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Non-Bornian Ion Solvation Energy. An Approach from Redox Potentials of Heteropoly Oxometalate Anions

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The first and second redox potentials (E_1° and E_2°) of Keggin-type heteropolytungstate anions (α-$[PW_{12}O_{40}]^{3-}$ and α-$[SiW_{12}O_{40}]^{4-}$) have been determined in various solvents by means of cyclic voltammetry. The difference ($\Delta E_{1,2}^\circ$) between E_1° and E_2°, being theoretically associated with the solvation energies of the polyanions, does not correlate with the permittivity of the solvent, in conflict with an expectation based on the Born-type electrostatic solvation model. In contrast, $\Delta E_{1,2}^\circ$ has been found to show some definite correlations with such empirical solvent parameters as acceptor numbers. This shows that the short-range interactions (i.e., donor–acceptor effects or hydrogen bonds) between the heteropolyanion and its primary solvents play the most significant role in the solvation of the heteropolyanions. We have thus proposed a new analytical equation for evaluating the short-range ion–solvent interaction energy.

In 1920 Born[1)] showed that the Gibbs free energy of solvation of an ion of charge ze (e the elementary charge) and radius r in a continuous medium of relative permittivity ε is

$$\Delta G_s^\circ(\mathrm{Born}) = -N_A z^2 e^2 (1-\varepsilon^{-1})/(8\pi\varepsilon_0 r), \tag{1}$$

where N_A is the Avogadro constant, and ε_0 the permittivity of a vacuum. However, the defects of this equation have been well known for at least 60 years, and attempts have been made by adjusting the (crystallographic) radii of the ions in a more-or-less empirical way until agreement with experiment is obtained,[2—10)] and/or by taking into account the dielectric saturation (i.e., the lowering of the permittivity of solvents adjacent to an ion due to the high electric field).[10—13)] Although there are an infinite variety of modifications, it is contemplated that the ion solvation energy estimated by any modified equation may show a certain dependence on the solvent permittivity, so far as the equation is based on a Born-type electrostatic model. Contrary to this contemplation, it has been known from old that the solvation free energy of ions, in most cases, shows no dependence on the solvent permittivity, but can be interpreted rather better in terms of empirical parameters for the electron-pair donating or accepting ability of solvents (e.g., the donor number or the acceptor number).[14,15)] In some attempts to improve the Born model (e.g., the mean spherical approximation theory[6—9)]), crystal ionic radii have been corrected by using the empirical solvent parameters.

Electrochemical measurements have been frequently employed for studies in this field. For example, Gutmann and coworkers[16)] studied solvent effects on the redox potentials of hexacyanoferrates and hexacyanomanganates, and observed that the changes in the redox potentials did not correlate with the dielectric properties, but with the empirical solvent parameters. Similar solvent effects were reported by Kadish et al.[17)] on the reduction of metalloporphyrins. Although these studies have drawn important conclusions, their arguments are based on the variation of the absolute value of the redox potential measured against the specified reference redox system (or the reference electrode). However, it should be noted that the reference redox system itself is solvent-dependent.

In 1991 Krishtalik et al.[18)] proposed a new electrochemical approach to the electrostatic ion–solvent interaction. This method is based on compensation of the solvophobic (non-electrostatic) effects in the difference (ΔE) of the redox potentials of two oxidation steps of large compact particles. Since the value of ΔE is independent of the reference electrode potential, this approach is superior to the earlier ones. Krishtalik et al. applied this to the cobaltocene and dicarbollylnickel systems, and showed that the solvation (or transfer) energy of the large ions in aprotic solvents obeyed the Born equation. In a similar manner, Kapturkiewicz[19)] showed the difference between the oxidation and reduction potentials of rubrene (5,6,11,12-tetraphenyltetracene) to depend linearly on $1/\varepsilon$, and interpreted the efficiencies of electrogenerated chemiluminescence of rubrene in terms of the Marcus theory.

Recently, we have determined the first and second one-electron redox potentials (E_1° and E_2°) of Keggin-type heteropolyanions (α,β-$[XM_{12}O_{40}]^z$; X=S, P, As, V, Si, Ge; M=W, Mo; z=2−, 3−, 4−) in aprotic solvents: acetone

(AC), acetonitrile (AN), 1,2-dichloroethane (DCE), dimethyl sulfoxide (DMSO), nitrobenzene (NB), and propylene carbonate (PC).[20)] It was then found that the difference (ΔE_1°) of the E_1° values for a pair of polyanions, whose ionic charge differs by unity (e.g., α-$[PW_{12}O_{40}]^{3-}$ and α-$[SiW_{12}O_{40}]^{4-}$), is independent of $1/\varepsilon$, in conflict with the Born equation. In the present study, measurements concerning α-$[PW_{12}O_{40}]^{3-}$ and α-$[SiW_{12}O_{40}]^{4-}$ (noted $PW_{12}{}^{3-}$ and $SiW_{12}{}^{4-}$) were extended to eight solvents, including protic ones, viz., benzonitrile (BN), *N,N*-dimethylacetamide (DMA), *N,N*-dimethylformamide (DMF), ethylene glycol (EG), ethanol (EtOH), formamide (FA), methanol (MeOH), and nitromethane (NM). Using the difference $\Delta E_{1,2}^\circ$ ($\equiv E_1^\circ - E_2^\circ$) between the first and second redox potentials (instead of ΔE_1°), its solvent effects have been examined in further detail. Although this approach with the potential difference between two reduction steps is analogous with that of Krishtalik et al.,[18)] our results did not obey the Born equation, in contrast to the previous observations,[18,19)] and then showed the importance of short-range ion–solvent interactions rather than the long-range electrostatic interaction. In this paper the reason why there are two cases for and against the Born equation is also discussed.

Experimental

The salts of α-$Na_3[PW_{12}O_{40}]\cdot 10H_2O$,[21)] α-$K_4[SiW_{12}O_{40}]\cdot 4.8H_2O$,[22)] and α-$(n\text{-}C_4H_9)_4[SiW_{12}O_{40}]$[22)] were prepared from the corresponding acids, which were distributed by Wako Pure Chemical Industries, Ltd. The sodium and potassium salts were dehydrated by heating at 120 °C before use. Analytical-grade solvents (all available from Wako) were dried over type 4A molecular sieves and then distilled under reduced pressure or at atmospheric pressure (for EtOH and MeOH). Their water contents were checked by means of the Karl–Fisher method. The salt of $(n\text{-}C_4H_9)_4NClO_4$, used as the supporting electrolyte for BN, DMA, DMF, and NM, was prepared and purified by a literature method.[23)] The supporting electrolyte for other solvents was anhydrous $NaClO_4$, which was prepared from the monohydrate (Wako) by successive recrystallizations from water and ethanol, followed by vacuum drying at 120 °C.

