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—Note—

MUTUAL RELATIONSHIP BETWEEN FREE ENERGIES OF SOLVATION OF MONOATOMIC CATIONS IN NON-AQUEOUS MEDIA AND IN WATER

By

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We reported in our previous work[1] an excellent linearity between the relative standard free energy of solvation $\boldsymbol{a}_{is} \equiv \frac{\bar{\alpha}^0_{is}}{z_i} - \frac{\bar{\alpha}^0_{js}}{z_j}$ and $\frac{\bar{\alpha}^0_{iw}}{z_i}$ using the Randles series for $\bar{\alpha}^0_{iw}$-values[2], where $\bar{\alpha}^0$'s with subscripts i and j were respectively the standard real free energies of solvation for monoatomic cations of species i of valency z_i and of a definite reference ion j of valency z_j, and subscripts s and w denoted non-aqueous and aqueous media, respectively. However, different values for $\bar{\alpha}^0_{iw}$ are reported among different authors[3]. In order to avoid the confusion due to the lack of conformity in the experimental values for $\bar{\alpha}^0_{iw}$, the empirical relationship in the previous work is expressed here in terms of $\boldsymbol{a}_{is}$ and $\boldsymbol{a}_{iw}$ which can readily be determined from the standard electromotive force associated with ion i.

Let us first consider $\boldsymbol{a}_{iw}$ referred to the standard real free energy of hydration of proton $\bar{\alpha}^0_{H^+,w}$

$$\boldsymbol{a}_{iw} = \frac{\bar{\alpha}^0_{iw}}{z_i} - \bar{\alpha}^0_{H^+,w} . \tag{1}$$

Splitting $\bar{\alpha}^0_{iw}$ into the chemical term α^0_{iw} and the electrostatic term $z_i\mathbf{F}\chi_w$ as

$$\bar{\alpha}^0_{iw} = \alpha^0_{iw} - z_i\mathbf{F}\chi_w , \tag{2}$$

$\boldsymbol{a}_{iw}$ can also be expressed in terms of the chemical terms

$$\boldsymbol{a}_{iw} = \frac{\alpha^0_{iw}}{z_i} - \alpha^0_{H^+,w} , \tag{3}$$

where χ_w is the surface potential of water and $\mathbf{F}$ is the Faraday.

On the basis of the thermodynamical relation

$$\Delta\mathscr{F}^0_i = \bar{\alpha}^0_{iw} + z_i\mathbf{F}\varphi^0_{iw} , \tag{4}$$

$\boldsymbol{a}_{iw}$ can be expressed in terms of the experimental quantities

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TABLE 1. The values of a_{is} in eV and β for monoatomic cations in non-aqueous and aqueous media at 25°C, **NM** : nitromethane, **DMSO** : dimethylsulfoxide,

