Solvation model for inner-sphere nuclear reorganization in the photoionization of univalent anions in solution[§]

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Abstract. The energy of inner-sphere reorganization for the photoionization of univalent anions in aqueous solution is calculated from a discrete model of solvation. A multipole expansion is used to account for electrostatic interactions, and only the terms corresponding to nuclear motion are retained in the expansion to the exclusion of induced moments. London dispersion, Born repulsion, cavity formation and hydrogen bonding are also taken into account. The theory is applied to eight inorganic anions. Calculated reorganization energies are compared to experimental values deduced from threshold energies for photoelectron emission by aqueous solutions of eight anions in the 6 to 11 eV range of photon energies. Standard reduction potentials for the corresponding radical-anion couples are calculated from threshold energies and theoretical reorganization energies.

Keywords. Anion; electron transfer; inner sphere; nuclear reorganization; outer sphere; photoelectron emission; radical; solvation; threshold energy.

1. Introduction

It is a pleasure to dedicate this paper to our distinguished colleague, K S G Doss, on the occasion of his eightieth birthday and as a tribute to his contributions to science and to electrochemistry in particular. The recently developed theory of inner-sphere reorganization (Delahay and Dziedzic 1986a) will be applied to the photoionization of eight inorganic univalent anions not previously considered. The results will be used in the calculation of the standard reduction potentials for radical-anion couples in solution. A brief introduction to photoelectron spectroscopy of aqueous solutions will be given first. Further details on this method can be found in an extensive review (Delahay 1984).

2. Photoelectron spectroscopy of aqueous solutions

Optical electron transfer can be investigated by measuring the current for photoelectron emission by aqueous solutions (salts, molecules) as a function of the photon energy E (6 to 11 eV). The current is measured by collecting electrons by means of an electrode in the gas phase above the liquid. A rotating disk target (figure 1) is used for continuous renewal of the irradiated surface of the solution. The yield is calculated as the number of collected electrons per incident photon,

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[§] Dedicated to Prof. K S G Doss on his eightieth birthday
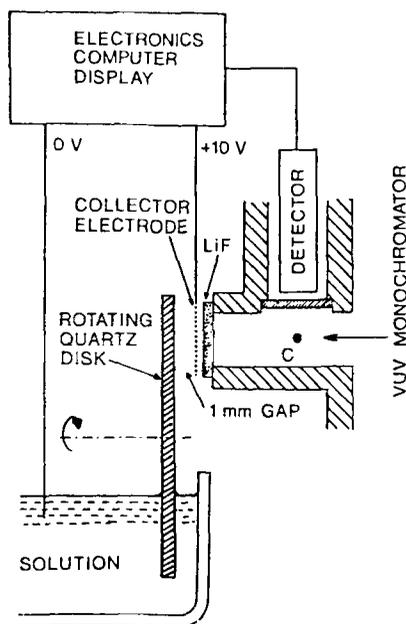* To whom all correspondence should be addressed.

Figure 1. Schematic diagram of instrument for the determination of emission spectra (Delahay 1982).

and results are displayed as a plot of the yield Y as a function of photon energy E (figure 2, curve A).

Theory (Brodsky and Tsarevsky 1976; Brodsky 1980) predicts and experiment confirms that plots of $Y^{1/2}$ against E are linear and extrapolate to the threshold energy E_t (figure 2, line B). The exponent 1/2 of the yield Y generally holds at photon energies exceeding the threshold energy by a few tenths of electronvolt (Brodsky 1980). Plots of $Y^{1/2}$ against E exhibit a fine structure consisting of "wiggles." This fine structure, which is primarily determined by the nature of the solvent, results from a nonequilibrium electronic contribution to the energetics of photoionization on account of dielectric dispersion (Delahay and Dziedzic 1986b). The effect of this contribution, in general, averages out over the usual extrapolation range 7 to 10 eV for aqueous solutions and represents a rather negligible (< 0.1 eV) error on threshold energies obtained by extrapolation from plots of $Y^{1/2}$ against E. This effect therefore is neglected in the following treatment. However, in the case of nonaqueous solvents the dispersion contribution may not be negligible and must be considered.