The acquisition and analysis of voltammetric data were performed using a microcomputer (NEC, PC9801) equipped with a 16-bit DA converter and a 12-bit AD converter. Through these converters a potentiostat (Hokuto Denko, HA-501) was connected to the microcomputer. A conventional three-electrode system was employed. A glassy carbon electrode (BAS, No. 11-2012; surface area=0.071 cm^2) and a platinum wire electrode were used as the working and counter electrodes, respectively. For each measurement the working electrode surface was freshly polished with a 0.25 μm diamond slurry, washed in an ultrasonic field successively with water and the solvent used for the measurement, and finally subjected to air-drying. An Ag/Ag^+ (0.01 $mol\,dm^{-3}$ $AgNO_3$ or $AgClO_4$) electrode was used as the reference electrode for all solvents except DMF and FA. In DMF and FA the Ag/Ag^+ electrode was not very stable; therefore, an aqueous Ag/AgCl (saturated KCl) electrode was used with a bridge to avoid water contamination. The dehydrated salt of a heteropolyanion was added to a test solution so that the concentration became 5×10^{-4} $mol\,dm^{-3}$. When the salt was not dissolved completely, the saturated solution was subjected to a voltammetric measurement. Unless otherwise noted, the concentration of the supporting electrolyte was 0.05 $mol\,dm^{-3}$. The test solution was always deaerated with N_2 gas. In cyclic voltammetry, the voltage scan rate was usually set at 0.1 $V\,s^{-1}$. The electrolytic cell was water-jacketed to maintain the temperature at 25±0.1°C.

Theoretical

In a preceding paper[20)] we showed experimentally that plots of E_1° and E_2° against z for Keggin-type heteropolymolybdates or -tungstates gave parallel straight lines in several aprotic solvents as well as water. Theoretical considerations showed that the common slope of the linear E_1° (or E_2°) vs. z plots, or, the difference (ΔE_1°) of the E_1° values for a pair of Keggin anions whose ionic charges differ by unity, should reflect the solvation energies of the polyanions (and its reduced anions). In this section, we demonstrate that the difference ($\Delta E_{1,2}^\circ$) between the first and second redox potentials of one Keggin anion is equally useful for studying the solvation energy. The following theoretical analysis is analogous to Krishtalik et al.'s one.[18)]

Let us consider a two-step one-electron redox process of a Keggin anion:

$$[XM_{12}^{VI}O_{40}]^{z} \xrightleftharpoons{+e^-} [XM^{V}M_{11}^{VI}O_{40}]^{z-1} \xrightleftharpoons{+e^-} [XM_2^{V}M_{10}^{VI}O_{40}]^{z-2}. \quad (2)$$

Using the Born–Haber cycle the standard redox potentials for the first and second steps can be expressed as

$$-FE_1^\circ = E_{a,z} - \Delta G_{s,z}^\circ + \Delta G_{s,z-1}^\circ - FE_{ref}, \quad (3)$$

$$-FE_2^\circ = E_{a,z-1} - \Delta G_{s,z-1}^\circ + \Delta G_{s,z-2}^\circ - FE_{ref}, \quad (4)$$

where $E_{a,x}$ and $\Delta G_{s,x}^\circ$ are, respectively, the electron affinity and the standard Gibbs energy of solvation of the Keggin anion with the ionic charge of x=z, $z-1$, or $z-2$ (shown by the subscript), and where E_{ref} is a constant which is determined only by the reference electrode employed.

By using Eqs. 3 and 4, we have the following expression for the difference between the first and second redox potentials:

$$\begin{aligned}\Delta E_{1,2}^\circ &\equiv E_1^\circ - E_2^\circ \\ &= -(E_{a,z} - E_{a,z-1})/F + (\Delta G_{s,z}^\circ - 2\Delta G_{s,z-1}^\circ + \Delta G_{s,z-2}^\circ)/F. \quad (5)\end{aligned}$$

Thus, the quantity $\Delta E_{1,2}^\circ$ comprises two terms, one being ascribed to the electron affinity and the other to the solvation energy. Because the first term is independent of the solvent, the second term is only affected by the solvent. It should also be noted that the quantity $\Delta E_{1,2}^\circ$ does not depend on the reference electrode potential.

As first noted by Pope,[24)] the reducibility of polyoxometalate anions requires the presence of MO_6 octahedra, each of which has one terminal oxygen atom. Such an MO_6 octahedron can be related to mononuclear MOL_5 complexes[25)] in which there is a single non-bonding metal d orbital corresponding to the lowest unoccupied molecular orbital (LUMO). In the successive reductions (Eq. 2) each electron is added to this non-bonding orbital of a separate MO_6 octahedron, and hence causes only a minor structural change.

It has also been noted that the interaction between reduced metal atoms is not appreciable, or that the added electrons are localized on certain metal atoms.[26,27] Accordingly, we may assume that there is no difference in the energy level of LUMO between the oxidized and one-electron reduced forms. However, because the electron affinity is defined as the energy needed to provide an electron for an isolated ion in a vacuum, the energy of the Coulomb interaction between the electron and the polyanion should be also taken into account. Thus, $E_{\mathrm{a},z}$ and $E_{\mathrm{a},z-1}$ are given, respectively, by

$$E_{\mathrm{a},z} = w_{\mathrm{n}} + w_z, \tag{6}$$

$$E_{\mathrm{a},z-1} = w_{\mathrm{n}} + w_{z-1}, \tag{7}$$

where w_{n} is the charge-independent term which is primarily governed by LUMO of the $\mathrm{MO_6}$ octahedron, and where w_z or w_{z-1} is the charge-dependent term standing for the Coulomb interaction energy. As shown in Eq. 5, the quantity $\Delta E^{\circ}_{1,2}$ is related to the difference of $E_{\mathrm{a},z}$ and $E_{\mathrm{a},z-1}$, which is equated with the difference of w_z and w_{z-1} (see Eqs. 6 and 7). In a previous paper,[20] w_z and w_{z-1} were formulated as

$$w_z = -N_{\mathrm{A}} z e^2/(4\pi\varepsilon_0 r), \tag{8}$$

$$w_{z-1} = -N_{\mathrm{A}}(z-1)e^2/(4\pi\varepsilon_0 r). \tag{9}$$

However, these equations seem to be oversimplifications, because the distribution of the electrons added to the polyanion is not properly taken into account. Accordingly, it seems inappropriate to use Eqs. 8 and 9 to evaluate w_z and w_{z-1}. Nevertheless, since the relevant quantity is the difference between w_z and w_{z-1}, we evaluated it in the following manner: In the first reduction step, an electron is added to one of the twelve equivalent metal atoms. In the second reduction step, another electron is most likely added to the metal atom being located farthest from the first reduced atom. The added electrons are not extensively delocalized.[26,27] Consequently, the difference of w_z and w_{z-1} (i.e., the difference of $E_{\mathrm{a},z}$ and $E_{\mathrm{a},z-1}$) can be represented by the energy of the Coulomb interaction between the two electrons being fixed on the metal atoms. We can then obtain an expression for the first term of Eq. 5:

$$-(E_{\mathrm{a},z} - E_{\mathrm{a},z-1})/F = e/(4\pi\varepsilon_0\varepsilon_{\mathrm{r}} d_{\mathrm{M-M}}), \tag{10}$$

where ε_{r} is the relative permittivity inside the polyanion, and $d_{\mathrm{M-M}}$ the distance between the reduced metal atoms. Though the quantity ε_{r} is unknown, its approximate value may be obtained by assuming the inside structure of the Keggin anion to be made up of twenty oxygen molecules, and by adopting the following well-known relation: $\varepsilon_{\mathrm{r}}=1+\chi=1+(\rho\alpha/\varepsilon_0)$, where χ is the electric susceptibility, being given by the polarizability (α) and the density (ρ) of the molecule. Using the value $\alpha=(4\pi\varepsilon_0)1.60\times10^{-30}\ \mathrm{m^3}$ for the oxygen molecule and the value $\rho=20/(4\pi r^3/3)$(with $r=0.56$ nm[28]), ε_{r} was calculated to be 1.55. The distance $d_{\mathrm{M-M}}$ in Eq. 10 was obtained to be 0.706 nm from the X-ray crystallographic data.[29] By introducing the estimated values of ε_{r} and $d_{\mathrm{M-M}}$ into Eq. 10, the contribution from the electron affinity to $\Delta E^{\circ}_{1,2}$ (i.e., the first term in Eq. 5) was finally evaluated to be ca. 1.3 V.