No.	Ion	NM	CH_3CN	PC	H_2O	CH_3OH	C_2H_5OH	$HCONH_2$
1	H^+	0.00	0.00	6.06#	0.00	0.00	0.00	0.00
2	Li^+	−5.52	−5.80	0.29	−6.00	−5.94	−5.99	−6.04#
3	Na^+	−6.34	−6.88	−0.66	−7.04	−7.03	−7.10	−7.09#
4	K^+	−7.09#	−7.56	−1.33	−7.80	−7.75#	−7.80#	−7.85
5	Rb^+	−7.30#	−7.85	−1.60	−8.03	−7.98#	−8.03#	−8.17
6	Cs^+	−7.60#	−8.22	−1.94	−8.36	−8.31#	−8.36#	−8.43#
7	Cu^+	−4.89	−5.25	0.92#	−5.39	−5.36#	−5.39	−5.42#
8	Cu^{2+}	−0.42#	−0.45	5.56#	−0.52	−0.51	−0.38	−0.45
9	Ag^+	−5.63	−5.77	0.00	−6.34	−6.30	−6.29	−6.38#
10	Au^+	−4.53#	−4.91#	1.28#	−5.01	−4.98#	−5.01#	−5.04#
11	Au^{3+}	3.29#	3.41#	9.42#	3.53	3.51#	3.53#	3.59#
12	Be^{2+}	1.18#	1.17#	7.23#	1.23	1.23#	1.23#	1.27#
13	Mg^{2+}	−1.16	−1.41#	4.70#	−1.42	−1.41#	−1.42#	−1.41#
14	Ca^{2+}	−2.73#	−3.16	3.18	−3.04	−3.02#	−3.04#	−3.05#
15	Sr^{2+}	−3.40#	−3.70#	2.46#	−3.77	−3.75#	−3.77#	−3.79#
16	Ba^{2+}	−4.02#	−4.36#	1.82#	−4.45	−4.42#	−4.45#	−4.47#
17	Ra^{2+}	−4.15#	−4.50#	1.68#	−4.59	−4.56#	−4.59#	−4.62#
18	Zn^{2+}	−0.67#	−0.82	5.30#	−0.79	−0.82	−0.92	−0.80
19	Cd^{2+}	−1.74#	−1.90	4.19#	−1.96	−1.94	−1.99	−1.96
20	Ho^{2+}	−1.61#	−1.80#	4.32#	−1.82	−1.81#	−1.82#	−1.82#
21	Al^{3+}	4.32#	4.50#	10.48#	4.65	4.63#	4.65#	4.73#
22	Ga^{2+}	−0.68#	−0.81#	5.29#	−0.80	−0.79#	−0.80#	−0.78#
23	Ga^{3+}	4.35#	4.54#	10.52#	4.69	4.67#	4.69#	4.77#
24	In^+	−6.90#	−7.42#	−1.17#	−7.59	−7.54#	−7.59#	−7.65#
25	In^{3+}	2.60#	2.68#	8.70#	2.78	2.77#	2.78#	2.83#
26	Tl^+	−7.04#	−7.57#	−1.27	−7.74	−7.70	−7.73	−7.73
27	Tl^{3+}	2.68#	2.77#	8.79#	2.87	2.86#	2.87#	2.93#
28	Sc^{3+}	2.13#	2.17#	8.21#	2.26	2.25#	2.26#	2.31#
29	Y^{3+}	0.98#	0.96#	7.02#	1.01	1.01#	1.01#	1.05#
30	La^{3+}	−0.09#	−0.18#	5.90#	−0.16	−0.16#	−0.16#	−0.14#
31	Ce^{3+}	0.90#	0.87#	6.93#	0.92	0.92#	0.92#	0.95#
32	Ce^{4+}	5.17#	5.41#	11.37#	5.58	5.55#	5.58#	5.67#
33	Nd^{3+}	0.70#	0.65#	6.72#	0.70	0.70#	0.70#	0 73#
34	Sm^{3+}	0.93#	0.90#	6.96#	0.95	0.95#	0.95#	0.98#
35	Gd^{3+}	1.04#	1.02#	7.08#	1.08	1.08#	1.08#	1.12#

Mutual Relation between Free Energies of Solvation of Cations

PC: propylene carbonate, **N-MF**: N-methylformamide,
DMF: dimethylformamide.
The reference ion is Ag^+ for **PC** and **DMF**, Li^+ for **N-MF**