Threshold energies of some common inorganic anions in aqueous solution are listed in table 1. All these values are below the threshold energy of liquid water, $E_t = 10.06$ eV, except for the fluoride ion. The value $E_t = 10.6$ eV for this anion was recently determined by subtracting at each photon energy the emission yield for water from the total yield measured for a 5 M potassium fluoride solution (Delahay and Dziedzic 1986a). A platinum rotating disk and a plastic-lined cell were used to avoid spurious emission resulting from leaching of glass under the action of fluoride solution.
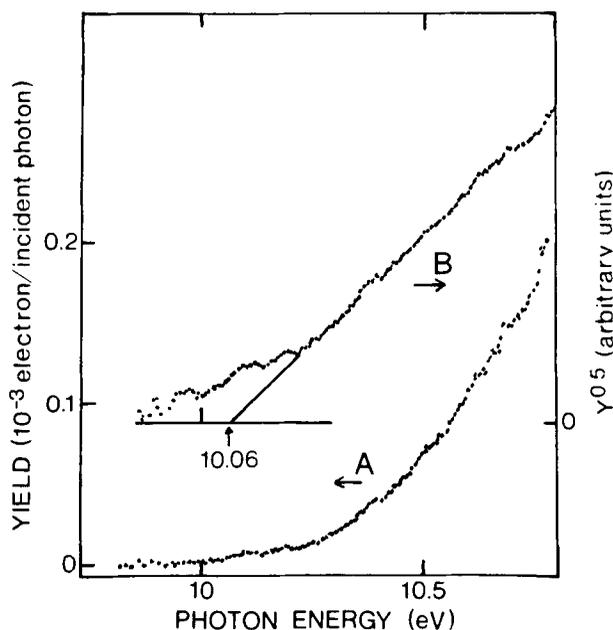
Figure 2. Photoelectron emission spectrum of liquid water at 1·5°C consisting of the plot of the yield Y against the photon energy E (curve A). Plot of $Y^{1/2}$ against E (line B). Extrapolated threshold energy $E_t = 10·06$ eV (Delahay and von Burg 1981).

Table 1. Experimental threshold energies (eV) of anions in aqueous solution*.

OH^- (8·6)
F^- (10·6), Cl^- (8·9), Br^- (8·15), I^- (7·4)
ClO_3^- (8·2), BrO_3^- (7·9), IO_3^- (7·4)
ClO_4^- (8·5)
NO_2^- (7·6), NO_3^- (8·5), N_3^- (7·4)
HCO_3^- (9·1), SCN^- (7·2)

*From Delahay and Dziedzic 1984a; Delahay and Dziedzic 1986a.

## 3. Energetics of photoionization in aqueous solution

3.1 *Threshold energy*

The following basic equation for the threshold energy E_t for photoionization emission by anions in aqueous solution is derived from a thermodynamic cycle and consideration of nuclear reorganization (von Burg and Delahay 1981; Delahay 1984):

$$E_t = \Delta G_H + \Delta G + R + |e|\Delta\chi \tag{1}$$

where the free energies $\Delta G_H (= 4·48$ eV) and ΔG pertain, respectively, to the

reactions

$$1/2H_2(g) = H^+(aq) + e^-(g),$$ (2)

$$A^-(aq) + H^+(aq) = A(aq) + 1/2H_2(g);$$ (3)
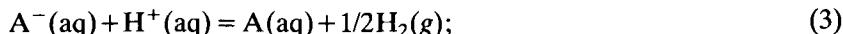
R is the free energy for nuclear reorganization of the product of photoionization; and $\Delta\chi$ is the difference between the surface potentials of the solution of A^- (aq) and water. The last term in (1) is generally very small (< 0.05 eV) and can be neglected. The contribution to E_t from nonequilibrium electronic polarization arising from dielectric dispersion is not included in (1) because it is generally negligible as noted in §2. The threshold energy E_t is equated in (1) to the free energy for electron emission. Equation (1) will be applied in §6.

The threshold energy E_t is also related to the electron affinity (EA) of the atom or radical $A(g)$ by the following equation derived from a thermodynamic cycle (Delahay 1982):

$$E_t \approx EA + \Delta G_n + \Delta G_s + R$$ (4)

where ΔG_n and ΔG_s are the solvation free energies of the species $A(g)$ and $A^-(g)$, respectively. Equation (4) is approximate because the electron affinity is an enthalpy and the equation should be written in terms of enthalpies rather than free energies. The error can be significant (e.g., 0.5 eV) if the entropy contribution to ΔG_s is important. Equation (4) will be applied in §6.