So far, the ion solvation energy has often been divided into two (or three) parts corresponding to electrostatic and non-electrostatic (and specific) ion–solvent interactions.[10,12,18] This division is to a certain degree arbitrary, since different effects may overlap: For example, electric polarization of the medium may influence significantly its structure. Nevertheless, such a division permits an evaluation of the individual effects. In the present theory we have divided for convenience the solvation energy of the heteropolyanion into two terms:

$$\Delta G^{\circ}_{\mathrm{s},z} = \Delta G^{\circ}_{\mathrm{s},z}(z\text{-dep}) + \Delta G^{\circ}_{\mathrm{s},z}(z\text{-indep}), \tag{11}$$

where $\Delta G^{\circ}_{\mathrm{s},z}(z\text{-dep})$ is the charge-dependent term, which comprises the electrostatic (long-range) ion–solvent interaction (i.e., charging energy) and/or the specific (short-range) interactions of an ion with solvents in its immediate vicinity (i.e., donor–acceptor effects or hydrogen bonds), and where $\Delta G^{\circ}_{\mathrm{s},z}(z\text{-indep})$ is the charge-independent term corresponding to the solvophobic interaction or the energy of the formation of a cavity in solvent. Since the solvophobic interaction depends not on the ionic charge, but exclusively on the ionic size,[30] we may assume that

$$\Delta G^{\circ}_{\mathrm{s},z}(z\text{-indep}) = \Delta G^{\circ}_{\mathrm{s},z-1}(z\text{-indep}) = \Delta G^{\circ}_{\mathrm{s},z-2}(z\text{-indep}). \tag{12}$$

Using this assumption and Eqs. 10 and 11, Eq. 5 can be rewritten as

$$\Delta E^{\circ}_{1,2} = e/(4\pi\varepsilon_0\varepsilon_{\mathrm{r}} d_{\mathrm{M-M}}) + [\Delta G^{\circ}_{\mathrm{s},z}(z\text{-dep}) - 2\Delta G^{\circ}_{\mathrm{s},z-1}(z\text{-dep}) + \Delta G^{\circ}_{\mathrm{s},z-2}(z\text{-dep})]/F. \tag{13}$$

As can be seen in this equation, the variation of $\Delta E^{\circ}_{1,2}$ with the solvent should reflect the difference in the charge-dependent component of the solvation energy.

Results and Discussion

Determination of the Standard Redox Potentials. Figure 1 shows a typical cyclic voltammogram for the two-step one-electron redox process (2). Such two successive waves were observed in all cases, except for $\mathrm{SiW_{12}}^{4-}$ in NM, in which the second wave merged into the reduction wave of the solvent. The peak separation, i.e., the difference between the cathodic and anodic peak potentials (E_{pc} and E_{pa}) is usually 0.06—0.11 V, indicating that the charge-transfer processes are reversible or quasi-reversible.[31] It follows that the midpoint potential ($E_{\mathrm{mid}}\equiv(E_{\mathrm{pc}}+E_{\mathrm{pa}})/2$) of the first or second wave can be adequately approximated to be the corresponding standard redox potential, E°_1 or E°_2.[20] In Table 1 the thus-determined values of E°_1 and E°_2 are shown for $\mathrm{PW_{12}}^{3-}$ and $\mathrm{SiW_{12}}^{4-}$ in eight of the solvents examined. Though the potential values in the table are reported to 1 mV, the values of E°_1 and E°_2 were reproducible to about ±5 mV, so that the value of $\Delta E^{\circ}_{1,2}$ has an uncertainty of ca. 0.01 V.

Correlation of $\Delta E^{\circ}_{1,2}$ with the Slope of the E°_1 vs. z Plot. In the preceding paper,[20] it was shown that plots of E°_1 and E°_2 against z for the Keggin anions gave parallel straight lines

Table 1. The First and Second Standard Redox Potentials, E°_{1} and E°_{2}, of PW_{12}^{3-} and SiW_{12}^{4-} in Eight Solvents

Solvent	Supporting electrolyte[a]	Reference electrode[b]	PW_{12}^{3-} E°_{1}/V	PW_{12}^{3-} E°_{2}/V	SiW_{12}^{4-} E°_{1}/V	SiW_{12}^{4-} E°_{2}/V
BN	A	C	−0.764	−1.116	−1.251	−1.792
DMA	A	C	−0.748	−1.358	−1.249	−1.848
DMF	A	D	−0.246	−0.843	−0.792	−1.354
EG	B	C	−0.701	−0.987	−0.934	−1.174
EtOH	B	C	−0.910	−1.104	−1.091	−1.213
FA	B	D	−0.061	−0.337	−0.279	−0.556
MeOH	B	C	−0.893	−1.147	−1.099	−1.282
NM	A	E	−0.989	−1.274	−1.445	—[c]

a) A, 0.05 mol dm^{-3} $(n\text{-}C_4H_9)_4NClO_4$; B, 0.05 mol dm^{-3} $NaClO_4$. b) C, Ag/0.01 mol dm^{-3} $AgNO_3$ electrode; D, aqueous Ag/AgCl (saturated KCl) electrode; E, Ag/0.01 mol dm^{-3} $AgClO_4$ electrode. c) The wave was not observed because of the reduction of solvent.

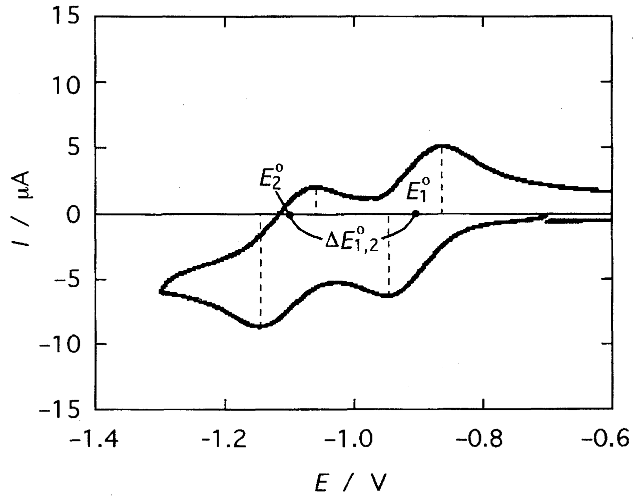

Fig. 1. Cyclic voltammogram of 5×10^{-4} mol dm^{-3} PW_{12}^{3-} in deaerated EtOH at the glassy carbon electrode. Supporting electrolyte: 0.05 mol dm^{-3} $NaClO_4$. Voltage scan rate: 0.1 V s^{-1}.