DMF	N_2H_4	DMSO	Pyridine	NH_3	HCOOH	N-MF	Quinoline
6.35#	0.00	0.00	0.00	0.00	0.00	6.29#	0.00
0.22	−6.83	−6.05	−5.79#	−6.79	−5.55	0.00	−6.43#
−0.84	−7.93	−6.96#	−6.78#	−7.74	−6.33	−1.04	−7.54#
−1.57	−8.70	−7.72#	−7.51#	−8.74	−7.36	−1.80	−7.35#
−1.90	−9.01	−7.95#	−7.74#	−9.05	−7.57	−2.09#	−8.59
−2.16#	−9.38#	−8.28#	−8.05#	−9.43	−7.94	−2.49	−8.94#
1.21	−5.09	−5.19	−5.20#	−5.28	−4.94#	0.66#	−5.78#
5.80#	−0.70#	−0.50	−0.54	−0.60	−0.31	5.75#	−0.63
0.00	−6.31	−6.22	−6.11	−6.37	−5.71	−0.33#	−6.79#
1.24#	−5.67#	−4.94#	−4.83#	−5.63#	−4.58#	1.06#	−5.37#
9.92#	3.78#	3.54#	3.37#	3.91#	3.59#	9.97#	3.72#
7.58#	1.24#	1.26#	0.70	1.34#	1.39#	7.57#	1.27#
4.89#	−1.70#	−1.38#	−1.38#	−1.62#	−1.15#	4.81#	−1.55#
3.22	−4.00	−2.99#	−2.94#	−4.27	−2.71	3.11#	−3.28#
2.50#	−4.30#	−3.71#	−3.64#	−4.25#	−3.39#	2.35#	−4.05#
1.81#	−5.05#	−4.39#	−4.30#	−5.01#	−4.05#	1.64#	−4.78#
1.67#	−5.20#	−4.53#	−4.43#	−5.16#	−4.18#	1.50#	−4.93#
5.53#	−1.15	−0.75#	−0.78#	−1.03	−0.51	5.46#	−0.88#
4.34#	−2.27	−1.91	−1.90#	−2.17	−1.62	4.24#	−2.13#
4.48#	−2.14#	−1.78#	−1.77#	−2.07#	−1.53#	4.39#	−1.98#
11.06#	5.02#	4.66#	4.45#	5.16#	4.66#	11.14#	4.92#
5.52#	−1.01#	−0.76#	−0.79#	−0.93#	−0.55#	5.45#	−0.89#
11.10#	5.07#	4.70#	4.49#	5.20#	4.70#	11.19#	4.96#
−1.38#	−8.53#	−7.51#	−7.31#	−8.51#	−7.05#	−1.64#	−8.12#
9.16#	2.95#	2.80#	2.65#	3.07#	2.87#	9.19#	2.93#
−1.44	−8.69#	−7.72	−7.46#	−8.68#	−7.19#	−1.79#	−8.28#
9.25#	3.05#	2.89#	2.74#	3.17#	2.96#	9.29#	3.02#
8.63#	2.38#	2.28#	2.15#	2.49#	2.37#	8.65#	2.37#
7.36#	0.99#	1.04#	0.95#	1.09#	1.18#	7.34#	1.04#
6.17#	−0.30#	−0.12#	−0.17#	−0.21#	0.06#	6.12#	−0.21#
7.27#	0.90#	0.95#	0.86#	0.99#	1.09#	7.25#	0.94#
12.00#	6.05#	5.58#	5.34#	6.20#	5.55#	12.11#	5.91#
7.04#	0.65#	0.73#	0.65#	0.75#	0.88#	7.02#	0.71#
7.30#	0.93#	0.98#	0.89#	1.02#	1.12#	7.28#	0.98#
7.43#	1.07#	1.11#	1.02#	1.17#	1.24#	7.42#	1.11#

Table 1.

No.	Ion	NM	CH_3CN	PC	H_2O	CH_3OH	C_2H_5OH	$HCONH_2$
36	Lu^{+3}	1.70#	1.72#	7.77#	1.80	1.79#	1.80#	1.84#
37	Th^{4+}	5.00#	5.23#	11.20#	5.40	5.37#	5.40#	5.48#
38	U^{3+}	0.65#	0.60#	6.67#	0.65	0.65#	0.65#	0.68#
39	U^{4+}	5.49#	5.75#	11.70#	5.93	5.90#	5.93#	6.02#
40	Sn^{2+}	−2.88#	−3.14#	3.01#	−3.20	−3.18#	−3.20#	−3.21#
41	Pb^{2+}	−3.19#	−3.55#	2.68#	−3.54	−3.47	−3.52	−3.55#
42	Ti^{2+}	−1.34#	−1.51#	4.61#	−1.52	−1.51#	−1.52#	−1.51#
43	Zr^{4+}	6.32#	6.63#	12.57#	6.84	6.80#	6.84#	6.94#
44	Hf^{4+}	5.52#	5.78#	11.73#	5.96	5.93#	5.96#	6.05#
45	As^{3+}	3.77#	3.93#	9.92#	4.06	4.04#	4.06#	4.13#
46	Sb^{3+}	1.81#	1.83#	7.87#	1.91	1.90#	1.91#	1.96#
47	Si^{3+}	1.15#	1.13#	7.19#	1.19	1.19#	1.19#	1.23#
48	V^{2+}	−1.51#	−1.69#	4.43#	−1.71	−1.70#	−1.71#	−1.70#
49	Nb^{3+}	3.73#	3.88#	9.87#	4.01	3.99#	4.01#	4.08#
50	Te^{4+}	8.20#	8.63#	14.52#	8.89	8.84#	8.90#	9.01#
51	Po^{2+}	−1.80#	−2.00#	4.13#	−2.02	−2.01#	−2.02#	−2.02#
52	Po^{3+}	2.24#	2.30#	8.33#	2.39	2.38#	2.39#	2.44#
53	Cr^{2+}	−1.43#	−1.61#	4.51#	−1.62	−1.61#	−1.62#	−1.61#
54	Cr^{3+}	3.46#	3.59#	9.60#	3.72	3.70#	3.72#	3.79#
55	Mn^{2+}	−1.60#	−1.79#	4.33#	−1.81	−1.80#	−1.81#	−1.81#
56	Fe^{2+}	−1.28#	−1.45#	4.66#	−1.46	−1.45#	−1.46#	−1.45#
57	Fe^{3+}	3.42#	3.55#	9.55#	3.67	3.65#	3.67#	3.73#
58	Ru^{2+}	−1.08#	−1.24#	4.87#	−1.24	−1.23#	−1.24#	−1.23#
59	Os^{2+}	−0.92#	−1.06#	5.05#	−1.06	−1.05#	−1.06#	−1.05#
60	Co^{2+}	−0.69#	−0.82#	5.28#	−0.81	−0.80#	−0.81#	−0.79#
61	Co^{3+}	4.59#	4.79#	10.77#	4.95	4.92#	4.95#	5.03#
62	Rh^{3+}	3.75#	3.90#	9.89#	4.03	4.01#	4.03#	4.10#
63	Ni^{2+}	−0.46#	−0.57#	5.52#	−0.56	−0.55#	−0.56#	−0.54#
64	Pd^{2+}	−0.90#	−1.04#	5.06#	−1.04	−1.03#	−1.04#	−1.03#
65	Pt^{2+}	−0.71#	−0.85#	5.26#	−0.84	−0.83#	−0.84#	−0.82#
β		0.916	0.974	0.953	1.000	0.994	1.000_3	1.011
SD, eV		0.06	0.07	0.03		0.03	0.07	0.05