Equations (1) and (4) give the threshold energy E_t for emission of electrons into the gas phase above the aqueous solution of $A^-(aq)$. The free energy for production of quasifree electrons in the *bulk of liquid water* by photoionization of species $A^-(aq)$ is given by $E_t - V_0$, where V_0 is the difference between the electron vacuum level and the bottom of the conduction band of liquid water. One has $V_0 \sim 1.2$ eV (Gurevich *et al* 1980) and consequently photoionization of a species in aqueous solution begins to occur in aqueous solution at photon energies lower by ≈ 1.2 eV than the threshold energy for emission into the gas phase by this species.

3.2 Free energy of nuclear reorganization

Photoionization of $A^-(aq)$ produces the species denoted by $A(aq)^*$ which initially has the solvation configuration of the ion $A^-(aq)$. Subsequent nuclear reorganization of this *nonequilibrium* solvation configuration yields the atom or radical $A(aq)$ having its equilibrium solvation configuration. The free energy for the spontaneous nuclear reorganization of the solvent about the photoionization product in the process $A(aq)^* \rightarrow A(aq)$ is $-R$, where R is taken to be a positive quantity. Additionally, a significant contribution from vibrational relaxation of $A(aq)^*$ may also be included in this term.

Two regions are distinguished about the ion being photoionized: (i) the inner-sphere region comprising the first layer of solvent molecules around the central ion, and (ii) the outer-sphere region beyond the inner-sphere region generally treated as a continuous medium. The boundary between these two regions is taken to be a sphere of radius

$$a = r_c + 2r_w,$$ (5)

where r_c and r_w are the crystallographic radii of the ion and the solvent, respectively ($r_w = 1 \cdot 38$ Å for water). Furthermore, nuclear motion is supposed to be uncorrelated between the inner- and outer-sphere regions, and consequently one writes

$$R = R_{IN} + R_{OUT} \tag{6}$$

where R_{IN} and R_{OUT} pertain to the inner- and outer-sphere regions, respectively.

The value of R_{OUT} was calculated first by Marcus (1956) who developed the required theory of *nonequilibrium* polarization of a continuous medium. Thus,

$$R_{OUT} = (\varepsilon_{op}^{-1} - \varepsilon_s^{-1})e^2/2a \tag{7}$$

where ε_{op} and ε_s are the optical and dielectric constants of the solvent, respectively, e is the electronic charge, and a is given by (5). The free energy R_{OUT} is determined by the *change* of ionic valence caused by photoionization rather than by the absolute values of the species involved in the photoionization process. Equation (7) shows that the free energy R_{OUT} is the difference between the free energies of electronic and total polarization of the continuous medium. Thus, R_{OUT} is the change in the free energy of orientation polarization of the medium resulting from the change of ionic valence upon photoionization.

The inner-sphere reorganization energy was calculated initially for thermal electron exchange between cations from a harmonic oscillator model of bond stretching (George and Griffith 1959). A transition state was assumed and the corresponding generalized coordinate was obtained by minimizing the energy of activation. This approach is *not* applicable directly to photoionization because no transition state is formed prior to optical electron transfer and there is reorganization about only *one* species, e.g., the ferric ion produced by photoionization of a ferrous ion. Conversely, there is reorganization about *two* species in thermal electron exchange, e.g., about the ferrous and ferric ions between which an electron is exchanged. The energy of inner-sphere reorganization U_{IN} for the photoionization of cations was calculated by Delahay and Dziedzic (1984b) for the harmonic oscillator model, and the resulting values agreed with experiment for hydrated transition metal cations and metal complexes. This matter will not be discussed further since inner-sphere reorganization about anions is treated by using a different model in the next section.

