reduction potential, $E°$, [reaction (2)] and, provided the

$$\mathrm{RH} \rightleftharpoons \mathrm{RH}^{\bullet +} + \mathrm{e}^- \qquad (2)$$

homolytic bond dissociation enthalpies $D°(\mathrm{R{-}H})$ are similar, by its $\mathrm{p}K_a$ [reaction (3)].

$$\mathrm{RH}^{\bullet +} \rightleftharpoons \mathrm{R}^{\bullet} + \mathrm{H}^+ \qquad (3)$$

The $E°$ values are approximately related to the corresponding gas-phase ionization potentials, IP, *via* eqn. (4) where the constant, 4.44 (±0.02) eV,[15] is the absolute potential of the hydrogen electrode in water,[16,17] $\Delta G°_{\mathrm{solv}}(\mathrm{RH})$ and $\Delta G°_{\mathrm{solv}}(\mathrm{RH}^{\bullet +})$ are the free energies of solvation of the neutral molecule and the radical cation, respectively, and F is the Faraday constant. It should be noted that the ionization potential is the enthalpy of ionization at 0 K; thus, the ionization entropy and the temperature correction are neglected in eqn. (4). However, these corrections are assumed to be fairly small. As can be seen from

$$\mathrm{IP} \approx 4.44(\pm 0.02) + E° + \frac{\Delta G°_{\mathrm{solv}}(\mathrm{RH}) - \Delta G°_{\mathrm{solv}}(\mathrm{RH}^{\bullet +})}{F} \qquad (4)$$

---

† Visiting Scientist 1995/96. Present address: Department of Chemistry, Nuclear Chemistry, Royal Institute of Technology, S-100 44 Stockholm, Sweden.

Table 1 Experimental and predicted one-electron reduction potentials in V relative to ferrocene

Solvent	$DABCO^{\bullet +}/DABCO$	$TMPD^{\bullet +}/TMPD$	$BQ/BQ^{\bullet -}$	$BQ^{\bullet -}/BQ^{2-}$	$MV^{2+}/MV^{\bullet +}$	$MV^{\bullet +}/MV$
i-PrOH	0.46 (0.46)^a (0.44)^b	−0.24 (−0.25)^c (−0.25)^d	−0.825 (−0.75)^e (−0.82)^f	−1.365 (−1.46)^g (−1.37)^h	—	—
EtOH	0.43 (0.43)^a (0.44)^b	−0.26 (−0.26)^c (−0.26)^d	—	—	—	—
THF	—	—	−1.025 (−1.04)^e (−1.11)^f	−1.655 (−1.75)^g (−1.66)^h	—	—
MeOH	0.44 (0.43)^a (0.45)^b	−0.26 (−0.27)^c (−0.26)^d	−0.565 (−0.54)^e (−0.66)^f	—	−0.825 (−0.81)^i	−1.282 (−1.27)^j
Acetone	0.30 (0.30)^a (0.31)^b	−0.28 (−0.28)^c (−0.28)^d	—	—	—	—
MeCN	0.35 (0.35)^a (0.34)^b	−0.28 (−0.28)^c (−0.28)^d	−0.885 (−0.82)^e (−0.94)^f	−1.610 (−1.71)^g (−1.61)^h	−0.835 (−0.85)^i	−1.240 (−1.27)^j
DMF	—	—	−0.905 (−0.87)^e (−0.96)^f	−1.710 (−1.81)^g (−1.70)^h	−0.900 (−0.89)^i	−1.280 (−1.27)^j
DMSO	0.25 (0.25)^a (0.24)^b	−0.30 (−0.30)^c (−0.31)^d	−0.835 (−0.83)^e (−0.90)^f	−1.700 (−1.81)^g (−1.71)^h	−0.920 (−0.92)^i	−1.270 (−1.27)^j

[a] Predicted from eqn. (6). [b] Predicted from eqn. (8). [c] Predicted from eqn. (7). [d] Predicted from eqn. (9). [e] Predicted from eqn. (15). [f] Predicted from eqn. 17. [g] Predicted from eqn. (16). [h] Predicted from eqn. (18). [i] Predicted from eqn. (13). [j] Predicted from eqn. (14).

the above equation, the parameters that govern the one-electron reduction potential of a radical cation are the difference in solvation free energy between the neutral molecule and the corresponding radical cation and the gas-phase ionization potential of the neutral molecule. Thus, differences in redox properties of radical cations in different solvents are due to differences in solvation and it is therefore reasonable to expect that solvent effects on redox potentials should follow linear solvation energy relationships.