Mutual Relation between Free Energies of Solvation of Cations

(Continued)

DMF	N_2H_4	DMSO	Pyridine	NH_3	HCOOH	N-MF	Quinoline
8.16#	1.87#	1.82#	1.71#	1.97#	1.93#	8.17#	1.88#
11.82#	5.85#	5.40#	5.17#	5.99#	5.38#	11.93#	5.72#
6.99#	0.60#	0.68#	0.61#	0.69#	0.83#	6.97#	0.66#
12.36#	6.44#	5.93#	5.68#	6.59#	5.88#	12.48#	6.29#
3.08#	−3.67#	−3.15#	−3.09#	−3.61#	−2.85#	2.95#	−3.45#
2.74#	−4.02	−3.43	−3.42#	−3.99	−2.95	2.59#	−3.81#
4.79#	−1.81#	−1.48#	−1.48#	−1.73#	−1.24#	4.70#	−1.66#
13.28#	7.45#	6.84#	6.55#	7.60#	6.75#	13.43#	7.25#
12.39#	6.47#	5.96#	5.71#	6.62#	5.91#	12.51#	6.31#
10.46#	4.37#	4.07#	3.88#	4.50#	4.09#	10.53#	4.29#
8.27#	1.99#	1.93#	1.82#	2.10#	2.04#	8.28#	2.00#
7.54#	1.19#	1.22#	1.12#	1.29#	1.35#	7.53#	1.23#
4.60#	−2.02#	−1.66#	−1.66#	−1.95#	−1.42#	4.50#	−1.86#
10.41#	4.32#	4.02#	3.83#	4.44#	4.05#	10.48#	4.24#
15.37#	9.72#	8.87#	8.52#	9.89#	8.71#	15.57#	9.44#
4.28#	−2.36#	−1.97#	−1.96#	−2.29#	−1.72#	4.18#	−2.19#
8.76#	2.52#	2.41#	2.28#	2.63#	2.50#	8.78#	2.51#
4.69#	−1.92#	−1.57#	−1.58#	−1.85#	−1.34#	4.60#	−1.76#
10.11#	3.99#	3.73#	3.56#	4.12#	3.77#	10.17#	3.93#
4.49#	−2.13#	−1.76#	−1.76#	−2.06#	−1.52#	4.40#	−1.97#
4.85#	−1.74#	−1.42#	−1.42#	−1.67#	−1.19#	4.76#	−1.59#
10.06#	3.94#	3.68#	3.51#	4.06#	3.72#	10.12#	3.87#
5.07#	−1.50#	−1.20#	−1.21#	−1.42#	−0.98#	4.99#	−1.36#
5.26#	−1.30#	−1.02#	−1.04#	−1.22#	−0.80#	5.18#	−1.17#
5.51#	−1.02#	−0.77#	−0.80#	−0.94#	−0.56#	5.44#	−0.90#
11.36#	5.36#	4.96#	4.74#	5.49#	4.94#	11.46#	5.24#
10.43#	4.34#	4.04#	3.85#	4.46#	4.07#	10.50#	4.26#
5.76#	−0.74#	−0.52#	−0.56#	−0.66#	−0.32#	5.70#	−0.63#
5.28#	−1.27#	−1.00#	−1.02#	−1.20#	−0.78#	5.20#	−1.14#
5.48#	−1.05#	−0.80#	−0.83#	−0.97#	−0.59#	5.41#	−0.93#
1.016	1.107	0.994	0.961	1.117	0.956	1.044	1.065
0.05	0.08	0.07	0.02	0.07	0.13	0.04	0.03