4. Solvation model for inner-sphere reorganization about univalent anions

The close relationship between solvation in the Born model and outer-sphere reorganization can be extended to inner-sphere reorganization in the photoionization of univalent anions (Delahay and Dziedzic 1984a). This relationship was fully developed recently (Delahay and Dziedzic 1986a). Thus, solvation of $A^-(g)$ can be regarded as the formation of a cavity of radius r_i in the solvent and the orientation of N_i solvent molecules in the inner-sphere region of $A^-(aq)$. Conversely, photoelectron emission by a solution of $A^-(aq)$ entails the removal of the charge $e^-(g)$ and a change of the cavity radius from r_i to the value r_f for the radical or atom thus produced. Nuclear reorganization of the inner-sphere shell changes the solvent configuration around the species produced by photoionization. The number of surrounding solvent molecules may also change from N_i to N_f. The energy U_{IN} for

inner-sphere reorganization therefore is

$$U_{\text{IN}} = U^f(\text{nucl}) - U^i(\text{nucl}) \tag{8}$$

where $U^f(\text{nucl})$ and $U^i(\text{nucl})$ represent, respectively, the terms in the equations for the hydration energies of A(aq) and $A^-(\text{aq})$ which correspond *only to nuclear motion* in the hydration of these species. The energy $U^f(\text{nucl})$ in (8) is the nuclear contribution to the solvation energy of the species A(aq) surrounded by the *equilibrium* inner-sphere shell of solvent. The energy $U^i(\text{nucl})$ in (8) is the nuclear contribution from the species A(aq)* surrounded by the *nonequilibrium* inner-sphere solvent shell of the ion $A^-(\text{aq})$.

The terms in the energies $U^f(\text{nucl})$ and $U^i(\text{nucl})$ in (8) are taken from a fairly standard model of ionic solvation involving a multipole expansion of the ionic field (*cf*, e.g., Morf and Simon 1971). The model is modified to take into account the different orientations of water molecules around cations and anions. One has (Delahay and Dziedzic 1986a)

$$U_{\text{IN}} = -U^i(ep) - U^i(eq) - U^i(pp) - U^i(pq) - U^i(qq)$$
$$+ \Delta U_{\text{disp}} + \Delta U_{\text{rep}} + \Delta U_v + \Delta U_c, \tag{9}$$

where the first five terms on the right hand side represent interaction energies involving the *change* (e) of ionic charge upon photoionization, solvent permanent dipoles (p) and quadrupoles (q). Each of the last four ΔU-terms are equal to the difference $U^f - U^i$ for the following processes: ΔU_{disp} for London water–water dispersion; ΔU_{rep} for Born water–water repulsion; ΔU_v for the volume change of the solvent upon solvation; ΔU_c for cavity formation and the breaking up of the solvent structure in the solvation process. Explicit forms of the terms in (9) are given by Delahay and Dziedzic (1986a).

5. Calculation of the reorganization energy U_{IN} for various univalent anions

The contributions to the inner-sphere reorganization energies U_{IN} are listed in table 2 for various inorganic anions not considered previously by Delahay and Dziedzic (1986a). The thermochemical radii (table 3) were used for all the anions except for ClO_4^- and N_3^- for which Pauling radii were available. The following assumptions were made in the calculation: (i) The radii r_i and r_f of the anion and radical, respectively, were assumed to be equal. This assumption affects only the calculation of ΔU_{disp} and ΔU_{rep} in (9). The former is negligible even for very different values of r_i and r_f (Delahay and Dziedzic 1986a) and the latter is not sensitive to the choice of radii. (ii) The values $N_i = 6$ and $N_f = 4$ were adopted. This choice is fully justified, for instance, for the halide ions (Delahay and Dziedzic 1986a) and it appears reasonable for the anions of table 2. (iii) The water orientation was assumed in which the field vector of the negative point charge of the anion and the dipole moment of water make a $52·23°$ angle. This orientation is justified for the halides (Delahay and Dziedzic 1986a) and it should also prevail for other anions. (iv) The electrical field of the anions was assumed to have spherical symmetry. This approximation seems justified for ClO_4^-, for instance, but is more tentative for a V-shaped ion like NO_2^- or a linear ion such as CNS^-, for example.

Table 2. Contribution to the inner-sphere reorganization energy U_{IN}*.

Anion	$-U^i(ep)$	$-U^i(eq)$	$-U^i(pp)$	$-U^i(pq)$	$-U^i(qq)$	ΔU_{rep}	ΔU_v	ΔU_c	U_{IN}
					(all units in eV)				
ClO_3^-	2·14	−0·61	−0·19	0·08	−0·02	−0·18	0·04	−0·27	0·99
BrO_3^-	2·40	−0·72	−0·23	0·10	−0·02	−0·19	0·15	−0·27	1·22
ClO_4^-	1·39	−0·32	−0·10	0·04	−0·01	−0·14	≈0	−0·27	0·59
NO_2^-	1·88	−0·50	−0·16	0·06	−0·01	−0·16	−0·23	−0·27	0·61
NO_3^-	2·03	−0·56	−0·18	0·07	−0·02	−0·17	0·05	−0·27	0·95
N_3^-	1·75	−0·45	−0·14	0·06	−0·01	−0·15	−	−0·27	0·79
HCO_3^-	2·36	−0·71	−0·23	0·10	−0·02	−0·19	0·03	−0·27	1·07
SCN^-	1·66	−0·42	−0·13	0·05	−0·01	−0·15	0·13	−0·27	0·86

