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## EMPIRICAL RELATION BETWEEN FREE ENERGIES OF HYDRATION AND IONIZATION POTENTIALS OF MONOATOMIC CATIONS<sup>\*)</sup>

By

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### Abstract

It is found that the monoatomic cationic species can be classified into (a), (b) and (c) groups on the basis of three types of linear relationship between their standard free energies of hydration relative to that of proton and their ionization potentials in the gas phase. The cationic species in the three groups are respectively characterized by (i) the position in the periodic table: (a) IA~VA groups, (b) VIA~VIB groups, and (c) IB~VIB groups in the 6th period; (ii) the electronic configuration: (a) the rare gas type, including lanthanides and actinides, (b) the number of d-electrons more than 3, and (c)  $5d^{10}+4f^{14}$  electrons; (iii) the standard electromotive force: (a) below  $-1.0$  V, and (b) and (c) above  $-1.0$  V; (iv) the free energy of ionization in aqueous medium: (a) negative, (b) and (c) positive.

Assuming that an ideal ion which has no ionization potential and no chemical interaction with surrounding water molecules in the hydration process belongs to (a) group cations which are characterized by the electronic configuration of the rare gas type, the absolute value of the standard chemical free energy of hydration of proton can be estimated to be 11.71 eV from the linear relationship for the (a) group cations.

### Introduction

Many attempts have been made from the thermodynamical point of view for the estimation of the ion-solvent interactions, but still there exists inconsistency among the values of the standard real free energy of hydration of single ions reported by different authors<sup>1)</sup>. Furthermore we have an essential difficulty in splitting the real free energy of solvation of a single ion into its chemical and electrostatic terms as pointed out by Guggenheim<sup>2)</sup>.

On the other hand, the ion-solvent interactions in solution have been studied theoretically in connection with the structure and the stability of the

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coordination compounds<sup>3)</sup>. The hydration bond for monoatomic ions can be explained quantitatively by the electrostatic theory in fairly good approximation<sup>4)</sup>. However, the static dielectric constant of aqueous and non-aqueous media has no direct correlation with the real free energy of solvation for monoatomic cations in a series of solvents<sup>5)</sup>. The crystal field correction for the electrostatic theory has been successfully applied to the explanation of the spectroscopic data and the stability of the coordination compounds of the transition elements<sup>6)</sup>, but it is not successful for the explanation of the bond energies of the coordination compounds in which  $\pi$ -bond is included. Although the molecular orbital theory can explain the fine structure of the coordination compounds, *e.g.* the NMR-spectra and spin-orbital coupling, but this theory is not accurate enough at present to predict the bond energy as a whole<sup>7)</sup>. The donor-acceptor concept has been introduced for the explanation of the molecular interactions<sup>8)</sup>, but this approach is limited at present to some ion-solvent systems in liquid media. The X-ray and neutron diffraction studies for the ionic solutions are also limited to some ionic systems<sup>9)</sup>. It seems therefore that the nature of the chemical interactions of an ion with surrounding solvent molecules in liquid media is essentially not clear at present from both of the theoretical and experimental points of view.

Recently we have found an excellent linear relationship between the relative standard free energies of solvation of single ions referred to proton in non-aqueous and aqueous media, which strongly suggests that the ion-solvent interaction in the solvation process is of the same type for any solvent<sup>5,14)</sup>. The present work is concerned with linear relationships between the relative free energies of hydration of monoatomic cations referred to proton and their ionization energies in the gas phase, which may enable us to estimate the chemical free energies of solvation of monoatomic cations not only for water but also for any solvent combined with the empirical rule reported in the previous work<sup>5,14)</sup>.

### Estimation of the relative standard free energy of hydration of a monoatomic cation

The standard real free energy of hydration  $\bar{\alpha}_{i,w}^0$  of a single ion of species  $i$  may be defined as the difference between the electrochemical potentials of the ion  $\bar{\mu}_{i,g}^0$  in the gas phase and  $\bar{\mu}_{i,w}^0$  in water as

$$\bar{\alpha}_{i,w}^0 = \bar{\mu}_{i,g}^0 - \bar{\mu}_{i,w}^0, \quad (1)$$

where superscript 0 means the standard state. Splitting the electrochemical

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potential into the chemical and electrostatic terms, we obtain

$$\bar{\alpha}_{i,w}^{\circ} = \alpha_{i,w}^{\circ} - z_1 F \chi_w, \quad (2)$$

where  $\alpha_{i,w}^{\circ}$  is the standard chemical free energy of hydration of ion  $i$ ,  $\chi_w$  is the surface potential of water,  $z_1$  is the valency of ion  $i$  and  $F$  is the Faraday.