One-electron reduction of neutral molecules usually results in formation of radical anions [reaction (5)].

$$RH + e^- \rightleftharpoons RH^{\bullet -} \qquad (5)$$

The one-electron reduction potential is related to the gas-phase electron affinity *via* an equation analogous to eqn. (4). Thus, solvent effects on the redox properties of radical anions directly reflect differences in solvation. Solvent effects on the one-electron reduction potentials of a number of neutral species have been thoroughly studied by Shalev and Evans.[18]

In this work, we have used our redox data for radical cations together with data for radical anions from Shalev and Evans to explore the applicability of the Kamlet–Taft expression to redox properties. Furthermore, we have measured the reduction potentials of 1,4-benzoquinone and the 1,4-benzoquinone radical anion and the first and second reduction potentials of methyl viologen in various solvents in order to study the solvation effects on the doubly charged anion and cation.

We have focused our attention on the applicability of the Kamlet–Taft expression on radical ions without trying to separate specific and non-specific effects. The objective of this work has been to find practically useful linear solvation energy relationships and to establish the physico-chemical properties of the solute radical ions governing the magnitude of these solvent effects.

Experimental

Cyclic voltammetry was performed with a PAR 273A Potentiostat/Galvanostat interfaced to a base PC using the EG&G Model 270 software package. The cell was a standard three electrode setup using a 3 mm diameter glassy carbon working electrode, a platinum coil counter electrode and a reference electrode consisting of a silver wire in a glass tube containing a 0.1 M solution of tetrabutylammonium perchlorate (TBAP) in acetonitrile. All solvents were of the purest grade available (Omnisolv). Acetonitrile was distilled from CaH_2 under 1 atm of argon prior to use. *N*,*N*-Dimethylformamide was distilled under reduced pressure from CaH_2. Acetone and methanol were distilled. THF was refluxed and distilled from P_2O_5 then from KOH and finally distilled over potassium. Propan-2-ol was refluxed with CaO and distilled. The supporting electrolyte, TBAP, was recrystallized three times from 10% hexane in ethyl acetate and dried in a vacuum oven (40 °C, 10 Torr). TBAP (0.1 M) was used as supporting electrolyte in all solvents except in propan-2-ol where 0.1 M $LiClO_4$ was used. All potentials were measured with respect to ferrocene as an internal reference. Full IR compensation was employed in all measurements. It was assumed that the solvent effect on the potential of ferrocene was small. For potential calibration ferrocene was used ($E° = 0.69$, 0.72 and 0.68 V *vs.* NHE in acetonitrile, DMF and DMSO, respectively).[19]

Results and discussion

The measured one-electron redox potentials (peak oxidation potential of DABCO and half-wave oxidation/reduction potentials of TMPD, 1,4-benzoquinone, 1,4-benzoquinone radical anion, methyl viologen dication and methyl viologen radical cation) relative to ferrocene are given in Table 1. The solvatochromic parameters α, β, π^* and δ_H for the solvents used in this study are given in Table 2.

The standard potentials in Table 1 are reported with respect to ferrocenium/ferrocene which was used as an internal reference. It has been pointed out that there are only small variations in the standard potential of ferrocenium in a number of aprotic solvents ($E° = 0.71 \pm 0.03$ V *vs.* NHE).[19] Small differences in the reported values have been attributed to changes in liquid junction potential. For the purposes of the following discussion, we will assume the redox potential of ferrocene to be invariant with solvent and use the average value suggested by Sawyer and co-workers.[19] While this assumption is not rigorously correct, the difference in redox potential for ferrocene

Table 2 Solvent parameters used in the Kamlet–Taft equation

Solvent	π^{*a}	α^a	β^a	$\delta_H{}^b$
i-PrOH	0.48	0.76	0.84	11.5
EtOH	0.54	0.86	0.75	12.7
THF	0.58	0	0.55	9.1
MeOH	0.60	0.98	0.66	14.5
Acetone	0.71	0.08	0.43	9.9
MeCN	0.75	0.19	0.40	11.9
DMF	0.88	0	0.69	12.1
DMSO	1	0	0.76	12

[a] Ref. 6. [b] Ref. 20.

between different solvents is small compared to the potential differences relevant to the analysis below.

