Ionization Potentials of Iodide, Bromide, and Thiocyanate Anions in Solvents: Solvent–Solvent Interactions in the Solvation Sphere

Iwao WATANABE,* Hajime TANIDA, Keiichi MAYA, Shigero IKEDA,† and Yu YOKOYAMA
Department of Chemistry, Faculty of Science, Osaka University, Toyonaka, Osaka 560
† Department of Materials Chemistry, Faculty of Science and Technology, Ryukoku University, Otsu, Shiga 520-21
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The solution-phase ionization potentials of I^-, Br^-, and SCN^- ions in 16 solvents including water have been measured by a photoelectron emission spectroscopic technique. The values obtained as the threshold energy E_t for halides are found to be correlated well with the Mayer–Gutmann acceptor number and better with the Riddle–Fowkes modified acceptor number of the solvent indicating that the electronic states of the halides are predominantly stabilized through the Lewis acid–base interaction. The reorganization energies ΔG_r of solvent after the photoionization of the halides are obtained from the E_t values. The experimental ΔG_r values are reproduced by using a simple model which incorporates the dipole–dipole repulsion and the bond formation energies in the first solvation layer. The solvation mechanism of SCN^- is somewhat different from those of the halides because its E_t depends less on the acceptor number and its ΔG_r values in alcohols are about half of those for the halides.

The vertical ionization potential of a solvated chemical species can be the measure of its reactivity in the solution phase. It is especially true if the reaction involves one-electron transfer in a rate-determining step. Nucleophilic reactivities of anions in solution have been found to be correlated with their vertical ionization potentials in solution.[1] This implies that an important activation process in the nucleophilic substitution reaction is the single-electron-transfer from the anion to the substrate. However, the vertical ionization potentials for solvated species became available only quite recently as the threshold photoionization energy E_t by photoelectron emission spectroscopy for solutions.[2]

The spectroscopic technique applied to a solution is able to provide E_t of almost any solvated species, organic or inorganic, neutral molecules, cations or anions in aqueous or nonaqueous solvents. The E_t in solution looks similar to either the ionization potential I_p in a vacuum or the standard redox potential E° in solution (referred to the vacuum level), but there are small differences between them, and the differences provide quite important information concerning the kinetics of electron-transfer reactions[3,4] and the effective solvation radius of molecules in the solvent.[5,6]

In this study we report the E_t values measured by the photoelectron emission method for iodide, bromide, and thiocyanate ions in a variety of solvents. These values have been reported by Delahay's group only for aqueous solutions.[7,8] They found a linear correlation of the E_t values for many anions in aqueous solution with the charge-transfer-to-solvent absorption energies.[7] They also treated, theoretically, the reorganization energies[9] pertaining to the relaxation process after the photoelectron emission. Thus, the E_t values have been predicted for the anions in aqueous solution. However, since their treatment requires a number of physical parameters for the ions and solvents, its applicability is limited almost entirely to aqueous solutions.

In this paper, the reorganization energies are predicted by using a simple model which includes the solvent–solvent interaction only in the first solvation sphere. In despite of the simplicity of the model, the reorganization energies for halides are essentially predicted. Thus, the reorganization mechanism and the solvation structure around the anions are discussed.

Experimental

The photoelectron emission spectrometer is composed of a hydrogen lamp, a vacuum UV monochromator, and an ionization chamber. The ionization chamber containing the sample solution is evacuated and sealed, thus the inside pressure is maintained at the equilibrium vapor pressure of the solvent. Then the surface of the solution is irradiated with monochromatized VUV light. There is an electrode a few millimeters above the solution surface that collects photoelectrons emitted from the surface. The E_t value is calculated from the photoelectron current vs. photon energy spectrum. The detailed instrumentation and procedures for measuring the E_t values have been described in earlier publications.[5,10] For the high E_t samples, MgF_2 was used as the window material, but a quartz window was used for the low E_t samples (<7 eV) to reduce high energy stray light. Optical dispersion correction[4,11] to E_t was not done since the optical data in the VUV range necessary for the correction of the solvents used here except for water are not available at present and the corrections have been considered to be rather small (<0.1 eV).[4]

Surface potentials of the solutions were also neglected. It has quite recently been reported by Barraclough and others that the surface potentials of pure liquids are best estimated to be 120±50, −150±50, and −100±60 mV for water, methanol, and acetonitrile, respectively, from their critical survey of the most reliable experimental data available.[12] It is also known that the surface potential is always reduced by the addition of electrolytes.[13] Therefore, we believe that the neglect of the surface potentials does not seriously affect the conclusion of this study.