*Thermochemical radii (table 3) used for all anions except ClO_4^- and N_3^- (Pauling radii). No calculation for IO_3^- because of uncertainty on the thermochemical radius. The value $\Delta U_v = 0·15$ eV for BrO_3^- is more likely to be comprised between the values of 0·04 and 0·10 eV for ClO_3^- and IO_3^-, respectively.

Table 3. Pauling and thermochemical radii*.

Anions	Pauling radius (Å)	Thermochemical radius (Å)
OH^-	1·47	1·33±0·03
F^-	1·36	1·26±0·03
Cl^-	1·81	1·72±0·05
Br^-	1·95	1·88±0·06
I^-	2·16	2·10±0·08
ClO_3^-	−	1·71±0·06
BrO_3^-	−	1·54±0·08
IO_3^-	−	1·22±0·72
ClO_4^-	2·45	2·40±0·05
NO_2^-	−	1·92±0·11
NO_3^-	−	1·79±0·06
N_3^-	2·04	1·95±0·02
HCO_3^-	−	1·56±0·02
CNS^-	−	2·13±0·10

*Pauling radii as given by Halliwell and Nyburg (1963); thermochemical radii according to Jenkins and Thakur (1979).

(v) Vibrational contribution to reorganization was neglected. This assumption is justified for NO_2^- (Warnek 1969) and N_3^- (Jackson *et al* 1981), for instance, but an additional vibrational contribution to U_{IN} of a few tenths of an electronvolt cannot be ruled out for some of the anions.

One has

$$U_v^i = -(v_{int} - v_{pm})/\beta_c \qquad (10)$$

where v_{int} and v_{pm} are the intrinsic and partial molar volumes of the anion, respectively, and β_c is the compressibility of water. The negative sign on the right hand side of (10) arises because the solvent is subject to electrostriction prior to

nuclear reorganization. This choice of sign is consistent with the convention of assigning a positive sign to R since $-R$ is the change of free energy for the spontaneous process $A(aq)^* \rightarrow A(aq)$. Removal of electrostriction around $A(aq)^*$ is also spontaneous and therefore the quantity
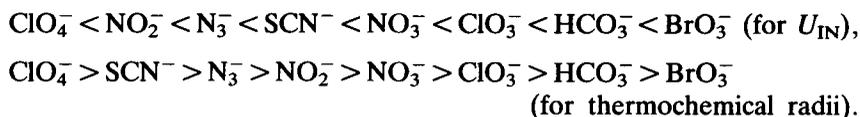
$$\Delta U_v = U_v^f - U_v^i \tag{11}$$

in (9) is taken as positive (just as R). The energy U_v^f in (11) is assumed to be equal to zero for the neutral species $A(aq)$. The required volumes were taken from tables (Akitt 1980; Marcus 1977; Padova 1964).

The term ΔU_c in (9) was obtained by noting that solvation of the radical $A(g)$ involves only the rotation of two of the four water molecules surrounding $A(aq)$ without a net change of the number of hydrogen bonds and with conservation of tetrahedral symmetry (Delahay and Dziedzic 1986a) for the value $N_f = 4$. Conversely, the substitution of $A(aq)$ by the ion $A^-(aq)$ involves a change from tetrahedral to octrahedral symmetry on the assumption that $N_i = 6$. This process involves the breaking of a bond. The reverse process therefore involves the net formation of a hydrogen bond and consequently $\Delta U_c = -0.27$ eV (Morf and Simon 1971).

It is seen from table 2 that the terms $-U^i(ep)$ and $-U^i(eq)$ in (9) are dominant in determining the energy U_{IN}. Thus, the energy U_{IN} is determined primarily by the charge-dipole and charge-quadrupole interactions. Next in importance come the contributions ΔU_c for hydrogen bonding, $-U^i(pp)$ for dipole–dipole interaction, and ΔU_{rep} for Born repulsion. The term ΔU_{disp} of (9) is equal to zero since the radii r_i and r_f were assumed to be equal. In any case, ΔU_{disp} is negligible (~ 0.01 eV) even when r_i and r_f are significantly different (e.g., for photoionization of halide ions).