Radical cations

Admittedly, the number of solvents used in this study (six) is not statistically sufficient for a fit to a four parameter equation. Bearing this in mind, multilinear regression of the potentials of DABCO and TMPD result in eqn. (6) and (7).

$$\Delta E^\circ_{\mathrm{DABCO}} = 0.27(\pm 0.02) - 0.34(\pm 0.04)\alpha + 0.17(\pm 0.02)\beta - 0.93(\pm 0.06)\pi^* + 0.065(\pm 0.005)\delta_H \quad (6)$$

$$\Delta E^\circ_{\mathrm{TMPD}} = -0.24(\pm 0.04) - 0.08(\pm 0.08)\alpha + 0.05(\pm 0.03)\beta - 0.22(\pm 0.12)\pi^* + 0.01(\pm 0.01)\delta_H \quad (7)$$

The redox potentials predicted from these equations are given in Table 1. For the multilinear regressions we get the following statistical parameters: $r^2 = 0.999$ and $F = 873$ for DABCO and $r^2 = 0.98$ and $F = 13$ for TMPD. The standard errors in the predicted potentials are 0.003 and 0.006 V for DABCO and TMPD, respectively. As can be seen in the equation for DABCO, the dominating contributions to the solvent effect are those of the solvent dipolarity/polarizability and the Hildebrand solubility parameter. Note that the Hildebrand solubility parameter is 10–20 times larger than the other solvatochromic parameters, thus, even though the coefficient, *h*, is smaller than the coefficients *a* and *b*, the impact is higher. We have therefore also performed multilinear regression using a reduced form of the Kamlet–Taft expression containing only the two most significant parameters. This resulted in eqn. (8) and (9).

$$\Delta E^\circ_{\mathrm{DABCO}} = 0.41(\pm 0.08) - 0.40(\pm 0.05)\pi^* + 0.019(\pm 0.006)\delta_H \quad (8)$$

$$\Delta E^\circ_{\mathrm{TMPD}} = -0.21(\pm 0.03) - 0.11(\pm 0.02)\pi^* + 0.001(\pm 0.002)\delta_H \quad (9)$$

The redox potentials predicted from these equations are also given in Table 1 for comparison. For the multilinear regressions we get the following statistical parameters: $r^2 = 0.97$ and $F = 51$ for DABCO and $r^2 = 0.93$ and $F = 19$ for TMPD. The standard errors in the predicted potentials are 0.02 and 0.007 V for DABCO and TMPD, respectively which are comparable to experimental errors in their determinations.

In Fig. 1 we have plotted the one-electron reduction potentials of the radical cations of DABCO and TMPD (*vs.* $Fc^{\cdot +}/Fc$) predicted from eqn. (8) and (9) against the corresponding experimental numbers. Roughly, the one-electron reduction potentials of the radical cations of both DABCO and TMPD decrease with increasing solvent dipolarity/polarizability.

Table 3 Effects of solvent polarity on the one-electron reduction potential of some radical cations

Radical cation	IP[22]	$\Delta E/\Delta\pi^*$
$CH_3OC_6H_5{}^{\cdot +}$	8.2	-1.12^a
$1,2\text{-}(CH_3O)_2C_6H_4{}^{\cdot +}$	7.8	-0.74^a
$1,4\text{-}(CH_3O)_2C_6H_4{}^{\cdot +}$	7.56	-0.82^a
$1,2,4\text{-}(CH_3O)_3C_6H_3{}^{\cdot +}$	7.5	-0.68^a
$DABCO^{\cdot +}$	7.32	-0.38
$TMPD^{\cdot +}$	6.1	-0.10
$(C_6H_5)_2NH^{\cdot +}$	7.19	-0.64^b
$C_6H_5NHCH_3{}^{\cdot +}$	7.32	-0.45^b
$C_6H_5NH_2{}^{\cdot +}$	7.72	-0.76^b

[a] Calculated from data given in ref. 12 and 23. [b] Calculated from data given in ref. 11.