Solutions were prepared by dissolving tetrabutylammoni-

um salts in most cases. However, whenever possible, lithium, sodium, and potassium salts were also tried. The salt solutions were measured at several different concentrations (e.g. 0.2, 0.1, and 0.05 mol dm^{-3}) to investigate the effects of ion-pair formation and ionic strength on the E_t values. It was thus confirmed within our experimental reproducibility (better than 0.05 eV) that there are no cation and salt concentration effects on E_t. This is in accordance with the assumption that the surface potentials are negligible since the surface potentials must depend on the kind and the concentration of the electrolyte used. The interesting exceptions were aqueous solutions of tetrabutylammonium salts, which gave strong photoelectron emissions at very low concentrations (10^{-6} mol dm^{-3}) indicating the segregation of the salt at the vapor/solution interface. Therefore the data for water used here are those of sodium and potassium salts.

Solvents were purified by standard procedures.[14] Water contents were measured by the Karl Fischer titration method. The contents were less than 15 mmol dm^{-3}. The E_t values were found not to depend on the water content at all in this concentration range.

To reduce the vapor pressure in the photoionization chamber, the solutions were cooled to: −20 °C/*N*-methyl-2-pyrrolidinone, −30 °C/pyridine, −10 °C/*N*,*N*-dimethylacetamide, room temperature (r.t.)/dimethyl sulfoxide, −20 °C/*N*,*N*-dimethylformamide, r.t./tetramethylene sulfone, r.t./nitrobenzene, −15 °C/propylene carbonate, −30 °C/acetonitrile, −10 °C/ethylene glycol, −20 °C/nitromethane, r.t./formamide, −25 °C/propyl alcohol, −25 °C/ethyl alcohol, −30 °C/methyl alcohol, 1 °C/water.

Results

There are two main difficulties for calculating the E_t values from the photoelectron emission spectra. (1) The subtraction of the base line current corresponding to zero photoelectron emission. There exists a background current, more or less, due to the stray light of high energy from the monochromator. (2) The selection of the photon energy range for obtaining the linear plot proposed by Brodsky and Tsarevsky of Y^n vs. $h\nu$,[15] where Y is the photoelectron yield, n the constant of 0.4 or 0.5, and $h\nu$ the photon energy. The ambiguity due to these difficulties may cause a 0.1 eV systematic error in the E_t value. The exponent n of 0.4 was selected throughout this study.

The E_t values measured with 16 different solvents are summarized in Table 1. The biggest E_t values are always given with water and the smallest with *N*-methyl-2-pyrrolidinone. The spans of the values amount about 1.5 eV for I^- and Br^- and about 1 eV for SCN^- over the broad selection of the solvents. The differences between the E_t values for I^- and Br^- are larger than the difference in the electron affinity E_A between the corresponding halogen atoms (3.06 and 3.36 eV for I^- and Br^-).[16] This indicates that the solvation stabilizes the electronic state of Br^- more effectively than I^-.

Table 1. Threshold Energies E_t for I^-, Br^-, and SCN^-

No.	Solvent		E_t/eV		
			I^-	Br^-	SCN^-
1	*N*-Methyl-2-pyrrolidinone	(NMP)	5.60	6.27	6.20
2	Pyridine	(Py)	5.70	6.55	6.36
3	*N*,*N*-Dimethylacetamide	(DMA)	5.71	6.27	6.22
4	Dimethyl sulfoxide	(DMSO)	5.79	6.46	6.38
5	*N*,*N*-Dimethylformamide	(DMF)	5.91	6.46	6.35
6	Tetramethylene sulfone	(TMS)	5.94	6.62	6.38
7	Nitrobenzene	(NB)	6.00	6.48	6.34
8	Propylene carbonate	(PC)	6.15	6.90	6.52
9	Acetonitrile	(AN)	6.28	7.11	6.60
10	Ethylene glycol	(EG)	6.49	7.16	6.74
11	Nitromethane	(NM)	6.50	7.16	6.66
12	Formamide	(FA)	6.56	7.32	6.60
13	Propyl alcohol	(PrOH)	6.61	7.36	6.51
14	Ethyl alcohol	(EtOH)	6.61	7.32	6.51
15	Methyl alcohol	(MeOH)	6.80	7.61	6.71
16	Water	(H_2O)	7.05	7.79	7.20