Let us now consider the relative standard free energy of hydration of ion  $i$  referred to a definite reference ion  $j$  which is defined as

$$\alpha_{i,w} = \frac{\bar{\alpha}_{i,w}^{\circ}}{z_1} - \frac{\bar{\alpha}_{j,w}^{\circ}}{z_j}, \quad (3)$$

with each divided by its valency.  $\alpha_{i,w}$  can be expressed by eq. (2) in terms of the chemical parts  $\alpha_{i,w}^{\circ}$  and  $\alpha_{j,w}^{\circ}$  as

$$\alpha_{i,w} = \frac{\alpha_{i,w}^{\circ}}{z_1} - \frac{\alpha_{j,w}^{\circ}}{z_j}. \quad (3')$$

The value of  $\alpha_{i,w}$  can be estimated from the standard electromotive force  $E_{ij}^{\circ}$  of the redox system associated with ion  $i$  and its pure element measured against the reference electrode composed of ion  $j$  and its pure element on the basis of the thermodynamical relation

$$\Delta \mathcal{F}_i^{\circ} = \bar{\alpha}_{i,w}^{\circ} + z_1 F \varphi_i^{\circ}, \quad (4)$$

where  $\Delta \mathcal{F}_i^{\circ}$  denotes the Gibbs Free energy of formation of ion  $i$  in the gas phase from its pure element,  $\varphi_i^{\circ}$  is the absolute electromotive force of the redox system associated with ion  $i$  referred to the standard state of the and gaseous electron. Applying eq. (4) to ion  $i$  and ion  $j$ , we obtain

$$\alpha_{i,w} = \frac{\Delta \mathcal{F}_i^{\circ}}{z_1} - \frac{\Delta \mathcal{F}_j^{\circ}}{z_j} - F E_{ij}^{\circ}, \quad (5)$$

where  $E_{ij}^{\circ} = \varphi_i^{\circ} - \varphi_j^{\circ}$ . The values of  $\alpha_{i,w}$  can therefore be estimated by eq. (5) using the values for  $\Delta \mathcal{F}_i^{\circ}$ ,  $\Delta \mathcal{F}_j^{\circ}$  and  $E_{ij}^{\circ}$  compiled in thermodynamical and electrochemical data books<sup>10,11</sup>.

**Empirical relation between  $\alpha_{i,w}$  and the ionization potential in the gas phase**

The value of the ionization potential  $I_i$  for ion  $i$  is given by the sum of the successive ionization potentials of the ion from its atomic state in the gas phase<sup>12</sup>.

Fig. 1 shows the relation between  $\alpha_{i,w}$  and  $I_i/z_1$  expressed in eV for monoatomic cations at 25°C, in which the hydrogen ion is chosen as the