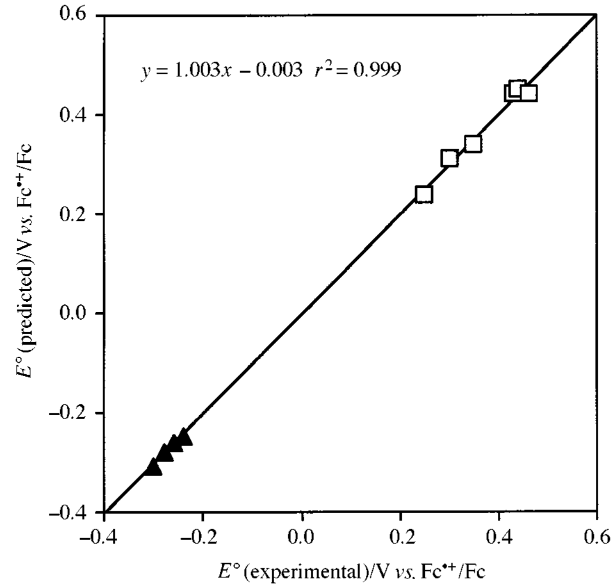

Fig. 1 The one-electron reduction potentials of the radical cations of DABCO (squares) and TMPD (filled triangles) predicted from eqn. (8) and (9), respectively, plotted against the corresponding experimental values.

It has previously been suggested that the higher the gas-phase ionization potential, the more localized is the charge on the radical cation which, in turn, leads to a more exergonic solvation of the radical cation.[21] Thus, the solvent has a leveling effect on the reduction potential, *i.e.* the difference in potential between two radical cations decreases when going from the gas phase to solution. This is also reflected by the difference in the magnitude of substituent effects on reduction potentials in different solvents. It is reasonable to expect that a stronger solvation would also result in an increased sensitivity to changes in solvent properties. The gas-phase ionization potential of DABCO is 7.32 eV[22] and that of TMPD is 6.1 eV[22] and, as expected, the magnitude of the solvent effects on the one-electron reduction potential of the corresponding radical cations is higher for DABCO. Using these data together with some previously published data[11,12,23] we can qualitatively check the relationship between ionization potential and the magnitude of the solvent effect for nine radical cations. For most of these radical cations, redox data are only available for two or three solvents. To quantify the solvent effects we have therefore simply used $\frac{\Delta E^\circ}{\Delta\pi^*}$. The magnitude of the solvent effects on the one-electron reduction potentials of the radical cations and the gas-phase ionization potentials of the corresponding neutral molecules are given in Table 3. The relationship between the magnitude of the substituent effect and the ionization potential is illustrated in Fig. 2 and the linear trend is given by eqn. (10).

$$\frac{\Delta E^\circ}{\Delta\pi^*} = 2.8(\pm 0.6) - 0.46(\pm 0.08)\mathrm{IP} \quad (10)$$

The statistical parameters for the linear regression are $r^2 = 0.82$, $F = 33$ and the standard deviation is 0.13. Despite

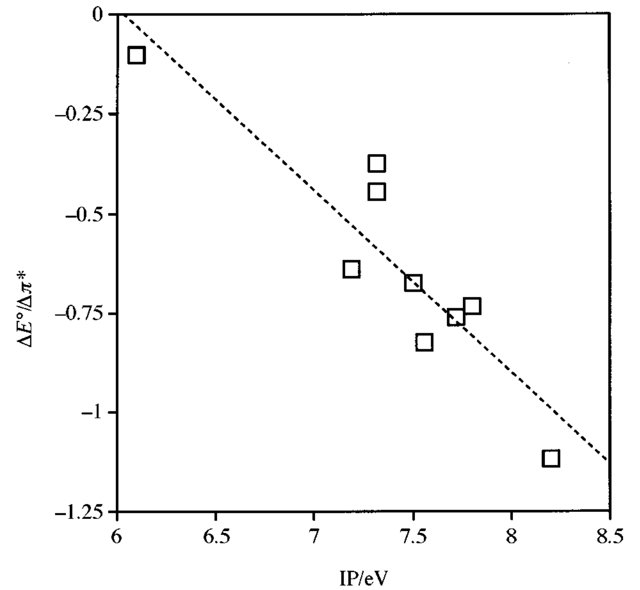

Fig. 2 The magnitude of solvent effects on the one-electron reduction potentials of radical cations plotted against the gas-phase ionization potentials of the corresponding neutral molecules.

the fact that these compounds are of a very different nature (aromatic and non-aromatic amines and methoxybenzenes), we obtain a linear trend. Clearly, this trend agrees with the above suggestion.