Discussion

Solvent Effects on E_t. The E_t could be considered as the HOMO energy of a cluster molecule consisting of an anion and several solvent molecules. Thus, the E_t energy should be expected to vary with the nature of the solvent. The problem we encounter here is to know what the mechanism of the solvent effect on E_t is. If stronger solvation gives greater stabilization of the HOMO energy, one would expect the correlation of E_t for an anion with its solvation free energy or solvation enthalpy. Or from the viewpoint of the Born equation, the dielectric constant of the solvent should correlate to E_t. Neither of them, however, was observed.

We have searched a large number of solvent parameters for the correlation with E_t and found that several solvent parameters do correlate with it. Some of them are the polarizability by the Clausius–Mossoti equation, the radius of the solvent molecule, and the Mayer–Gutmann acceptor number A_N.[17] However, the fact that the greater polarizability of the solvent molecule gives a smaller E_t value seems not to lead to a rational explanation for the presence of the correlation between them.

One of the best correlations found is that with A_N as shown in Fig. 1. If the points for I^- are shifted vertically by 0.7 eV, I^- and Br^- behave in quite the same manner against A_N. It is important to note that the points for aprotic solvents, the solvents with the A_N value less than 25, can be spread out by using the E_t value, implying that E_t discriminates between the aprotic solvents better than A_N. This reminds us of the recent work by Riddle and Fowkes concerning the modification of the A_N value.[18] They pointed out that the A_N value reflects not only the electrophilic ability of the solvent but the van der Waals contribution A_N^d to the electron donor–solvent interaction. Their conclusion is that A_N^*, proportional to $(A_N - A_N^d)$, better represents the acid–base interaction between the solvent and the electron donor. Figure 2 is the plot of E_t

against A_N^*. It is clear that the correlations found for the high A_N solvents now extend over the low A_N solvents. The presence of the correlation with A_N^* indicates that the electronic energy states of the solvated halide anions are mainly stabilized through the (Lewis)acid–base interaction between the anion and the adjacent solvent molecules for which the acidity is influenced by the next neighbor solvent molecules. It is expected that the acid–base interaction may also be represented by the index α the hydrogen-bond-donor acidity, which is one of the Kamlet–Taft solvatochromic parameters.[19] Taft and coworkers have shown that A_N is satisfactorily expressed in terms of the α and π^*, the scale of polarity/polarizability.[19,20] Their result resembles the analysis by Riddle and Fowkes. However, the correlation of E_t with α is poorer than that of E_t vs. A_N^* shown in Fig. 2.

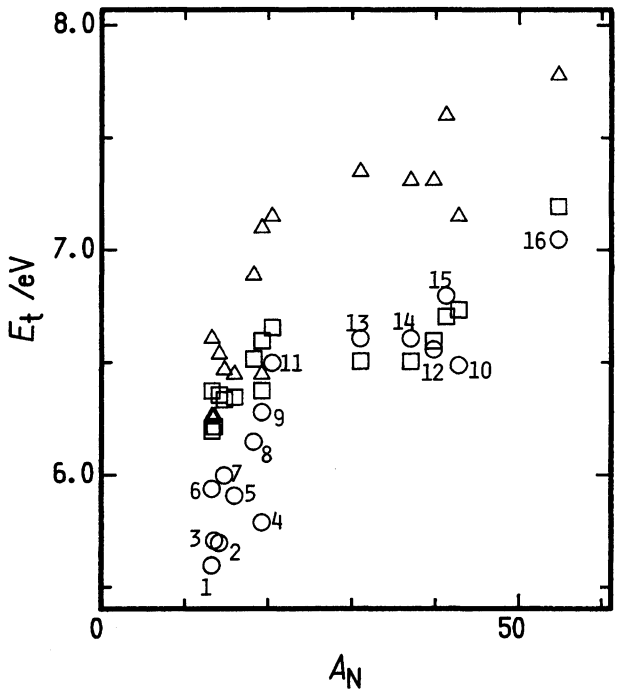

Fig. 1. Threshold energies E_t vs. acceptor number A_N for I^- (○), Br^- (△), and SCN^- (□).