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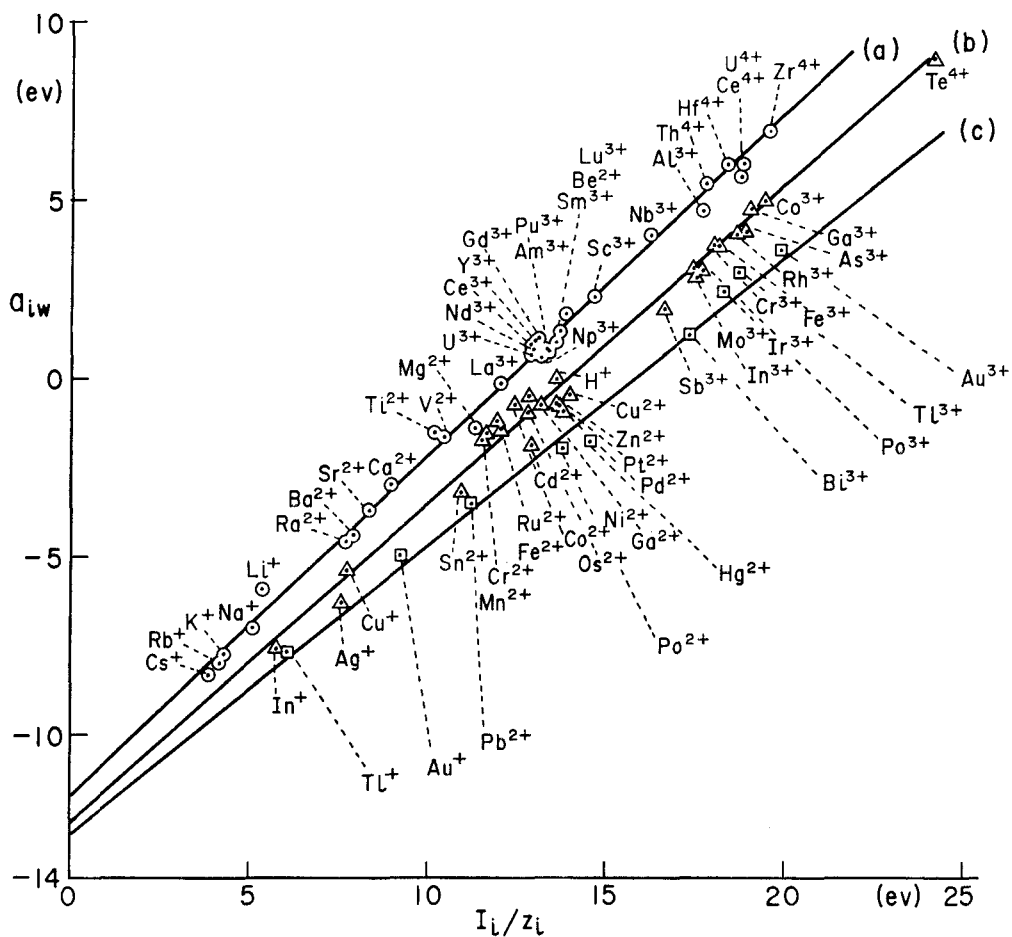


Fig. 1. The relation between  $\alpha_{i,w} = \frac{\alpha_{i,w}^0}{z_i} - \alpha_{H^+,w}^0$  and  $I_i/z_i$  for monoatomic cations at 25°C.

reference ion, *i. e.*  $\alpha_{i,w} = \frac{\alpha_{i,w}^0}{z_i} - \alpha_{H^+,w}^0$ . As seen from this figure, there exists three types of linearity which can be expressed by the equation

$$\alpha_{i,w} = \rho \frac{I_i}{z_i} - k. \quad (6)$$

The values of coefficient  $\rho$  for these three straight lines are estimated as 0.95, 0.88 and 0.82 respectively and those for constant  $k$  are 11.71, 12.53 and 12.75 eV with the correlation coefficients 0.9954, 0.9858 and 0.9885 respectively.

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Group	IA	IIA	IIIA	IVA	VA	VIA	VIIA	VIII	IB	IIB	IIIB	IVB	VB	VIB	VIIA	0		
1 1s	1 H	(a) (b) (c)														2 He		
2 2s2p	3 Li	4 Be	□			□			□			5 B	6 C	7 N	8 O	9 F	10 Ne	
3 3s3p	11 Na	12 Mg											13 Al	14 Si	15 P	16 S	17 Cl	18 Ar
4 4s3d	19 K	20 Ca	21 Sc	22 Ti	23 V	24 Cr	25 Mn	26 Fe	27 Co	28 Ni	29 Cu	30 Zn	31 Ga	32 Ge	33 As	34 Se	35 Br	36 Kr
5 5s4d5p	37 Rb	38 Sr	39 Y	40 Zr	41 Nb	42 Mo	43 Tc	44 Ru	45 Rh	46 Pd	47 Ag	48 Cd	49 In	50 Sn	51 Sb	52 Te	53 I	54 Xe
6 6s(4f)5d6p	55 Cs	56 Ba	57 ~71	72 Hf	73 Ta	74 W	75 Re	76 Os	77 Ir	78 Pt	79 Au	80 Hg	81 Tl	82 Pb	83 Bi	84 Po	85 At	86 Rn
7 7s(5f)6d	87 Fr	88 Ra	89 ~103															
Lanthanide 4f	57 La	58 Ce	59 Pr	60 Nd	61 Pm	62 Sm	63 Eu	64 Gd	65 Tb	66 Dy	67 Ho	68 Er	69 Tm	70 Yb	71 Lu			
Actinide 5f	89 Ac	90 Th	91 Pa	92 U	93 Np	94 Pu	95 Am	96 Cm	97 Bk	98 Cf	99 Es	100 Fm	101 Md	102 No	103 Lr			