The two one-electron reduction steps of methyl viologen [reactions (11) and (12)] are relatively insensitive to differences in solvent properties.

$$MV^{2+} + e^{-} \rightleftharpoons MV^{\cdot +} \qquad (11)$$

$$MV^{\cdot +} + e^{-} \rightleftharpoons MV \qquad (12)$$

Multilinear regression of these two sets of data resulted in reduced Kamlet–Taft equations [eqn. (13) and (14)]. The redox

$$\Delta E°(MV^{2+}) = -0.6(\pm 0.2) - 0.28(\pm 0.15)\pi^{*} - 0.001(\pm 0.004)\delta_{H} \qquad (13)$$

$$\Delta E°(MV^{\cdot +}) = -1.25(\pm 0.2) - 0.01(\pm 0.2)\pi^{*} - 0.0005(\pm 0.006)\delta_{H} \qquad (14)$$

potentials predicted from these equations are also given in Table 1 for comparison. For the multilinear regressions we get the following statistical parameters: $r^2 = 0.91$ and $F = 5.2$ for MV^{2+} and $r^2 = 0$ and $F = 0$ for $MV^{\cdot +}$, *i.e.* no correlation in the latter case. The standard error in the predicted potentials is 0.02 for MV^{2+}.

For the first reduction step the solvent effect is significant which indicates that, as expected, the solvation free energy of the dication, MV^{2+} is more strongly solvent dependent than the solvation free energy of the radical cation, $MV^{\cdot +}$. Thus, the solvent dependence appears to increase with the charge of the cation. In fact, this agrees with the suggestion that the solvation energy of more strongly solvated species is more sensitive to differences in solvent properties.

From eqn. (14) and the data in Table 1 we see that the second reduction step is virtually solvent independent which is well in line with the previously presented trend (Fig. 2) since this reduction step corresponds to a low ionization potential.

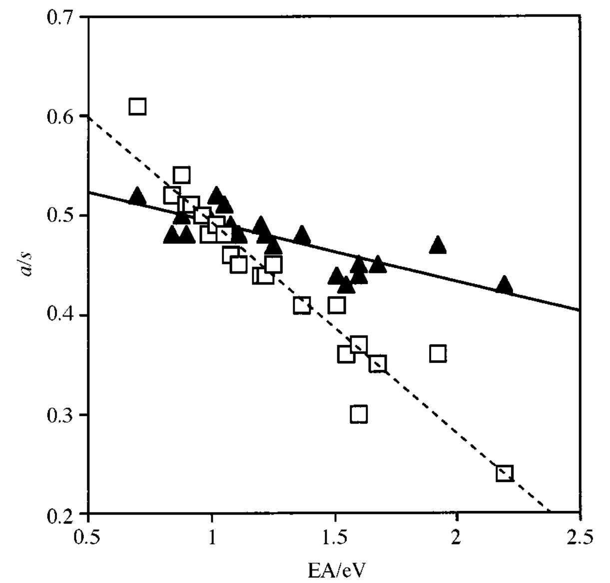

Fig. 3 The magnitude of the effects of solvent hydrogen bond donation ability, a, and solvent dipolarity/polarizability, s, on the one-electron reduction potentials of 22 nitrobenzenes plotted against the gas-phase electron affinities, EA, of the nitrobenzenes.

Radical anions

Applying the Kamlet–Taft equation to the first and second reduction steps for 1,4-benzoquinone (Table 1) results in eqn. (15) and (16). As for the radical cations, there are not enough data for a four parameter equation. For the multilinear regression of the first reduction step we get the following statistical parameters: $r^2 = 0.96$ and $F = 6.7$. For the second reduction step we do not have enough data to get any statistics. The potentials predicted using eqn. (15) and (16) are also given in Table 1.

$$\Delta E°(BQ) = -1.4(\pm 0.5) + 0.4(\pm 0.5)a - 0.09(\pm 0.3)\beta + 0.4(\pm 0.8)\pi^{*} + 0.02(\pm 0.08)\delta_{H} \qquad (15)$$

$$\Delta E°(BQ^{-}) = -1.5 + 0.5a - 0.05\beta + 0.09\pi^{*} - 0.03\delta_{H} \qquad (16)$$

As can be seen from eqn. (15), the hydrogen bond donor (HBD) ability, a, and the solvent dipolarity/polarizability, π^*, are the dominating contributions to the solvent effects. Using a reduced Kamlet–Taft equation containing only these two parameters we obtain eqn. (17) and (18).

$$\Delta E°(BQ) = -1.4(\pm 0.1) + 0.45(\pm 0.06)a + 0.5(\pm 0.1)\pi^{*} \qquad (17)$$

$$\Delta E°(BQ^{-}) = -1.59(\pm 0.04) + 0.37(\pm 0.03)a - 0.12(\pm 0.04)\pi^{*} \qquad (18)$$