$$a_{iw} = \frac{1}{z_i} \Delta\mathcal{F}_i^0 - \Delta\mathcal{F}_{H^+}^0 - FE_{iw}^0 , \qquad (5)$$

where $\Delta\mathcal{F}_i^0$ is the free energy of formation of ion i in the gas phase from its pure element and $\Delta\mathcal{F}_{H^+}^0$ is that for proton, φ_{iw}^0 is the standard electromotive force referred to the standard state of the gaseous electron for the redox system associated with ion i and its pure element and E_{iw}^0 is the difference $\varphi_{iw}^0 - \varphi_{H^+w}^0$.

The relative value a_{is} for ion i referred to proton in non-aqueous medium s can also be expressed by eq. (5) with subscript s in place of w.

The values of a_{is} and a_{iw} calculated by eq. (5) using the values of $\Delta\mathcal{F}_i^0$, $\Delta\mathcal{F}_{H^+}^0$, E_{is}^0 and E_{iw}^0 in the thermodynamical and electrochemical data books[4,5] are listed in

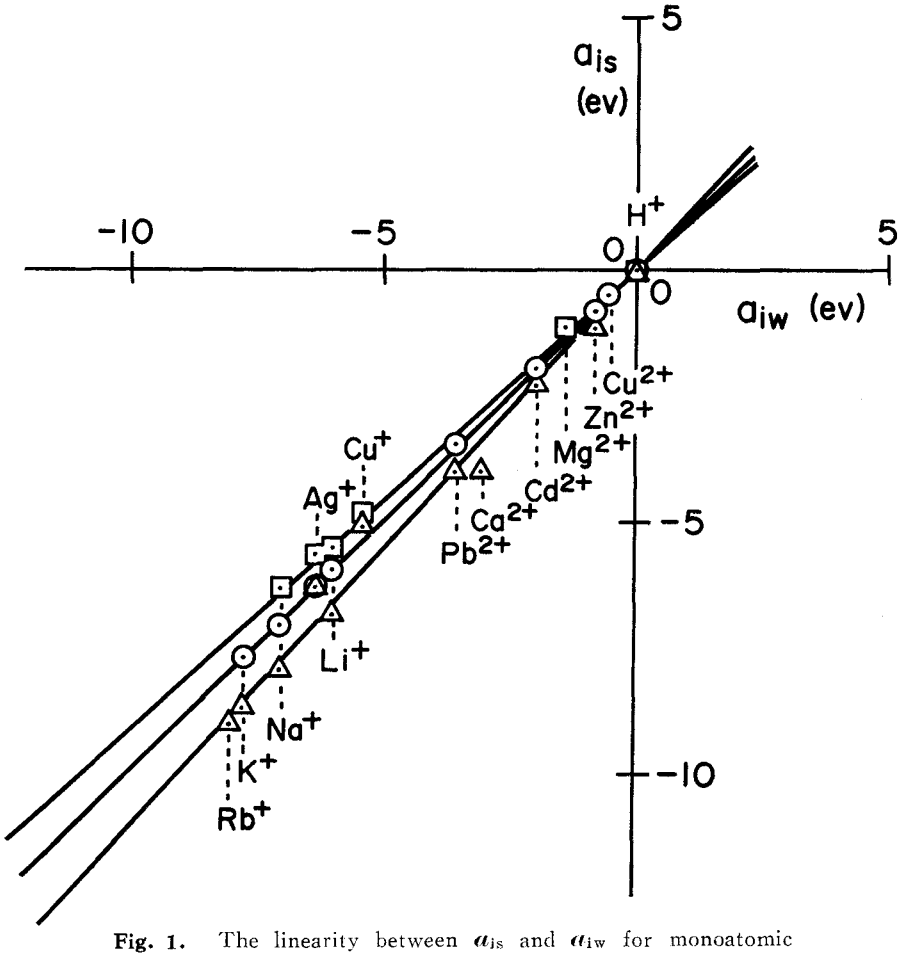

Fig. 1. The linearity between a_{is} and a_{iw} for monoatomic cations in nitromethane (⊡), methanol (⊙) and hydrazine (△), H^+ ion being taken as the reference ion.