Table 2. The Difference, $\Delta E^{\circ}_{1,2}$, between the First and Second Standard Redox Potentials of PW_{12}^{3-} and SiW_{12}^{4-} and the Difference, ΔE°_{1}, between the First Standard Redox Potentials of the Two Heteropolyanions for Various Solvents

No.	Solvent	$\Delta E^{\circ}_{1,2}$/V PW_{12}^{3-}	$\Delta E^{\circ}_{1,2}$/V SiW_{12}^{4-}	ΔE°_{1}/V	Reference
1	AC	0.540	0.518	0.481	20
2	AN	0.514	0.510	0.452	20
3	BN	0.352[a]	0.541	0.487	This study
4	DCE	0.496	0.511	0.438	20
5	DMA	0.610	0.554	0.546	This study
6	DMF	0.597	0.562	0.546	This study
7	DMSO	0.559	0.551	0.497	20
8	EG	0.286	0.240	0.233	This study
9	EtOH	0.194	0.122	0.181	This study
10	FA	0.276	0.277	0.218	This study
11	H_2O	0.259	0.256	0.201	20
12	MeOH	0.254	0.183	0.206	This study
13	NM	0.285[a]	—	0.456	This study
14	PC	0.504	—	0.436	20

a) The deviation from the corresponding ΔE°_{1} value is over 0.08 V.

for various solvents. The common slope of the linear plots, being denoted as ΔE°_{1} or ΔE°_{2} in Ref. 20, is given by the same formula as $\Delta E^{\circ}_{1,2}$, i.e., Eq. 5. As shown in Eq. 15 or 21 (see below), $\Delta E^{\circ}_{1,2}$ is expected to be independent of z in the same way as ΔE°_{1} or ΔE°_{2}.[20] In Table 2 the values of $\Delta E^{\circ}_{1,2}$ and ΔE°_{1} for PW_{12}^{3-} and SiW_{12}^{4-} in various solvents, being determined in the present study and also in the preceding study,[20] are summarized. Mostly, the $\Delta E^{\circ}_{1,2}$ values of the two polyanions with different ionic charges agree well with each other, and further with the corresponding value of ΔE°_{1}. The deviations are not more than 0.08 V, except in BN and NM for PW_{12}^{3-}. This suggests that in most cases, $\Delta E^{\circ}_{1,2}$ as well as ΔE°_{1} properly reflects the solvation energy of the polyanion in accordance with Eq. 5.

Influences of the Supporting Electrolytes. In the preceding paper,[20] it was shown that there are no significant effects of the supporting electrolytes on the ΔE°_{1} values of Keggin anions for AN and H_2O. Such effects on the $\Delta E^{\circ}_{1,2}$ values determined here for other solvents are probably not significant in most cases. This is supported by the above-mentioned good correlation between $\Delta E^{\circ}_{1,2}$ and ΔE°_{1}. For insurance, however, we have made supplementary measurements for EtOH and also solvents (BN and NM) in which the $\Delta E^{\circ}_{1,2}$ values (for PW_{12}^{3-}) differ from the values of ΔE°_{1}. The results are summarized in Table 3. The $\Delta E^{\circ}_{1,2}$ values of PW_{12}^{3-} and SiW_{12}^{4-} in EtOH showed almost no dependence on the concentration of the supporting electrolyte, varying by less than 0.01 V. This is the case for SiW_{12}^{4-} in BN. However, the $\Delta E^{\circ}_{1,2}$ values of PW_{12}^{3-} for BN and NM were significantly affected by the concentration of the supporting electrolyte, indicating that the ion-pair formation between the supporting electrolyte cation $(n\text{-}C_4H_9)_4N^+$ and PW_{12}^{3-} (and/or the reduced forms) influenced the redox potentials to a considerable extent. In these cases, $\Delta E^{\circ}_{1,2}$ is no longer given by Eq. 5. Accordingly, these data will be excluded in the following analysis, based on Eq. 5 or 13.

Discussion

Non-Validity of the Simple Born Model. If we assume

Table 3. Influences of the Supporting Electrolytes on E°_1, E°_2, and $\Delta E^\circ_{1,2}$ of $PW_{12}{}^{3-}$ and $SiW_{12}{}^{4-}$ in BN, EtOH, and NM

Solvent	Supporting electrolyte[a)]	$PW_{12}{}^{3-}$ E°_1/V	E°_2/V	$\Delta E^\circ_{1,2}$/V	$SiW_{12}{}^{4-}$ E°_1/V	E°_2/V	$\Delta E^\circ_{1,2}$/V
BN	A (0.01 mol dm^{-3})	−0.799	−1.068	0.269	−1.273	−1.816	0.543
	A (0.05 mol dm^{-3})	−0.794	−1.116	0.352	−1.251	−1.792	0.541
	A (0.10 mol dm^{-3})	−0.743	−1.142	0.399	−1.223	−1.766	0.543
	A (0.20 mol dm^{-3})	−0.737	−0.158	0.421	−1.219	−1.769	0.550
EtOH	B (0.01 mol dm^{-3})	−0.950	−1.155	0.205	−1.129	−1.246	0.117
	B (0.05 mol dm^{-3})	−0.910	−1.104	0.194	−1.091	−1.213	0.122
	B (0.10 mol dm^{-3})	−0.891	−1.090	0.199	−1.066	−1.187	0.121
	B (0.20 mol dm^{-3})	−0.871	−1.067	0.196	−1.052	−1.167	0.115
NM	A (0.01 mol dm^{-3})	−1.018	−1.241	0.223			
	A (0.05 mol dm^{-3})	−0.989	−1.274	0.285	−1.445	—[b)]	—
	A (0.10 mol dm^{-3})	−0.989	−1.317	0.328			
	A (0.20 mol dm^{-3})	−0.967	−1.355	0.388			

a) A, $(n\text{-}C_4H_9)_4NClO_4$; B, $NaClO_4$. b) The wave was not observed because of the reduction of solvent.

that the charge-dependent term of the solvation energy for the heteropolyanions is given by the simple Born equation (Eq. 1), i.e.,

$$\Delta G^\circ_{s,z}(z\text{-dep}) = \Delta G^\circ_s(\text{Born}) \tag{14}$$

$\Delta E^\circ_{1,2}$ expressed by Eq. 13 should be given by

$$\Delta E^\circ_{1,2} = e/(4\pi\varepsilon_0\varepsilon_r d_{\text{M-M}}) - e(1-\varepsilon^{-1})/(4\pi\varepsilon_0 r). \tag{15}$$

In Fig. 2 the values of $\Delta E^\circ_{1,2}$ determined for (A) $PW_{12}{}^{3-}$ and (B) $SiW_{12}{}^{4-}$ in various solvents are plotted against $1/\varepsilon$ (the values of ε[32,33)] are shown in Table 4 together with some solvent parameters[32,34—38)] being used in the subsequent analysis). As seen in the figure, there are no correlations between $\Delta E^\circ_{1,2}$ and $1/\varepsilon$. This shows that the assumption of Eq. 14 is invalid, or, that at least the simple Born equation cannot be applied to the solvation energy of the polyanions. As described above, many types of modifications of the Born model have so far been presented.[2—13)] However, any model based on the electrostatic ion–solvent interaction could not essentially improve the dispersed plots in Fig. 2, since there are no clear-cut dependencies on ε. We would like to add that $\Delta E^\circ_{1,2}$ also showed no definite dependencies on the dipole moment (μ) of the solvent molecules, though it showed some dependencies on their polarizability (α); the correlation coefficients, R, are 0.771 for $PW_{12}{}^{3-}$ (the number of data, n=11; the standard deviation, SD=0.104 V) and 0.699 for $SiW_{12}{}^{4-}$ (n=11; SD=0.127 V) (plots not shown).