For the multilinear regressions we get the following statistical parameters: $r^2 = 0.95$ and $F = 28$ for the first reduction step and $r^2 = 0.996$ and $F = 242$ for the second reduction step. The standard errors in the predicted potentials are 0.04 and 0.01 V for the first and second reduction step, respectively. The potentials predicted using eqn. (17) and (18) are also given in Table 1. From eqn. (18) we can draw the conclusion that the solvent dependence on the free energy of solvation of the dianion is stronger than for the monoanion, analogous to the cation case.

In the original paper, Shalev and Evans found a correlation between the one-electron reduction potential and the solvent acceptor number (AN).[18] Here, we have applied the reduced Kamlet–Taft equation (*i.e. versus* π^* and a) to their original data on the one-electron reduction potentials of 22 nitrobenzenes in five different solvents. The resulting parameters are given in Table 4 along with the corresponding electron affinities. For the multilinear regressions we get the following range of statistical parameters: $r^2 = 0.991$–0.999 and $F = 108$–721.

As can be seen, the dipolarity/polarizability contribution is relatively invariant with electron affinity whereas the contribution from the hydrogen bond donor (HBD) ability decreases significantly with increasing electron affinity (Fig. 3).

Table 4 Electron affinities and solvent independent coefficients for nitrobenzenes

Nitrobenzene	EA/eV[24]	*a*	*s*
2,4,6-$(CH_3)_3C_6H_2NO_2$	0.70	0.61	0.52
2,3-$(CH_3)_2C_6H_3NO_2$	0.84	0.52	0.48
4-$CH_3OC_6H_4NO_2$	0.88	0.54	0.50
2-$CH_3C_6H_4NO_2$	0.90	0.51	0.48
4-$CH_3C_6H_4NO_2$	0.92	0.51	0.51
3-$CH_3C_6H_4NO_2$	0.96	0.50	0.50
$C_6H_5NO_2$	0.99	0.48	0.50
3-$CH_3OC_6H_4NO_2$	1.02	0.49	0.52
2-$FC_6H_4NO_2$	1.05	0.48	0.51
4-$FC_6H_4NO_2$	1.08	0.46	0.49
2-$ClC_6H_4NO_2$	1.11	0.45	0.48
3-$FC_6H_4NO_2$	1.20	0.44	0.49
4-$ClC_6H_4NO_2$	1.22	0.44	0.48
3-$ClC_6H_4NO_2$	1.25	0.45	0.47
3-$CF_3C_6H_4NO_2$	1.37	0.41	0.48
3-$CNC_6H_4NO_2$	1.51	0.41	0.44
2-$CNC_6H_4NO_2$	1.55	0.36	0.43
1,3-$(NO_2)_2C_6H_4$	1.60	0.37	0.44
1,2-$(NO_2)_2C_6H_4$	1.60	0.30	0.45
4-$CNC_6H_4NO_2$	1.68	0.35	0.45
1,4-$(NO_2)_2C_6H_4$	1.92	0.36	0.47
3,5-$(NO_2)_2C_6H_3CN$	2.19	0.24	0.43

The trends can be described by eqn. (19) and (20).

$$s = 0.55(\pm 0.01) - 0.06(\pm 0.01)\mathrm{EA} \qquad (19)$$

($F = 40$, $r^2 = 0.67$ and standard error 0.02)

$$a = 0.71(\pm 0.02) - 0.21(\pm 0.01)\mathrm{EA} \qquad (20)$$

($F = 203$, $r^2 = 0.91$ and standard error 0.03)

It is not unexpected that radical anions should be hydrogen bond acceptors. The extent to which they are should be related to the extent of delocalization of the charge; *i.e.* the charge on a radical anion corresponding to a molecule with high electron affinity (more positive standard potential) is generally more delocalized than the charge on a radical anion with a lower electron affinity (more negative standard potential). In the latter case, the more localized charge will lead to a stronger solvent-to-solute hydrogen bond and thereby also to increased sensitivity to the hydrogen bond donation ability of the solvent, *a*. From Table 4 it is also evident that at higher electron affinities the dominating contributor to the solvent effects changes from the hydrogen bond donation ability to the dipolarity/polarizability. The overall solvent effect on the solvation free energy of the radical anion also decreases with increasing electron affinity. This is well in line with the observations on the solvent effects on the solvation free energy of radical cations, *i.e.* the more stable the radical ion is in itself, the less sensitive it is to variations in the solvent properties. This compensating effect of π^* and *a* can also be understood in terms of the more localized (*i.e.* lower EA) anions being better hydrogen bond acceptors.