Table 1. Fig. 1 shows a few example for the a_{1s} vs. a_{1w} plots obtained from Table 1. We can find an excellent linear relation between a_{1s} and a_{1w} pointing to the origin which can be expressed by the equation

$$a_{1s} = \beta a_{1w}, \tag{6}$$

for monoatomic cations in any solvent for which E^0_{1s} is known experimentally, with a few exceptions Ag^+, Cu^+ and Ca^{++} ions in hydrazine and ammonia (cf. Fig. 8 in ref. 1 a), Ag^+ ion in acetonitrile (cf. Fig. 8 in ref. 1 a), and Be^{++} ion in pyridine (cf. Fig. 5 in ref. 1 b), which show a slight deviation from eq. (6). The standard deviation (SD) from eq. (6) for the cations in each solvent is shown in Table 1. The values of coefficient β are also shown in the table. It is found that they are in the range $1 \sim 0.9$.

Eq. (6) is rewritten using eq. (3) in terms of the chemical terms α^0_{1s} and α^0_{1w}

$$\frac{1}{z_1}\alpha^0_{1s} - \alpha^0_{H^+,s} = \beta\left(\frac{1}{z_1}\alpha^0_{1w} - \alpha^0_{H^+,w}\right) \tag{7}$$

Let us now assume an ideal ion which has no chemical interaction with any solvent, *i. e.*,

$$\alpha^0_{1s}(\text{ideal}) = 0, \tag{8}$$

and postulate on the basis of eq. (6) that the ideal ion is located on the straight line. It follows from eqs. (7) and (8)

$$\alpha^0_{1s} = \beta\alpha^0_{1w}. \tag{9}$$

In this way we find an excellent linearity between α^0_{1s} and α^0_{1w} under the presumption of the ideal ion. Eq. (9) strongly suggests that the ion-solvent interaction in the solvation process is of the same type for any cation in any solvent with a few exceptions described above, and the values of α^0_{1s} for a given ion in different solvents are quite close to each other.

At the present stage the experimental values for E^0_{1s} in non-aqueous media are known for a limited number of cations. However, using the values of a_{1w}, it may be possible to estimate the values of a_{1s} by eq. (6) for the cations in any non-aqueous solvent for which the experimental values for E^0_{1s} are not known. The values of a_{1s} calculated in this way are also shown in Table 1 with symbol $\sharp$.

Thus it may be better to express the mutual relation between the free energies of solvation in non-aqueous and aqueous media by eq. (6) in terms of a_{1s} and a_{1w} rather than a_{1s} and $\frac{1}{z_1}\bar{\alpha}^0_{1w}$ because eq. (6) does not include any uncertainty due to the lack of conformity in the experimental values for $\bar{\alpha}^0_{1w}$ and can readily be proved by the experimental values for E^0_{1s}.

Let us discuss here briefly the concept for the ideal ion. The ideal ion can be regarded as an ion of infinite size and consequently of infinitesimally small charge density on its surface. as seen from the comparison of the a_{1s}-values in Fig. 1 for the cations

of the same valency. It may therefore be reasonable to assume that $\alpha_{Is}^{0}(\text{ideal})=0$, but the electrostatic work $z_I F\chi_s$ in the solvation process of the ideal ion cannot be ignored since the electrostatic work does not depend on the size of the ion. In our previous work[1] we assumed $\bar{\alpha}_{Is}^{0}(\text{ideal})=0$ for the ideal ion in place of $\alpha_{Is}^{0}(\text{ideal})=0$, but this assumption was not correct. Accordingly, $-\frac{1}{z_I}\alpha_I^0$ and φ_I^0 in the previous work should be read as $\frac{1}{z_I}\alpha_{Is}^{0}-\mathbf{F}(\beta\chi_w-\chi_s)$ and $\varphi_{Is}^{0}+\mathbf{F}(\beta\chi_w-\chi_s)$, respectively.

The numerical estimation for α_{Is}^{0} will be discussed elsewhere[6].

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