Thus, it has been concluded that the solvent effects of $\Delta E^\circ_{1,2}$ for the polyanions cannot be elucidated in terms of dielectric properties of solvents. Contrary to this view, however, it may be claimed that some modern modifications of

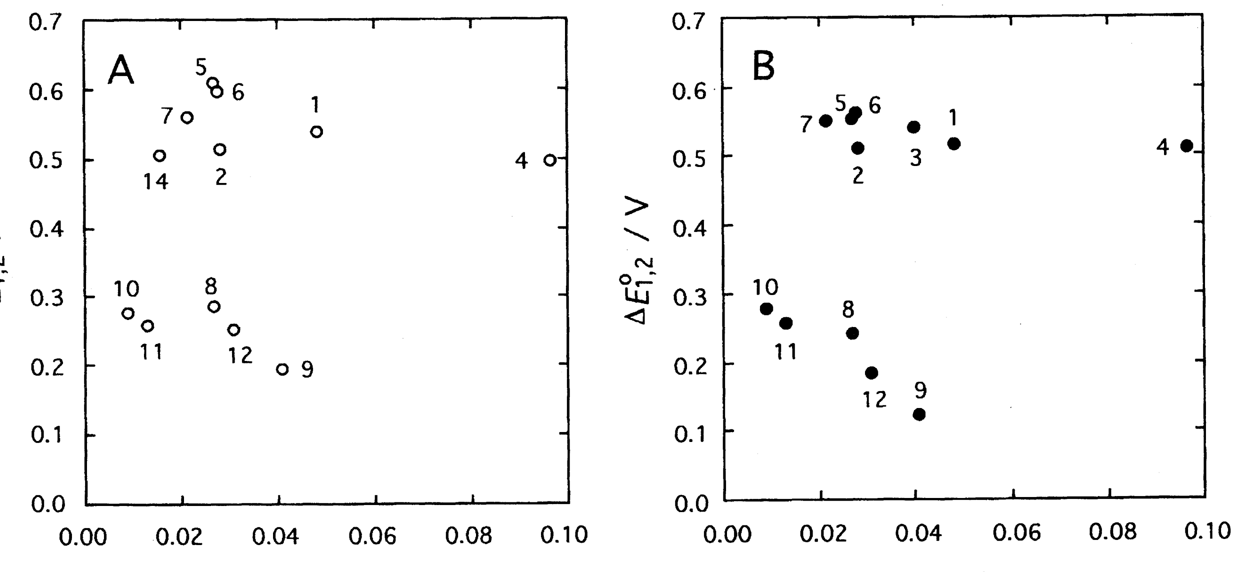

Fig. 2. Plots of the values of $\Delta E^\circ_{1,2}$ for (A) $PW_{12}{}^{3-}$ and (B) $SiW_{12}{}^{4-}$ in various solvents against $1/\varepsilon$.

Table 4. Relative Permittivities, ε, Dipole Moments, μ, Polarizabilities, α, Acceptor Numbers, A_N, Dimroth-Reichardt's E_T-values, E_T, Kosower's Z-values, Z, and Standard Gibbs Energies of the Transfer of BPh_4^- from Water to Organic Solvent, $\Delta G_{tr}^{o,W\rightarrow S}(BPh_4^-)$, for solvents at 25 °C

No.	Solvent	ε[a)]	μ[32)]	α[32)]	A_N[34)]	E_T[35,36)]	Z[37)]	$\Delta G_{tr}^{o,W\rightarrow S}(BPh_4^-)$[38)]
			D	10^{-30} m^3		kcal mol^{-1}	kcal mol^{-1}	kJ mol^{-1}
1	AC	20.70	2.69	6.41	12.5	42.2	65.7	−32
2	AN	35.95	3.44	4.41	18.9	46.0	71.3	−32.8
3	BN	25.20	4.05	12.54	15.5	42.0		
4	DCE	10.36	1.86	8.33	16.7	41.9		−33
5	DMA	37.78	3.72	9.63	13.6		66.9	−38.7
6	DMF	36.71	3.86	7.90	16.0	43.8	68.5	−38.5
7	DMSO	46.6	3.9	7.99	19.3	45.0	71.1	−37.4
8	EG	37.7	2.28	5.73		56.3	85.1	−21
9	EtOH	24.55	1.66	5.13	37.1	51.9	79.6	−21.2
10	FA	111.0	3.37	4.23	39.8			−23.9
11	H_2O	78.39	1.834	1.456	54.8	63.1	94.6	
12	MeOH	32.70	2.87	3.26	41.3	55.5	83.6	−24.1
13	NM	35.94	3.56	4.95	20.5	46.3		
14	PC	64.4	4.98	8.56	18.3	46.6		−36.0

a) From the compilation of Marcus[32)] except in the case of AN, DMSO, NM, and PC.[33)]

the Born equation, e.g., the mean spherical approximation (MSA) theory,[6—9)] could improve our understanding of the present results. In the MSA, the Gibbs solvation energy is corrected by adding a constant as an adjusting parameter to the ionic radii in the Born equation. The constant called "the MSA distance parameter" depends on the nature of the solvent and also on whether the solvated ion is an anion or a cation, and is connected with empirical scales measuring solvent basicity and acidity. Since the distance parameter for the multivalent polyanions has not been provided, we cannot readily examine the utility of the MSA theory in the present system. However, even if the attempt to apply the MSA theory succeeds, we have to recognize that in the MSA, non-electrostatic (i.e., specific) ion–solvent interactions are taken into account to the full extent for evaluating the solvation energy of ions.

Correlations of $\Delta E_{1,2}^{\circ}$ with Empirical Solvent Parameters. The electrostatic model represented by the Born equation is not the only approach to ion–solvent interactions. There is an alternative approach which recognizes the coordinative bonds that may be formed between an ion and solvent molecules in the first solvation shell. So far, various empirical parameters for the electrophilic properties of solvents have been proposed. Gutmann and co-workers[34)] have proposed a well-known solvent parameter, i.e., the acceptor number (A_N) which has been derived from ^{31}P NMR solvent shifts of triethylphosphine oxide (Et_3PO). In Fig. 3 the values of $\Delta E_{1,2}^{\circ}$ for (A) PW_{12}^{3-} and (B) SiW_{12}^{4-} in various solvents are plotted against A_N (the plot for solvent **8** is omitted due to the lack of its A_N-value). In contrast to the plots (Fig. 2) based on the Born model, some definite correlations have been found between $\Delta E_{1,2}^{\circ}$ and A_N; R=0.910 (n=11; SD=0.069 V) for PW_{12}^{3-} and R=0.880 (n=11; SD=0.085 V) for SiW_{12}^{4-}.

Taft and coworkers[39)] have concluded that A_N is, in fact, a combined measure of the solvent polarity/polarizability and hydrogen-bond donicity. Although Taft's analysis of A_N, in which he separates polarity effects from hydrogen bond donicity, is not appropriate, as discussed by Fawcett,[8,9)] it is instructive to recognize a significant role of hydrogen bonds in A_N. As can be seen in Fig. 3, the protic solvents (**9**—**12**) with higher A_N's, which are capable for forming hydrogen bonds, give smaller $\Delta E_{1,2}^{\circ}$ values than the aprotic solvents (**1**—**7** and **14**). Thus, hydrogen bonds play a very important role in the solvation of the polyanions in protic solvents.

Though the plots are not shown here, similar correlations of $\Delta E_{1,2}^{\circ}$ have been observed with other solvent parameters, i.e., Z-values[37)] and E_T-values,[35,36)] which are known to show good linear correlations with A_N. However, the correlation coefficients are not very good (R=0.81 to 0.86; SD=0.085 to 0.114 V).