Conclusions

In this work we have shown that the solvent effects on one-electron reduction potentials of dications, radical cations, neutral molecules and radical anions can be quantitatively described by reduced Kamlet–Taft relationships leading to simple predictive relationships. The main factors affecting the magnitude of the solvent effects are the gas-phase redox properties of the corresponding neutral molecule (ionization potential and electron affinity) and the charge. In general, the magnitude of the solvent effects on solution redox properties of radical ions decreases with increasing redox stability of the radical ion, reflected by low ionization potential of the corresponding neutral molecule for radical cations and by high electron affinity of the corresponding molecule for radical anions. The solvent sensitivity also increases with charge of the ion.

Acknowledgements

M. J. thanks the Swedish Natural Science Research Council for financial support. We also thank the referees for pointing out some serious problems in the original manuscript.

References

1 Issued as NRCC publication No. 40905.
2 C. Reichardt, in *Solvents and Solvent Effects in Organic Chemistry*, 2nd edn., VCH, Weinheim, 1988.
3 J. M. Tanko, in *Chemistry of Double Bonded Functional Groups; Supplement A3*, S. Patai (ed.), Wiley, New York, 1997.
4 L. Valgimigli, J. T. Banks, K. U. Ingold and J. Lusztyk, *J. Am. Chem. Soc.*, 1995, **117**, 9966.
5 Y. Marcus, *Chem. Soc. Rev.*, 1993, 409 and refs. therein.
6 M. J. Kamlet, J.-L. M. Abboud, M. H. Abraham and R. W. Taft, *J. Org. Chem.*, 1983, **48**, 2877.
7 W. R. Fawcett, in *Quantitative Treatments of Solute/Solvent Interactions*, P. Politzer and J. S. Murray (ed.), Elsevier, Amsterdam, 1994, pp. 183–212.
8 I. A. Koppel and V. A. Palm, in *Advances in Linear Free Energy Relationships*, N. B. Chapman and J. Shorter, ed., Plenum, London, 1972, Ch. 5.
9 R. S. Drago, *J. Chem. Soc.*, *Perkin Trans. 2*, 1992, 1827.
10 R. S. Drago, M. S. Hirsch, D. C. Ferris and C. W. Chronister, *J. Chem. Soc.*, *Perkin Trans. 2*, 1994, 219.
11 M. Jonsson, D. D. M. Wayner and J. Lusztyk, *J. Phys. Chem.*, 1996, **100**, 17539.
12 M. Jonsson, J. Lind, T. Reitberger, T. E. Eriksen and G. Merényi, *J. Phys. Chem.*, 1993, **97**, 11278.
13 M. Jonsson, J. Lind, G. Merényi and T. E. Eriksen, *J. Chem. Soc.*, *Perkin Trans. 2*, 1995, 67.
14 L. Engman, J. Persson, C. M. Andersson and M. Berglund, *J. Chem. Soc.*, *Perkin Trans. 2*, 1992, 1309.
15 S. Trasatti, *Pure Appl. Chem.*, 1986, **58**, 955.
16 R. G. Pearson, *J. Am. Chem. Soc.*, 1986, **108**, 6109.
17 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 this terminology as suggested by Pearson (ref. 16).
18 H. Shalev and D. H. Evans, *J. Am. Chem. Soc.*, 1989, **111**, 2667.
19 W. C. Barrette, H. W. Johnson Jr. and D. T. Sawyer, *Anal. Chem.*, 1984, **56**, 1890.
20 A. F. M. Barton, *Chem. Rev.*, 1975, **75**, 731.
21 D. D. M. Wayner, B. A. Sim and J. J. Dannenberg, *J. Org. Chem.*, 1991, **56**, 4853.
22 NIST Standard Reference Database Number 69-March 1998 Release.
23 A. Zweig, W. G. Hodgson and W. H. Jura, *J. Am. Chem. Soc.*, 1964, **86**, 4124.
24 S. Chowdhury, E. P. Grimsrud and P. Kebarle, *J. Phys. Chem.*, 1987, **91**, 2551.

Paper 8/09499C