Fig. 2. The classification of monoatomic cations of (a), (b) and (c) groups in the periodic table.

It will be seen that the cations on each straight line (a), (b) and (c) in Fig. 1 can be classified according to their electronic configurations, standard electromotive forces and ionization free energies in aqueous medium. Fig. 2 shows the classification in the periodic table. The electronic configurations and the standard electromotive forces for the cations in the three groups are listed in Table 1.

It is found that:

(i) the cations on the straight line (a) belong to IA-VA groups in the periodic table and they have the electronic configuration of the rare gas type, including lanthanides and actinides, but with exceptions of three ionic species  $Ti^{2+}$ ,  $V^{2+}$  and  $Nb^{3+}$  which have  $3d^2$ ,  $3d^3$  and  $4d^2$  electrons respectively,

(ii) the cations on the straight line (b) belong to VIA-VIB groups in the periodic table which are characterized by d-electrons more than 3;

(iii) the cations in the straight line (c) belong to IB-VIB groups in the 6th period which are characterized by  $5d^{10}+4f^{14}$ , but with an exception of  $Au^{3+}$  ion which has the same electronic configuration with  $Pt^{2+}$  in (b) group,

(iv) most of the cations in (b) and (c) groups are known to form aqua-complexes.

TABLE 1. The standard electrode potentials referred to the standard hydrogen electrode at 25°C and the electronic configurations of monoatomic cations in (a), (b) and (c) groups