Correlations with the Transfer Energies of Other Common Anions. Furthermore, we have examined the correlations of with the Gibbs energies ($\Delta G_{tr}^{o,W\rightarrow S}$) of the transfer of other common anions (Cl^-, Br^-, I^-, and BPh_4^-) from water to organic solvents.[38)] Although some correlations (R=0.70 to 0.97) were observed with the $\Delta G_{tr}^{o,W\rightarrow S}$ for any anion, the large BPh_4^- ion was found to show the best correlation to $\Delta E_{1,2}^{\circ}$. Plots are shown in Fig. 4. The correlation coefficients are R=0.967 (n=11; SD=0.041 V) for PW_{12}^{3-} and R=0.953 (n=10; SD=0.057 V) for SiW_{12}^{4-}, being slightly better than those for A_N (R=0.908 and 0.880, respectively). The worse correlation between A_N and $\Delta E_{1,2}^{\circ}$ seems to be owing to the difference in the number of the solvent molecules which directly determine the quantities A_N and $\Delta E_{1,2}^{\circ}$. It has been revealed that Et_3PO, being used for determining A_N, has three primary solvent molecules in water and one or two in alcohols.[40)] As compared with these, the numbers of the primary solvents around the Keggin anion (r=0.56 nm[28)]) used for determining $\Delta E_{1,2}^{\circ}$ and around BPh_4^- (r=0.421 nm[32)]) for

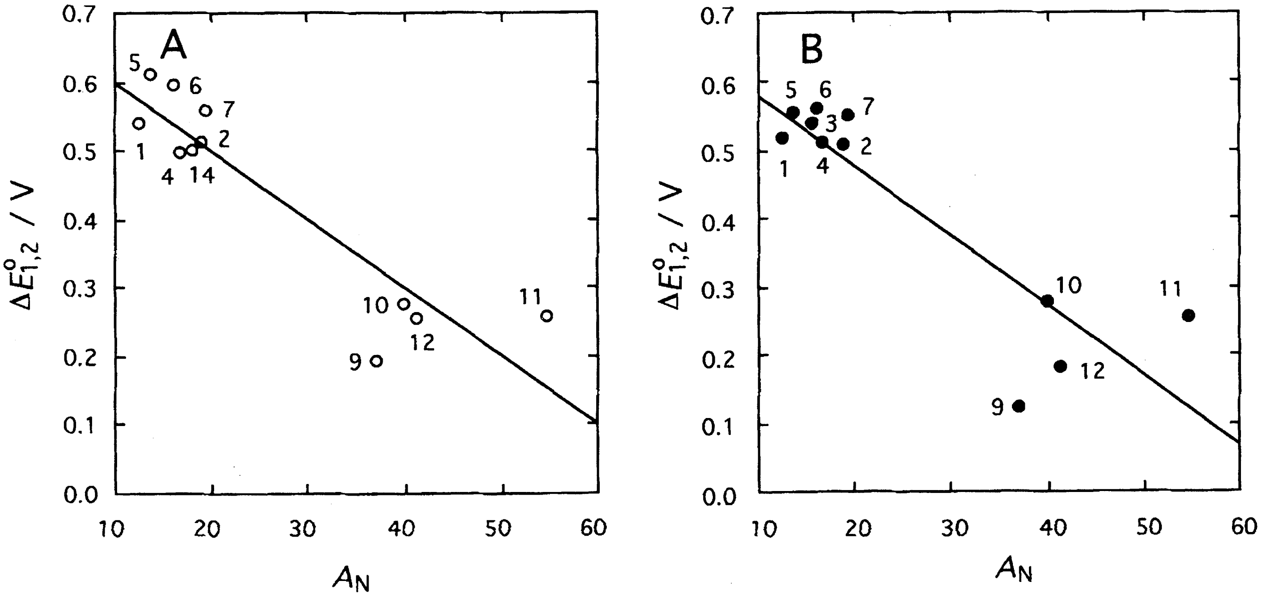

Fig. 3. Plots of the values of $\Delta E^{\circ}_{1,2}$ for (A) PW_{12}^{3-} and (B) SiW_{12}^{4-} in various solvents against A_N. Each straight line shows a regression line.

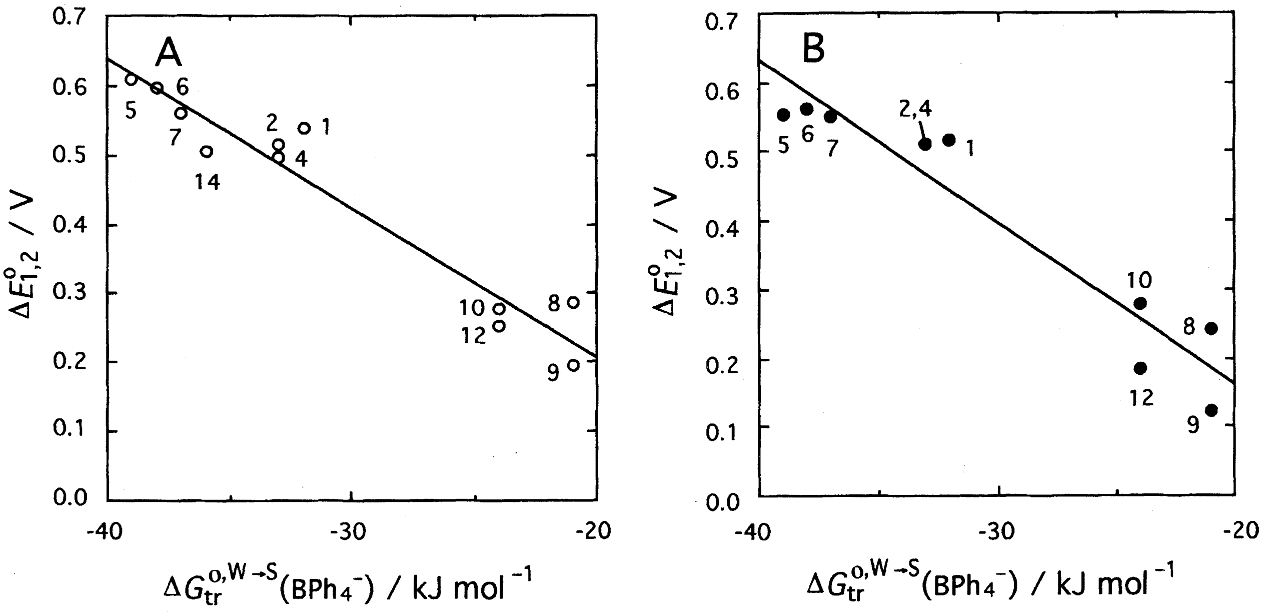

Fig. 4. Plots of the values of $\Delta E^{\circ}_{1,2}$ for (A) $PW_{1,2}^{3-}$ and (B) SiW_{12}^{4-} in various solvents against $\Delta G_{tr}^{o,W\to S}(BPh_4^-)$. Each straight line shows a regression line.

$\Delta G_{tr}^{o,W\to S}(BPh_4^-)$ are probably much larger. Accordingly, it appears that the value of $\Delta E^{\circ}_{1,2}$ as well as $\Delta G_{tr}^{o,W\to S}(BPh_4^-)$ is useful for a measure of the solvation energy of "larger" anions.