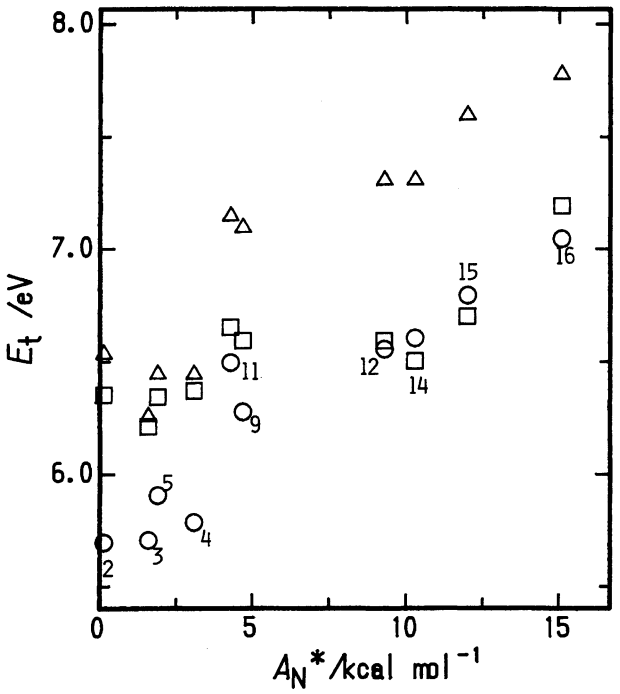

Fig. 2. Threshold energies E_t vs. Riddle–Fowkes acceptor number A_N^* for I^- (○), Br^- (△), and SCN^- (□).

The dependence of E_t for SCN^- on A_N is fairly smaller than that for I^- or Br^-. The electronic charge on SCN^- ion is known to be distributed over the both ends of S and N,[21] thus the electrostatic interaction with solvent must be weaker, even though its thermochemical ionic radius (2.13 Å) is similar to that of I^- (2.10 Å).[22]

Reorganization Energies. As the energy scheme in Fig. 3 indicates, E_t can be used to obtain the reorganization energy ΔG_r, which is released after the photoelectron emission as follows.[23]

$$\Delta G_r = E_A - E_t - \Delta G_s + \Delta G_n, \quad (1)$$

or

$$\Delta G_r = E^\circ \text{ (vs. V.L.)} - E_t, \quad (2)$$

where E_A is the electron affinity of the atom X°, ΔG_s and ΔG_n the solvation energies of X^- and X°, respectively, E° (vs. V.L.) the standard redox potential for the X^-(solv)/X°(solv) couple with respect to the vacuum level. We use the N.H.E. potential of −4.5 eV with respect to the vacuum level here.[24] For the halides the E_A values are known accurately, thus the ΔG_r values are calculated by combining the solvation energies. The

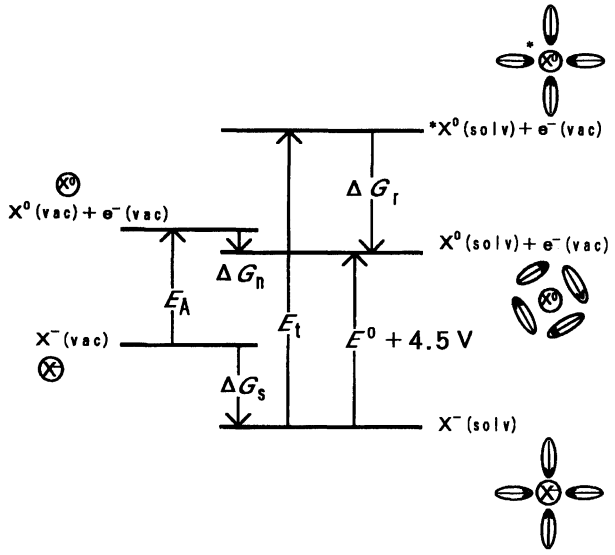

Fig. 3. Schematic representation of the energies for the one-electron loss process, $X^- \rightarrow X^\circ + e^-$ in vacuum and in solution.

value for ΔG_s in nonaqueous solvent is the sum of ΔG_s for water and the transfer energy ΔG_{tr} from water to the given solvent.