The charge-dipole energy $U^i(ep)$ is inversely proportional to the square of the cavity radius r_i, that is, to the sum of the ionic radius and the crystallographic radius of water (1.38 Å). Likewise, the charge-quadrupole interaction energy is inversely proportional to r_i^3. Since $-U^i(ep)$ and $-U^i(eq)$ are the dominant terms in (9), one can expect a monotonic decrease of U_{IN} with increasing ionic radius. The following sequences hold for the data of tables 2 and 3:

$$ClO_4^- < NO_2^- < N_3^- < SCN^- < NO_3^- < ClO_3^- < HCO_3^- < BrO_3^- \text{ (for } U_{IN}),$$

$$ClO_4^- > SCN^- > N_3^- > NO_2^- > NO_3^- > ClO_3^- > HCO_3^- > BrO_3^-$$
$$\text{(for thermochemical radii)}.$$

The expected trend is essentially observed except for NO_2^-. The N_3^-/SCN^- inversion is minor, and may arise from the neglect of the unavailable value of ΔU_v in the calculation of U_{IN} for N_3^-. The exception for NO_2^- arises from the abnormally large thermochemical radius of this ion. Evidence from lyotropic numbers (Morris 1958) suggests that NO_2^- is smaller than NO_3^- whereas the opposite conclusion follows from the radii of table 2. The term $\Delta U_v = -0.23$ eV for NO_2^- is also abnormal in comparison with the ΔU_v's for the other anions in table 2. The NO_2^- ion is V-shaped, the ONO angle being $115°$ (Cotton and Wilkinson 1980), and this pronounced departure from the spherical symmetry inherent to a point-charge model may account for the abnormal results for NO_2^-. Further comments on NO_2^- are made in §6.

6. Comparison of experimental free energies R_{IN} with theoretical energies U_{IN}

Good agreement was obtained by Delahay and Dziedzic (1986a) between the theoretical values of U_{IN} and experimental values of R_{IN} for the halide and hydroxide ions. The R_{IN}-values were computed from (1), (6) and (7). Three additional experimental values of R_{IN} will be calculated for NO_2^-, NO_3^- and N_3^-.

The values $R_{IN} = 1.27$ and 0.85 eV for NO_2^- and NO_3^-, respectively, were calculated from (1) for $E_t = 7.6$ and 8.5 eV (table 1), $\Delta G = 1.0$ and 2.3 eV (Berdnikov and Bazhin 1970), and $R_{OUT} = 0.85$ and 0.87 eV [from (7) for the thermochemical radii of table 3]. The free energy ΔG for the N_3^-/N_3 couple is not available, and R_{IN} was obtained from (4). The value $\Delta G_n = 0.15$ eV was taken by analogy with solvation of other radicals. The value $\Delta G_s = -2.92$ eV was computed from the solvation enthalpy -3.09 eV of N_3^- (Halliwell and Nyburg 1963) and the entropy correction of 0.17 eV calculated from data in Friedman and Krishnan (1973). Furthermore, one has $E_t = 7.4$ eV (table 1) for N_3^-, EA $= 2.70$ eV (Jackson *et al* 1981), $R_{OUT} = 0.82$ eV for $r_c = 2.40$ Å (Conway 1981), and consequently $R_{IN} = 0.81$ eV from (4). The N–N distances in $N_3^-(g)$ and $N_3(g)$ are the same within 0.006 Å and the NNN angle is the same according to Jackson *et al* (1981). The vibrational contribution to R_{IN} therefore should be minor.

Values of R_{IN} thus obtained are listed in table 4. These free energies R_{IN} calculated from threshold energies by means of (1) are essentially *experimental* quantities since only model considerations enter in the calculation of R_{OUT} and the contribution of this term is not sensitive to r_c ($R_{OUT} = 0.96$ eV for F^- vs $R_{OUT} = 0.80$ for I^-). Furthermore, the continuous medium model used in calculating R_{OUT} is fully satisfactory for the outer-sphere region. Values of R_{IN} and U_{IN} in table 4 agree very well with the error of $\approx \pm 0.1$ eV on R_{IN} except for NO_2^-. The error on R_{IN} arises from the uncertainty in the extrapolation procedure used to obtain threshold energies and the error on the free energy ΔG appearing in (1). The entropy contribution to R_{IN} is probably within the error on this quantity. The theory should hold best for anions such as the halide ions which exhibit spherical symmetry, but the agreement between R_{IN} and U_{IN} is also good for ions not

Table 4. Experimental free energies R_{IN} versus theoretical energies U_{IN}*.