A New Theoretical Treatment of Short-Range Ion–Solvent Interaction Energies. The above-mentioned correlations of $\Delta E^{\circ}_{1,2}$ with such empirical solvent parameters as A_N show a more important role of short-range ion–solvent interactions than the electrostatic (long-range) interaction. In view of establishing a new analytical equation of the ion solvation energy in place of the Born equation, a theoretical consideration has been presented in this section.

Because the short-range (i.e., chemical) interactions recognize some overlap of the electron orbitals of the ion and the solvent molecule in its immediate vicinity, they should be elucidated on quantum chemical considerations. In ab initio molecular orbital studies,[41] the self-consistent field (SCF) energy of the ion–molecule interaction, U_{SCF}, is partitioned into several terms, e.g., Coulomb (COU), exchange (EX), polarization (POL), and charge-transfer (CHT) terms:

$$U_{SCF} = U_{COU} + U_{EX} + U_{POL} + U_{CHT}. \tag{16}$$

Although such energy partitioning is to a certain degree arbitray and still controversial, it seems to shed light on the present discussion. The term U_{COU} in Eq. 16 is identical with the empirical energy of ion–dipole interaction. If a solvent molecule is fixed on an ion, U_{COU} is given by $-\mu E\cos\theta$ (with μ the dipole moment of the solvent molecule; E the surface field strength of the ion, θ the angle between the dipole axis and the line connecting point dipole and point charge).[42] Similarly, U_{POL} is identical with the semi-classical electrostatic energy of ion–induced dipole interaction, being given by $-\alpha E^2/2$ (with α the electronic polarizability of the solvent).[42] The term U_{CHT} is the energy for the intermolecular electron transfer between the ion and the solvent. Although the dependence of U_{CHT} on the ionic charge and size may be considered very hard to derive, Osakai and Ebina[43] have recently used the model Hamiltonian approach to show that U_{CHT} ($=-\Delta W$ in Ref. 43) per primary solvent, for an ion such as the polyanion, is a function of E, approximately a quadratic equation:

$$U_{\mathrm{CHT}} = -\zeta_0 - \zeta_1 E - \zeta_2 E^2. \tag{17}$$

This approximate equation can be applied under the conditions that the radius of the ion is much larger than that of the solvent molecule. The coefficients ζ_0, ζ_1, and ζ_2 (denoted as α_0, α_1, and α_2 in Ref. 43) should be affected by various molecular properties which include, for the anion–solvent interaction, the ionization potential of the surface atoms of the ion (e.g. oxygen atom for polyanions), the electron affinity of the solvent, and the charge-transfer distance. Then, the coefficients can be used to evaluate the charge-transfer interaction energy. The remaining term, U_{EX} in Eq. 16, represents the non-classical repulsion term. Its major part, which probably arises from the kinetic energies of electrons, is inherently independent of z or E. From these considerations, it may be concluded that the short-range interaction energy per primary solvent, U(sr), can be given by a function of E as

$$U(\mathrm{sr})(=U_{\mathrm{SCF}}) = -AE^2 - BE - C, \tag{18}$$

with $A=\alpha/2+\zeta_2$, $B=\mu\cos\theta+\zeta_1$, and $C=\zeta_0-U_{\mathrm{EX}}$. We have examined the utility of this equation on the basis of the following quantitative analysis.

In Eq. 18, it should be noted that U(sr) represents the interaction energy per primary solvent. When the ion is much larger than the solvent, one can assume that the number (N) of solvent molecules adjacent to the ion, i.e., in the first solvation shell, is proportional to the surface area of the ion: $N=4\pi r^2\rho$, where ρ is the number of solvent molecules per unit surface area of the ion. Because E is given by $ze/(4\pi\varepsilon_0 r^2)$, the contribution of the short-range interactions to the ion solvation energy, ($\Delta G^{\circ}_{\mathrm{s},z}$ (sr)) can then be written in the form:

$$\begin{aligned}\Delta G^{\circ}_{\mathrm{s},z}(\mathrm{sr}) &= N\cdot U(\mathrm{sr})\\ &= -A[z^2e^2\rho/(4\pi\varepsilon_0^2 r^2)] - B(ze\rho/\varepsilon_0) - C(4\pi r^2\rho).\end{aligned} \tag{19}$$

Since the first and second terms thus depend on z, the charge-dependent term of the solvation energy can be set as

$$\Delta G^{\circ}_{\mathrm{s},z}(z\text{-dep}) = -A[z^2e^2\rho/(4\pi\varepsilon_0^2 r^2)] - B(ze\rho/\varepsilon_0). \tag{20}$$

Substituting this in Eq. 13 finally yields the expression for $\Delta E^{\circ}_{1,2}$:

$$\Delta E^{\circ}_{1,2} = e/(4\pi\varepsilon_0\varepsilon_r d_{\mathrm{M-M}}) - 2A[e\rho/(4\pi\varepsilon_0^2 r^2)]. \tag{21}$$

The first term is independent of solvent, and therefore $\Delta E^{\circ}_{1,2}$ is affected only by the second term, accordingly by A. Since A is given by $A=\alpha/2+\zeta_2$ as described above, it is expected that $\Delta E^{\circ}_{1,2}$ is influenced by the solvent polarizability and electron acceptability, or, the abilities for intra- and inter-molecular electron transfers. This expectation is in harmony with the above-mentioned correlation of $\Delta E^{\circ}_{1,2}$ with A_{N}.

As shown in the Theoretical section, the first term in Eq. 21 has been evaluated to be ca. 1.3 V. The second term in Eq. 21 can be evaluated at least for water as follows: The polarizability α of a water molecule is reported to be $(4\pi\varepsilon_0)1.456\times10^{-30}$ m^3 ($=1.62\times10^{-40}$ C V^{-1} m^2),[38] while the value of ζ_2 is reported to be 2.052×10^{-22} (eV) V^{-2} m^2 ($=3.29\times10^{-41}$ C V^{-1} m^2).[43] Then, A is calculated to be 1.14×10^{-40} C V^{-1} m^2. Using this value and the values of ρ ($=9.4\times10^{18}$ molecules m^{-2})[43] and r (=0.56 nm),[28] the second term in Eq. 21 is obtained to be 1.11 V. Consequently, $\Delta E^{\circ}_{1,2}$ is roughly evaluated to be ca. 0.2 V (=1.3—1.11 V). It should be stressed that this value is close to the experimental value of ca. 0.26 V for water.

The present estimation of $\Delta E^{\circ}_{1,2}$ for water cannot be readily extended to other solvents because the ζ_2-values concerning the CHT interaction are lacking at the present stage. The theoretical estimatation of the ζ_2-values for different solvents based on quantum chemical models is possible, but cumbersome. However, the ζ_2-values would be estimated in a more-or-less empirical way. Although it seems premature to come to a conclusion, the above-mentioned near agreement of the theoretical and experimental values of $\Delta E^{\circ}_{1,2}$ for water does show a potential utility of Eq. 18.

In What Cases Is the Born Equation Valid or Invalid? The present results have shown that the solvation energies (more properly, the $\Delta E^{\circ}_{1,2}$-values) of Keggin anions do not obey the Born equation. In contrast to our results, however, Krishtalik et al.[18] observed that the solvation energies of cobaltocene and dicarbollylnickel in aprotic solvents obeyed the Born equation, or, depended linearly on $1/\varepsilon$. Kapturkiewicz[19] also reported the linear dependence of the solvation energy of rubrene on $1/\varepsilon$. Why do their results differ from our results?