For the E_A values of SCN^- ion, scattered values have been reported.[25] The SCN^- ion is possible to give a vertical or adiabatic E_A value, or the compromise of these values depending on the experimental method. For the SCN^- ion we choose the $E°$ value of 1.66 V (vs. N.H.E.) because three independent reports have given values close to this.[26]

In Table 2 are summarized the ΔG_r^{exp} values obtained from Eq. 1 or Eq. 2 together with the solvation energies used. Here, the ΔG_n term and the surface potential at the gas/solution interface[2] are neglected. These approximations have been considered not to give serious errors. In any case, we do not have good data of these quantities for the wide variety of solvents used here, and since the absolute values for these quantities should not be large, the conclusions concerning the relative energies for anions and solvents should not be greatly affected by these approximations. This seems to be supported by the fact that the ΔG_r^{exp} values for I^- and Br^- in a given solvent are quite the same for the wide variety of solvents. We think an additional support comes from the fact that there is neither a cation effect nor a concentration effect on E_t.

The ΔG_r^{exp} values are plotted against A_N in Fig. 4. If the points for ethylene glycol and formamide are removed, the points for I^- and Br^- make a single line smoother than that of the E_t vs. A_N plot. The ΔG_r^{exp} for SCN^- behaves in a somewhat different manner, however. In aprotic solvents the ΔG_r^{exp} values are not different from those for halides, but they are about a half of those for the halides in alcohols and formamide. This indicates that the solvation structure around the SCN^- ion in aprotic solvents is similar to those around I^- and Br^-, but this is not the case in alcohols and formamide.

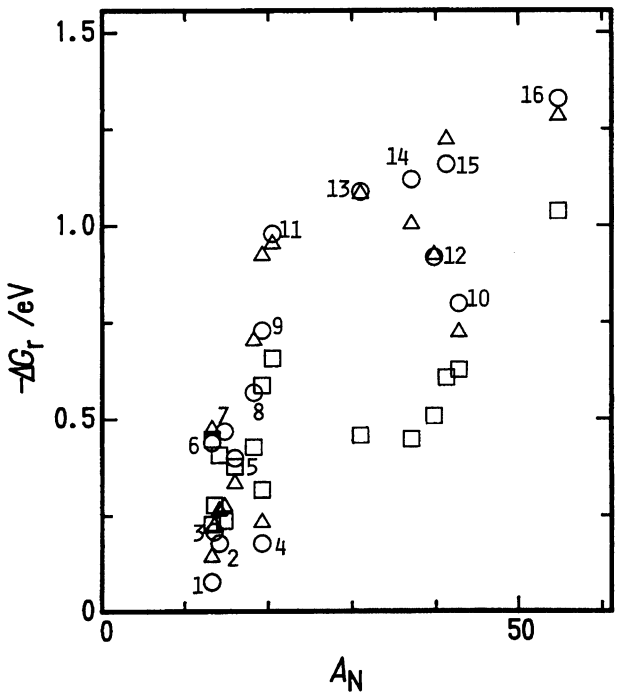

Fig. 4. Reorganization energies ΔG_r^{exp} vs. acceptor number A_N for I^- (○), Br^- (△), and SCN^- (□).

Calculation of ΔG_r. Delahay and Dziedzic calculated the ΔG_r values for anions in aqueous solution.[4,9,27] Their treatment involves the calculation of a number of interaction energies; in the first solvation (inner) sphere, the interactions between the charge on anion and the dipoles and quadrupoles of water molecules, and of the dipole–dipole and dipole–quadrupole among the ligand water molecule, and in the outer sphere, the calculation of the Marcus reorganization energy ΔG_r(out) by the following Born equation.

$$\Delta G_r(\text{out}) = -(\varepsilon_{op}^{-1} - \varepsilon_s^{-1})e^2/2a, \qquad (3)$$

where ε_{op} and ε_s are the optical and static dielectric constants of water, respectively, and a is the radius of the inner sphere.