(a)-Group	E°, v	Elec. Config.	(b)-Group	E°, v	Elec. Config.	(c)-Group	E°, v	Elec. Config.
1 Li/Li <sup>+</sup>	-3.024	He	1 Mn/Mn <sup>2+</sup>	-1.05	Ar+3d <sup>5</sup>	1 Tl/Tl <sup>+</sup>	-0.338	Xe+5d <sup>10</sup> +4f <sup>14</sup> +6s <sup>2</sup>
2 Cs/Cs <sup>+</sup>	-3.02	Xe	2 Cr/Cr <sup>2+</sup>	-0.9	Ar+3d <sup>4</sup>	2 Pb/Pb <sup>2+</sup>	-0.126	Xe+5d <sup>10</sup> +4f <sup>14</sup> +6s <sup>2</sup>
3 Rb/Rb <sup>+</sup>	-2.99	Kr	3 Zn/Zn <sup>2+</sup>	-0.762	Ar+3d <sup>10</sup>	3 Bi/Bi <sup>3+</sup>	0.2	Xe+5d <sup>10</sup> +4f <sup>14</sup> +6s <sup>2</sup>
4 K/K <sup>+</sup>	-2.924	Ar	4 Cr/Cr <sup>3+</sup>	-0.71	Ar+3d <sup>3</sup>	4 Po/Po <sup>3+</sup>	0.56	Xe+5d <sup>10</sup> +4f <sup>14</sup> +6s <sup>2</sup> +6p <sup>2</sup>
5 Ra/Ra <sup>2+</sup>	-2.92	Rn	5 Ga/Ga <sup>3+</sup>	-0.52	Ar+3d <sup>10</sup>	5 Po/Po <sup>2+</sup>	0.65	Xe+5d <sup>10</sup> +4f <sup>14</sup> +6s <sup>2</sup> +6p <sup>2</sup>
6 Ba/Ba <sup>2+</sup>	-2.90	Xe	6 Ga/Ga <sup>2+</sup>	-0.45	Ar+3d <sup>10</sup> +4s	6 Tl/Tl <sup>3+</sup>	0.71	Xe+5d <sup>10</sup> +4f <sup>14</sup>
7 Sr/Sr <sup>2+</sup>	-2.89	Kr	7 Fe/Fe <sup>2+</sup>	-0.441	Ar+3d <sup>6</sup>	7 Hg/Hg <sup>2+</sup>	0.854	Xe+5d <sup>10</sup> +4f <sup>14</sup>
8 Ca/Ca <sup>2+</sup>	-2.87	Ar	8 Cd/Cd <sup>2+</sup>	-0.402	Kr+4d <sup>10</sup>	8 Au/Au <sup>3+</sup>	1.50	Xe+5d <sup>8</sup> +4f <sup>14</sup>
9 Na/Na <sup>+</sup>	-2.714	Ne	9 In/In <sup>3+</sup>	-0.340	Kr+4d <sup>10</sup>	9 Au/Au <sup>+</sup>	1.70	Xe+5d <sup>10</sup> +4f <sup>14</sup>
10 Ce/Ce <sup>3+</sup>	-2.48	Xe+4f	10 Co/Co <sup>2+</sup>	-0.277	Ar+3d <sup>7</sup>			
11 Nd/Nd <sup>3+</sup>	-2.44	Xe+4f <sup>3</sup>	11 In/In <sup>+</sup>	-0.25	Kr+4d <sup>10</sup> +5s <sup>2</sup>			
12 Sm/Sm <sup>3+</sup>	-2.41	Xe+4f <sup>5</sup>	12 Ni/Ni <sup>2+</sup>	-0.250	Ar+3d <sup>8</sup>			
13 Gd/Gd <sup>3+</sup>	-2.40	Xe+4f <sup>7</sup>	13 Mo/Mo <sup>3+</sup>	-0.2	Kr+4d <sup>3</sup>			
14 La/La <sup>3+</sup>	-2.37	Xe	14 Sn/Sn <sup>2+</sup>	-0.140	Kr+4d <sup>10</sup>			
15 Y/Y <sup>3+</sup>	-2.37	Kr	15 Fe/Fe <sup>3+</sup>	-0.036	Ar+3d <sup>5</sup>			
16 Mg/Mg <sup>2+</sup>	-2.34	Ne	16 ½H <sub>2</sub> /H <sup>+</sup>	0				
17 Am/Am <sup>3+</sup>	-2.32	Rn+5f <sup>6</sup>	17 Sb/Sb <sup>3+</sup>	0.24	Kr+4d <sup>10</sup> +5s <sup>2</sup>			
18 Lu/Lu <sup>3+</sup>	-2.225	Xe+4f <sup>14</sup>	18 As/As <sup>3+</sup>	0.3	Ar+3d <sup>10</sup>			
19 Sc/Sc <sup>3+</sup>	-2.08	Ar	19 Cu/Cu <sup>2+</sup>	0.345	Ar+3d <sup>9</sup>			
20 Pu/Pu <sup>3+</sup>	-2.07	Rn+5f <sup>5</sup>	20 Co/Co <sup>3+</sup>	0.4	Ar+3d <sup>6</sup>			
21 Th/Th <sup>4+</sup>	-1.90	Rn	21 Ru/Ru <sup>2+</sup>	0.45	Kr+4d <sup>6</sup>			
22 Np/Np <sup>3+</sup>	-1.86	Rn+5f <sup>4</sup>	22 Cu/Cu <sup>+</sup>	0.522	Ar+3d <sup>10</sup>			
23 U/U <sup>3+</sup>	-1.80	Rn+5f <sup>3</sup>	23 Te/Te <sup>4+</sup>	0.568	Kr+4d <sup>10</sup> +5s <sup>2</sup>			
24 Ti/Ti <sup>2+</sup>	-1.75	Ar+3d <sup>2</sup>	24 Os/Os <sup>2+</sup>	0.7	Xe+5d <sup>6</sup> +4f <sup>14</sup>			
25 Be/Be <sup>2+</sup>	-1.70	He	25 Ag/Ag <sup>+</sup>	0.799	Kr+4d <sup>10</sup>			
26 Hf/Hf <sup>4+</sup>	-1.70	Xe+4f <sup>14</sup>	26 Pd/Pd <sup>2+</sup>	0.80	Kr+4d <sup>8</sup>			
27 Al/Al <sup>3+</sup>	-1.67	Ne	27 Rh/Rh <sup>3+</sup>	0.8	Kr+4d <sup>6</sup>			
28 Zr/Zr <sup>4+</sup>	-1.53	Kr	28 Ir/Ir <sup>3+</sup>	1.0	Xe+5d <sup>6</sup> +4f <sup>14</sup>			
29 Ce/Ce <sup>4+</sup>	-1.46	Xe	29 Pt/Pt <sup>2+</sup>	1.0	Xe+5d <sup>8</sup> +4f <sup>14</sup>			
30 U/U <sup>4+</sup>	-1.40	Rn+5f <sup>2</sup>						
31 V/V <sup>2+</sup>	-1.18	Ar+3d <sup>3</sup>						
32 Nb/Nb <sup>3+</sup>	-1.1	Kr+4d <sup>2</sup>						