Here, we would like to point out that the redox systems of Krishtalik et al. and Kapturkiewicz share two similarities: One is that their redox systems are studied in aprotic solvents. Krishtalik et al.[18] have also described that strong deviations from Bornian dependence are observed for protic media in which specific ion–solvent interactions (or, formation of hydrogen bonds) are predominant. The second similarity is that their redox systems are written as

$$\mathrm{R}^+ \underset{}{\overset{+e^-}{\rightleftarrows}} \mathrm{R} \underset{}{\overset{+e^-}{\rightleftarrows}} \mathrm{R}^- \tag{22}$$

Thus, the electric charge of the redox species changes in such a way that $+1\rightarrow0\rightarrow-1$. The changes in the sign of charge suggest dramatic changes in the orientation of solvent molecules around the redox species, which leads to larger values of ΔE (=ca. 1—3 V) for two redox couples. In the present heteropolyanion system, however, there are no changes in the sign of charge of the redox species. The negative charge of the polyanion (here, -3 or -4) is only raised by the stepwise reduction in such a way that $-3 \rightarrow -4 \rightarrow -5$ (for $PW_{12}{}^{3-}$). Accordingly, the orientation of solvent molecules around the polyanion would not be changed significantly by the stepwise reduction. It should also be noted that the values of $\Delta E^{\circ}_{1,2}$ are much smaller (ca. 0.2—0.6 V) compared to the above systems.

So far as we know, there are no other redox studies, except the above two cases, which support the simple Born equation. Probably, Krishtalik's and Kapturkiewicz's systems were rare cases in which the above two conditions were both satisfied. Applying the MSA theory to a variety of redox systems, Fawcett[8] has found that the standard potentials for almost redox systems depend primarily on the solvent acidity and/or basicity, but only secondarily on the solvent polarity.

References

1) M. Born, *Z. Phys.*, **1**, 45 (1920).

2) D. D. Eley and M. G. Evans, *Trans. Faraday Soc.*, **34**, 1093 (1938).

3) W. M. Latimer, K. S. Pitzer, and C. M. Slansky, *J. Chem. Phys.*, **7**, 108 (1939).

4) R. M. Noyes, *J. Am. Chem. Soc.*, **84**, 513 (1962).

5) J. F. Coetzee and J. J. Campion, *J. Am. Chem. Soc.*, **89**, 2513 (1967).

6) W. R. Fawcett and L. Blum, *J. Chem. Soc., Faraday Trans.*, **88**, 3339 (1992).

7) L. Blum and W. R. Fawcett, *J. Phys. Chem.*, **96**, 408 (1992).

8) W. R. Fawcett, *J. Phys. Chem.*, **97**, 9540 (1993).

9) W. R. Fawcett, in "Quantitative Treatments of Solute/Solvent Interactions," ed by P. Politzer and J. S. Murray, Elsevier, Amsterdam (1994), p. 183.

10) Y. Marcus, *J. Chem. Soc., Faraday Trans.*, **87**, 2995 (1991).

11) A. D. Buckingham, *Discuss. Faraday Soc.*, **24**, 151 (1957).

12) M. H. Abraham and J. Liszi, *J. Chem. Soc., Faraday Trans. 1*, **74**, 1604 (1978).

13) M. H. Abraham, J. Liszi, and L. Mészáros, *J. Chem. Phys.*, **70**, 2491 (1979).

14) V. Gutmann, "The Donor–Acceptor Approach to Molecular Interactions," Plenum, New York (1978).

15) K. Burger, "Solvation, Ionic an Complex Formation Reactions in Non-Aqueous Solvents—Experimental Methods for Their Investigation," Akadémiai Kiadó, Budapest (1983), Chap. 4.

16) G. Gritzner, K. Danksagmüller, and V. Gutmann, *J. Electroanal. Chem.*, **72**, 177 (1976); **90**, 203 (1978).

17) K. M. Kadish, J.-L. Cornillon, C.-L. Yao, T. Malinski, and G. Gritzner, *J. Electroanal. Chem.*, **235**, 189 (1987).

18) L. I. Krishtalik, N. M. Alpatova, and E. V. Ovsyannikova, *Electrochim. Acta*, **36**, 435 (1991).

19) A. Kapturkiewicz, *J. Electroanal. Chem.*, **372**, 101 (1994).

20) K. Maeda, H. Katano, T. Osakai, S. Himeno, and A. Saito, *J. Electroanal. Chem.*, **389**, 167 (1995).

21) M. T. Pope and G. M. Varga, Jr., *Inorg. Chem.*, **5**, 1249 (1996).

22) C. Rocchiccioli-Deltcheff, M. Fournier, R. Franck, and R. Thouvenot, *Inorg. Chem.*, **22**, 207 (1983).

23) K. Izutsu, *Denki Kagaku*, **48**, 530 (1980).

24) M. T. Pope, *Inorg. Chem.*, **11**, 1973 (1972).

25) C. J. Ballhausen and H. B. Gray, *Inorg. Chem.*, **1**, 111 (1962).

26) E. N. Dorokhova and L. P. Kazanskii, *Dokl. Chem.*, **229**, 489 (1976); translated from *Dokl. Akad. Nauk SSSR*, **229**, 622 (1976).

27) L. P. Kazanskii, *Bull. Acad. Sci. USSR, Div. Chem. Sci.*, **27**, 238 (1978); translated from *Izv. Akad. Nauk SSSR, Ser. Khim.*, **27**, 278 (1978).

28) T. Kurucsev, A. M. Sargeson, and B. O. West, *J. Phys. Chem.*, **61**, 1567 (1957).

29) J. F. Keggin, *Proc. R. Soc. London*, **A144**, 75 (1934).

30) A. Ben-Naim, "Hydrophobic Interactions," Plenum, New York (1980), Chap. 2.

31) A. J. Bard and L. R. Faulkner, "Electrochemical Methods," Wiley, New York (1980), Chap. 6.

32) Y. Marcus, "Ion Solvation," Wiley, Chichester (1985).

33) G. J. Janz and R. P. T. Tomkins, "Nonaqueous Electrolytes Handbook," Academic Press, New York (1972), Vol. 1.

34) U. Mayer, V. Gutmann, and W. Gerger, *Monatsch. Chem.*, **106**, 1235 (1975).

35) K. Dimroth, C. Reichardt, T. Siepmann, and F. Bohlmann, *Liebigs Ann. Chem.*, **661**, 1 (1963).

36) C. Reichardt, *Angew. Chem., Int. Ed. Engl.*, **4**, 29 (1965).

37) E. M. Kosower, "An Introduction to Physical Organic Chemistry," Wiley, New York (1968), p. 259.

38) Y. Marcus, *Pure Appl. Chem.*, **55**, 977 (1983).

39) R. W. Taft, J. Pienta, M. J. Kamlet, and E. M. Arnett, *J. Org. Chem.*, **46**, 661 (1981).

40) H. L. Robinson and M. C. R. Symons, *J. Chem. Soc., Faraday Trans. 1*, **1985**, 2131; M. C. R. Symons, *Pure Appl. Chem.*, **58**, 1121 (1986).

41) A. Karpfen and P. Schuster, in "The Chemical Physics of Solvation, Part A," ed by R. R. Dogonadze, E. Kálmán, A. A. Kornyshev, and J. Ulstrup, Elsevier, Amsterdam (1985), Chap. 7.

42) J. N. Israelachvili, "Intermolecular and Surface Forces," Academic Press, London (1985).

43) T. Osakai and K. Ebina, *J. Electroanal. Chem.*, **412**, 1 (1996).