We do not, however, follow their treatment for calculating ΔG_r for the following reasons. (1) Many of the physical solvent parameters and the knowledge of the solvation structure necessary for the treatment are not available for many nonaqueous solvents, thus the inner sphere contribution cannot be obtained. (2) The outer sphere contribution by Eq. 3 is found to be too large compared to the ΔG_r^{exp} value. For protic solvents, the ΔG_r(out) values by Eq. 3 take most of the ΔG_r^{exp} values, hence there is not much room left to place the inner sphere contribution. The applicability of Eq. 3 is even worse for aprotic solvents, since the equation already overestimates the total ΔG_r^{exp} values. Of course, one can introduce a modified Born equation[28] containing an additional parameter r_s, the size of the solvent molecule, which increases the sphere radius as $(a+r_s)$ in place of a in Eq. 3. The similar modification to this has been quite successful for calculating ion solvation energies in various solvents,[29] and given a theoretical interpretation.[30] This type of modification is very attractive since the correlation of ΔG_r^{exp} with the solvent radius found in this study can be qualitatively understood with the introduction of r_s. However, the improvement is not enough and because of reason 1, we abandoned the Delahay–Dziedzic treatment.

In this work, we estimate the ΔG_r energy by using the following simple model. (1) The anion as a hard sphere with radius r_i is coordinated by four or six solvent molecules which are also hard spheres with radius r_s having dipole moment μ at the center. (2) The solvents in the inner sphere are arranged tetrahedrally or octahedrally with the dipoles oriented toward the anion. (3) During the reorganization process, only the orientation of solvent dipoles is rearranged so that the

Table 2. Transfer Energies ΔG_{tr} (aq→nonaq)/eV,[a] Solvation Energies ΔG_s (vac→solv)/eV,[b] and Experimental Reorganization Energies ΔG_r^{exp}/eV for I^-, Br^-, and SCN^-

No.	Solvent	I^-			Br^-			SCN^-		
		ΔG_{tr}	$-\Delta G_s$	$-\Delta G_r^{exp}$	ΔG_{tr}	$-\Delta G_s$	$-\Delta G_r^{exp}$	ΔG_{tr}	$-\Delta G_s$	$-\Delta G_r^{exp}$
1	NMP	0.20	2.46	0.08	0.38	2.76	0.15	0.19	2.84	0.23
2	Py	0.20	2.46	0.18	0.22	2.92	0.27	0.21	2.82	0.41
3	DMA	0.03	2.44	0.21	0.46	2.68	0.23	0.22	2.81	0.28
4	DMSO	0.11	2.55	0.18	0.28	2.86	0.24	0.10	2.93	0.32
5	DMF	0.21	2.45	0.40	0.38	2.76	0.34	0.19	2.84	0.38
6	TMS	0.22	2.44	0.44	0.36	2.78	0.48	0.23	2.80	0.45
7	NB	0.19	2.47	0.47	0.30	2.84	0.28	0.06	2.97	0.24
8	PC	0.14	2.52	0.57	0.31	2.83	0.71	0.07	2.96	0.43
9	AN	0.17	2.49	0.73	0.32	2.82	0.93	0.15	2.88	0.59
10	EG	0.03	2.63	0.80	0.07	3.07	0.73	0.05	2.98	0.63
11	NM	0.20	2.46	0.98	0.30	2.84	0.96	0.16	2.87	0.66
12	FA	0.08	2.58	0.92	0.11	3.03	0.93	0.07	2.96	0.51
13	PrOH	0.20	2.46	1.09	0.23	2.91	1.09	0.10[d]	2.92	0.46
14	EtOH	0.23	2.43	1.12	0.19	2.95	1.01	0.11[d]	2.93	0.45
15	MeOH	0.08	2.58	1.16	0.12	3.02	1.23	0.06	2.97	0.61
16	H_2O	0	2.66	1.33	0	3.14	1.29	0	3.03	1.04

a) Based on the TATB assumption. From Ref. 34. b) From Refs. 28 and 34, and J. D. Lamb, J. J. Christensen, S. R. Izatt, K. Bedke, M. S. Astin, and R. M. Izatt, *J. Am. Chem. Soc.*, **102**, 3399 (1980). c) Solvent numbering and abbreviations are the same in Tables and Figures. d) Estimated from the linear solvation energy relationships in Ref. 34.

unfavorable dipole–dipole interactions in $^*X^\circ$(solv) as shown in Fig. 3 disappear. The interactions caused by the quadrupoles and higher multipoles are neglected. (4) The reorientation of the dipoles is assumed not to change such interaction energies as the dispersion energy between the solvent–solvent and the X°–solvent, but to create new bonds between solvents. The new bond is represented by the hydrogen bond here.