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The standard electromotive forces referred to the standard hydrogen electrode for the cations in (a) group rank below those for cations in (b) and (c) groups with boundary at about  $-1.0$  v as seen from Table 1.

The free energy of ionization  $I_{iw}$  for ion  $i$  in aqueous medium estimated by the following equation<sup>12)</sup>

$$I_{iw} = z_i F(E_i^\circ - E_e^\circ) - A, \quad (7)$$

is plotted in Fig. 3 against  $I_i/z_i$  in the gas phase. In eq. (7)  $A$  is the free energy of atomization from the pure element for ion  $i$ ,  $E_i^\circ$  and  $E_e^\circ$  are respectively the standard electromotive forces for ion  $i$  and the hydrated electron and  $E_e^\circ$  is taken as  $-2.77$  V<sup>13)</sup>.

It is found that  $I_{iw}$  is negative for every cation in (a) group, while it is positive for the cations in (b) and (c) groups with an exception of  $\text{Os}^{2+}$  ion only, and the cations in (c) group have high values of  $I_{iw}$  as compared with those in (b) group. From the energetic point of view a general trend can be seen from Fig. 3 that the atomic species in (a) group can readily dissociate into the ion and hydrated electron in aqueous media, in fact as is known for alkali and alkali earth metals, and most of atomic species in (b) group have a possibility to dissociate into the ion and hydrated electron