Anions	R_{IN} (eV)	U_{IN} (eV)
OH^-	1·38	1.24
F^-	1·56	1·42
Cl^-	1·00	0·94
Br^-	0·83	0·84
I^-	0·72	0·71
NO_2^-	1·27	0·61
NO_3^-	0·85	0·95
N_3^-	0·81	0·79

*Results for the halide and hydroxide ions from Delahay and Dziedzic (1986a).

Table 5. Change of free energy ΔG for reaction (1) for various anion–radical couples in aqueous solution*.

Anion	E_t	R_{IN}	R_{OUT}	ΔG
		(all in eV)		
ClO_3^-	8·2	0·99	0·89	1·8
BrO_3^-	7·9	1·22	0·92	1·3
ClO_4^-	8·5	0·59	0·76	2·7
NO_3^-	8·5	0·95	0·87	2·2
N_3^-	7·4	0·79	0·82	1·3
HCO_3^-	9·1	1·07	0·92	2·6
SCN^-	7·2	0·86	0·81	1·1

*E_t-values from table 1; R_{IN} from table 2; R_{OUT} computed from (7) for the thermochemical radii of table 3 except for ClO_4^- and N_3^- (Pauling radii).

satisfying conditions, i.e., OH^- (linear), N_3^- (linear) and NO_3^- with D_{3h}-symmetry (Cotton and Wilkinson 1980).

The decrease of U_{IN} with increasing ionic radius discussed in §5 is confirmed for R_{IN} except for NO_2^-. The following sequences prevail:

$$I^- < N_3^- < Br^- < NO_3^- < Cl^- < NO_2^- < OH^- < F^- \quad \text{(for } R_{IN}),$$

$$I^- > N_3^- > NO_2^- > Br^- > NO_3^- > Cl^- > OH^- > F^-$$
$$\text{(for thermochemical radii).}$$
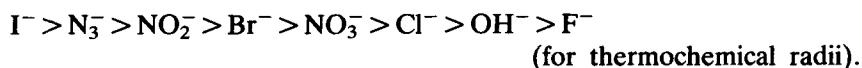
The values of R_{IN} for OH^-, NO_2^- and Cl^- in table 4 indicate that either the ionic radius of NO_2^- is comprised between the radii of OH^- and Cl^- and/or that the point-charge model is inadequate for this V-shaped ion (§5).

7. Calculation of the free energy charge ΔG for radical-anion couples

Values of ΔG computed from (1) and the threshold energies of table 1 are listed in table 5. The values of U_{IN} of table 2 were used instead of R_{IN} and the free energies R_{OUT} were computed from (7). The free energies ΔG in table 5 show that the radicals produced by photoionization of anions in aqueous solution are generally powerful oxidizing agents. Thus, the values $\Delta G = 2·7$ eV for $ClO_4(aq)/ClO_4^-(aq)$ and $\Delta G = 2·6$ eV for $HCO_3(aq)/HCO_3^-(aq)$ may be compared with $\Delta G = 2·55$ eV for $Cl^-(aq)/Cl(aq)$. The value $\Delta G = 2·2$ eV for $NO_3^-(aq)/NO_3(aq)$ agrees very well with the value $2·3 \pm 0·1$ eV given by Berdnikov and Bazhin (1970). This is to be expected in view of the agreement between R_{IN} and U_{IN} for NO_3^- in table 4.

Conclusion

The solvation model of inner-sphere nuclear reorganization yields results in agreement with experiment in the photoionization of univalent anions in aqueous solution. The development of the present theory shows how a central theme of

electrochemistry, namely ionic solvation, could be transposed to the study of nuclear reorganization in the photoionization in solution. Furthermore, application of the solvation model to photoionization allows the calculation of the free energy change ΔG characterizing the energetics of anion/radical couples in aqueous solution.

Acknowledgement

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