All of the dipole–dipole interactions[31] in the inner sphere are summed to give the reorganization energy ΔG_{dd} corresponding to the process 3 mentioned above and the result is

$$\Delta G_{dd} = -c\mu^2/(r_i + r_s)^3 \text{ eV debye}^{-2}\,\text{Å}^3, \quad (4)$$

where c is the constant of 4.441 or 1.423 for the octahedral or tetrahedral geometry, respectively, and μ is the dipole moment of the solvent molecule.

The hydrogen bond formation energy ΔG_{HB} among the solvent molecules corresponding to process 4 is estimated from the following equation,

$$\Delta G_{HB} = -\delta_h^2(4\pi/3)\{(r_i + r_s)^3 - r_i^3\} \text{ eV cal}^{-1}\,\text{cm}^3\,\text{Å}^{-3}, \quad (5)$$

where δ_h is the hydrogen bond component of the solubility parameter by Barton.[32] The term δ_h^2 corresponds to the cohesive energy per unit volume of solvent originating only from the hydrogen bond formation. We calculate the ΔG_{HB} energy here for the solvent shell volume in the inside of the sphere of radius $(r_i + r_s)$. Water is treated in a different manner because it has two hydrogen atoms directed one to the anion and the other to the solvent of the second layer so that it already forms a hydrogen bond with the other water molecules. If water directs both hydrogens toward the anion, its oxygen can easily make the hydrogen bond with the second layer waters. Therefore, a half of the calculated value is used as a rough estimate.

The ΔG_{dd} and ΔG_{HB} values thus obtained are summarized in Table 3 together with ΔG_r^{calc} which is the sum of the two components. The ΔG_{HB} contribution dominates for protic solvents while only the ΔG_{dd} contribution accounts for ΔG_r for some of the aprotic solvents such as acetonitrile or nitromethane. There is no adjustable parameter in the above calculation, but we must estimate the solvation number for each solvent. The solvation numbers used are six for smaller solvents such as water, alcohols, acetonitrile, and nitromethane, and four for the other solvents except for ethylene glycol.

The calculated ΔG_r values are compared with the experimental ones in Fig. 5. The agreements for the I^- and Br^- cases are surprisingly good if the approximation used for measuring ΔG_r^{exp} and the very simple model for the calculation of ΔG_r^{calc} are considered. The dashed line indicates the position where the values are the same. There must be fortunate cancellation among the neglected contributions. In any case, the success of this model is considered as the basis which allows us to use the photoelectron emission technique as the method for study of the solvation structure around anions.

The ΔG_r^{calc} values for I^- and Br^- in ethylene glycol used in Fig. 5 are obtained by reducing the solvation number to three and the ΔG_{HB} value to a half of its original, then the experimental values could be reproduced. This is interpreted as supporting the idea of the chelate structure of anion–ethylene glycol complex.[33]

Table 3. Calculation of the Reorganization Energies ΔG_r^{calc}/eV for I^-, Br^-, and SCN^-

No.	Solvent	I^-			Br^-			SCN^-		
		$-\Delta G_{dd}$[a)]	$-\Delta G_{HB}$[b)]	$-\Delta G_r^{calc}$	$-\Delta G_{dd}$[a)]	$-\Delta G_{HB}$[b)]	$-\Delta G_r^{calc}$	$-\Delta G_{dd}$[a)]	$-\Delta G_{HB}$[b)]	$-\Delta G_r^{calc}$
1	NMP	0.21	0.14	0.35	0.23	0.13	0.36	0.20	0.14	0.35
2	Py	0.08	0.09	0.16	0.09	0.08	0.17	0.07	0.08	0.16
3	DMA	0.17	0.28	0.46	0.20	0.25	0.45	0.17	0.29	0.46
4	DMSO	0.24	0.24	0.48	0.27	0.21	0.49	0.24	0.24	0.48
5	DMF	0.14	0.31	0.45	0.17	0.27	0.44	0.14	0.31	0.45
6	TMS	0.29			0.33			0.28		
7	NB	0.19	0.05	0.24	0.22	0.04	0.26	0.19	0.05	0.24
8	PC	0.32	0.04	0.36	0.37	0.04	0.40	0.32	0.04	0.36
9	AN	0.66	0.07	0.73	0.76	0.06	0.83	0.65	0.07	0.72
10	EG	0.04	0.67[c)]	0.71	0.04	0.59[c)]	0.64	0.03	0.68[c)]	0.71
11	NM	0.66	0.05	0.71	0.77	0.05	0.81	0.66	0.05	0.71
12	FA	0.22	0.60	0.82	0.26	0.52	0.78	0.22	0.60	0.82
13	PrOH	0.42	0.72	1.14	0.48	0.64	1.12	0.42	0.73	1.14
14	EtOH	0.14	0.77	0.90	0.16	0.68	0.84	0.14	0.78	0.92
15	MeOH	0.49	0.83	1.32	0.58	0.72	1.30	0.49	0.84	1.33
16	H_2O	0.29	0.96[c)]	1.25	0.34	0.83[c)]	1.18	0.28	0.97[c)]	1.26