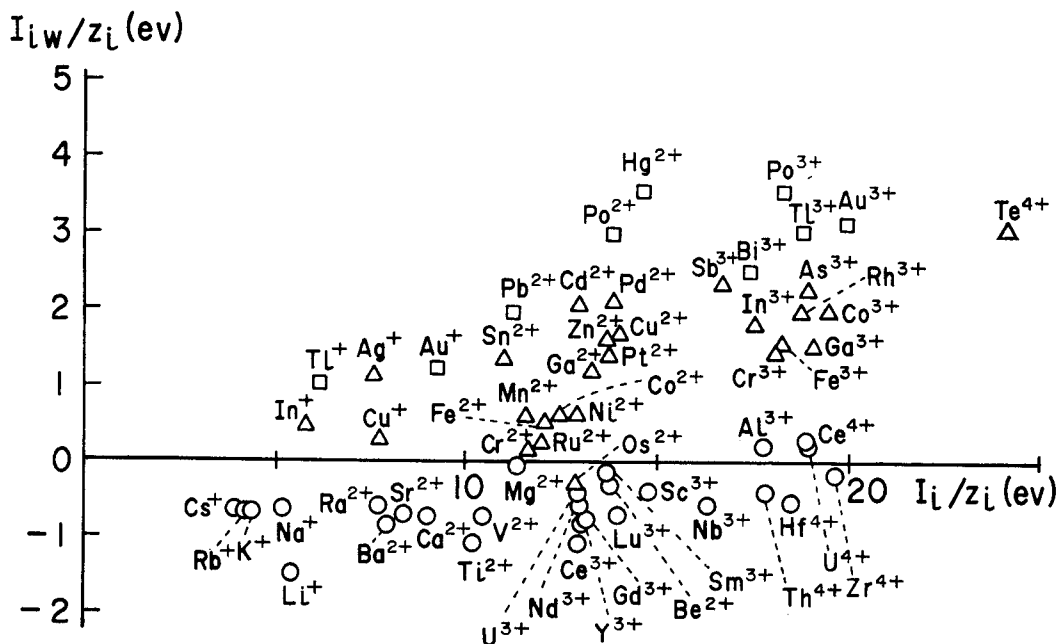


Fig. 3. The relation between the ionization energy  $I_{iw}/z_i$  in aqueous medium and  $I_i/z_i$  in the gas phase for monoatomic cations.



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TABLE 2. The list of criteria for the classification of monoatomic cations into (a), (b) and (c) groups

group	(a)	(b)	(c)
criteria	(32)	(29)	(9)
periodic table	IA-VA	VIA-VIB	IB-VIB (6-period)
electronic configuration	X	X+d <sup>4~10</sup>	X+5d <sup>10</sup> +4f <sup>14</sup>
standard potential (E <sub>i</sub> <sup>o</sup> )	< -1.0 v	> -1.0 v	> -1.0 v
ionization free energy in aq. medium	negative	positive	positive

X: rare gas type

by photoexcitation with visible ray, but most of the atomic species in (c) group show a difficulty for photo-dissociation in aqueous medium. The criteria for the classification of cations into (a), (b) and (c) groups are summarized in Table 2.

It may be possible to estimate the chemical free energy of hydration of proton  $\alpha_{\text{H}^+,\text{w}}^{\circ}$  directly from the linear relationship for the cations in (a) group which have simple electronic configuration of the rare gas type. Let us consider an ideal ion which has no chemical interaction with surrounding water molecules, *i. e.*  $\alpha_{i,\text{w}}^{\circ}$  (ideal)=0. For such an ideal ion the ionization potential may also be assumed to be zero, because the ideal ion can be regarded as an ion of infinite size. We assume here that the ideal ion is located on the extension of the linear relation (a) in Fig. 1. Then we obtain from constant  $k$  in eq. (6) for the (a) group cations  $\alpha_{\text{H}^+,\text{w}}^{\circ}=11.71$  eV with the standard deviation 0.30 eV. The value of  $\alpha_{i,\text{w}}^{\circ}$  for ion  $i$  can then be estimated by eq. (3') on the basis of  $\alpha_{\text{H}^+,\text{w}}^{\circ}=11.71$  eV.

On the other hand, we have found that the chemical free energy of solvation  $\alpha_{i,\text{s}}^{\circ}$  for ion  $i$  in a non-aqueous solvent  $s$  shows an excellent linear relationship with  $\alpha_{i,\text{w}}^{\circ}$  which can be expressed by the equation<sup>14)</sup>

$$\alpha_{i,\text{s}}^{\circ} = \beta \alpha_{i,\text{w}}^{\circ}, \quad (8)$$

where coefficient  $\beta$  is a constant which is characteristic to the solvent. The value of  $\alpha_{i,\text{s}}^{\circ}$  for any solvent can therefore be estimated by eq. (8) using the value for  $\alpha_{i,\text{w}}^{\circ}$  estimated in the present treatment. The ion-solvent interactions in the solvation process will be discussed elsewhere on the basis of the donor-acceptor concept introduced by Gutmann<sup>8)</sup> using the  $\alpha_{i,\text{s}}^{\circ}$ -values obtained

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by the present empirical approach.

In conclusion, for the estimation of the free energy of solvation of an ion by such an extrapolation method as proposed in the present treatment, we should take into consideration another kind of work in the solvation process of an ion which originates from the formation of the new boundary surface around the ion or from the van der Waals interaction between the ion and the surrounding solvent molecules, as pointed out by Frumkin<sup>15)</sup>. We can expect an anomalous increase of such work with increasing ionic radius. But such kind of size effect may be ruled out from the present treatment, since the linearity in Fig. 1 covers a wide range of ionic species from monovalent to polyvalent cations of small size.

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