a) Dipole–dipole repulsion energies. The parameters used are, r_i=2.16, 1.95, and 2.175 Å for I^-, Br^-, and SCN^-, respectively, and the solvent radii are calculated from the density d as $r_s=(1/2)(M/dN_A)^{1/3}$, where M is the molecular weight and N_A the Avogadro's number. Solvation numbers are, 6 for all anions in AN, NM, PrOH, EtOH, MeOH, and H_2O, 3 for halides in EG, and 4 for others. b) Hydrogen-bond formation energies. c) Half of the calculated value.

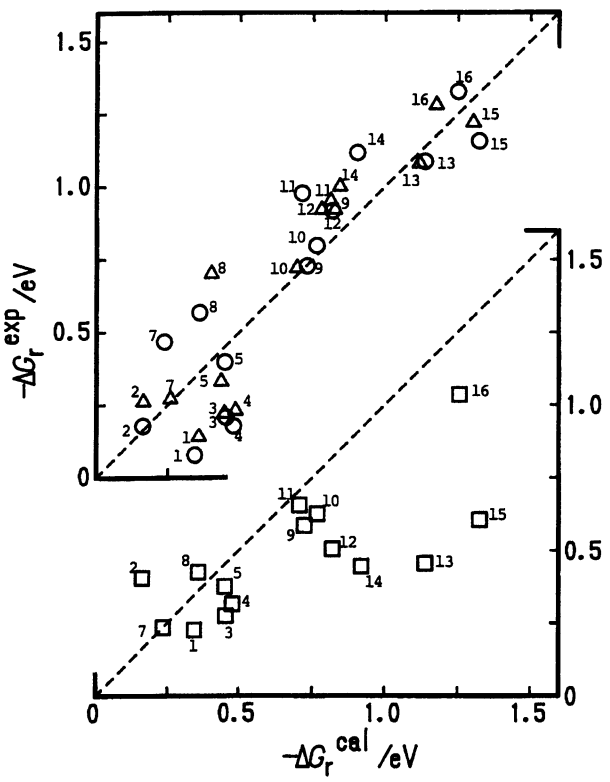

Fig. 5. Correlations between experimental and calculated reorganization energies ΔG_r^{exp} vs. ΔG_r^{calc} for I^- (○), Br^- (△), and SCN^- (□). The dashed lines indicate where the values are the same.

For SCN^- the model with the tetrahedral solvation structure, hence one OH group in a molecule toward the anion and the other OH toward outside, gives an excellent ΔG_r value indicating that the SCN^- ion does not form a chelate complex with ethylene glycol. In alcoholic solvents SCN^- behaves in a quite different manner from halides. As already mentioned in the previous section, SCN^- must have a weaker tendency toward the hydrogen bond compared to the halides.

The fact that the ΔG_r values for I^- and Br^- are quite the same in any solvent can be understood from the data in Table 3 as resulting from the cancellation of the two components, i.e. the larger ion gives a weaker solvent dipole–dipole repulsion due to larger separation between the solvents and a lager hydrogen bond formation energy due to larger solvent volume around the anion.

The model calculation should be considered as giving not free energy but enthalpy. Therefore, the ΔH_s values were collected from the literature[28,34] to obtain ΔH_r^{exp} and again the values by the model calculation are compared to ΔH_r^{exp}. Although the availability of the enthalpy data is limited, the result is quite similar to that found for ΔG_r except that ΔH_r^{exp} is constantly smaller than ΔG_r^{exp}.

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