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CLASSIFICATION OF MONOATOMIC CATIONS BY THE NATURE OF SOLVATION BONDING*

By

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Abstract

The numerical values of the standard chemical free energies of solvation of monoatomic cations have been estimated for 70 ionic species in 15 solvents on the basis of the empirical rules proposed previously.

It has been shown that the classification of monoatomic cations in the periodic table by the nature of the solvation bonding practically coincides with the classification of these ions by the hard and soft concept as the Lewis acids.

Introduction

In recent years non-aqueous solvents have achieved a great importance in electrochemistry as reaction media for electrolytes. However, we have not yet reached a final conclusion on the free energy of solvation of a single ion in non-aqueous media as well as in aqueous medium, although many theories and experimental procedures have been advanced for the estimation of the ion-solvent interactions in the solvation process.[1]

Recently we have found two empirical rules for the relative free energies of solvation of monoatomic cations which may enable us to determine the chemical free energies of solvation of these ions.[2,3] In the present work the numerical values of the standard chemical free energies of solvation of monoatomic cations estimated on the basis of the empirical rules will be reported and the classification of monoatomic cations by the nature of the solvation bonding will be compared with that proposed on the basis of the hard and soft acids and bases (HSAB) concept of the monoatomic cations as the Lewis acids.[4,5]

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Estimation of the standard chemical free energies of solvation of monoatomic cations

Let us consider a relative quantity $a_{ij,s}$ for the solvation free energy of monoatomic cation i in solvent s which can be defined by the following equation

$$a_{ij,s}=\frac{\overline{\alpha^0_{i,s}}}{z_i}-\frac{\overline{\alpha^0_{j,s}}}{z_j}=\frac{\alpha^0_{i,s}}{z_i}-\frac{\alpha^0_{j,s}}{z_j}, \tag{1}$$

where $\overline{\alpha^0_{i,s}}$ is the standard real free energy of solvation of ion i in solvent s, $\alpha^0_{i,s}$ its chemical part, z_i the valency of ion i and subscript j denotes a definite reference ion of valency z_j. $\overline{\alpha^0_{i,s}}$ can, in principle, be split into the chemical and electrostatic terms

$$\overline{\alpha^0_{i,s}}=\alpha^0_{i,s}-z_i\mathbf{F}\chi_s, \tag{2}$$

where χ_s is the surface potential of solvent s, the sign of which is taken positive when the surface dipole of the solvent turns its negative end towards the gas phase, and $\mathbf{F}$ the Faraday.

On the basis of a thermodynamic cycle $a_{ij,s}$ can be evaluated numerically by the following equation as reported previously[2]

$$a_{ij,s}=\frac{\Delta F^0_i}{z_i}-\frac{\Delta F^0_j}{z_j}-\mathbf{F}E^0_{ij,s}, \tag{3}$$

where ΔF^0_i is the free energy of formation of ion i in the gas phase from its pure element, ΔF^0_j is that for ion j, and $E^0_{ij,s}$ is the standard electromotive force of the redox system of ion i and its pure element in solvent s which is measured against the reference electrode of ion j and its pure element in the same solution.

We have recently found an excellent proportionality between $a_{ij,s}$ for any solvent and that for water $a_{ij,w}$[2]

$$a_{ij,s}=\beta_s a_{ij,w}, \tag{4}$$

where β_s is a constant for a given solvent which falls in the range 0.92～1.12 depending on the solvent, *e.g.*, 0.916 for nitromethane and 1.17 for ammonia. The standard deviation of the value of $a_{ij,s}$ from the straight line eq. (4) obtained by the least square method is less than 0.07 eV for any solvent except formic acid for which the standard deviation attains 0.13 eV. Eq. (4) was called "empirical rule I" for the solvation of monoatomic cations.

We have found furthermore three types of linear relationship between $a_{ij,s}$ and the ionization energy I_i for i in the gaseous state which can be expressed by the equation[3]

$$a_{ij,s} = \rho_s \frac{I_i}{z_i} - k_s , \qquad (5)$$

and the monoatomic cations can be classified into three groups (a), (b) and (c) by eq. (5) with different values for coefficient ρ_s and constant k_s. The cations of different groups are characterized by their electronic configurations of the outer shell: group (a) cations — the rare gas type, the lanthanides and the actinides, group (b) cations — the number of d-electrons in the outer shell more than 3, and group (c) cations — $5d^{10}+4f^{14}$ type. Eq. (5) was called "empirical rule II" for the solvation of monoatomic cations.

The numerical values of β_s in eq. (4), and those of ρ_s and k_s for (a), (b) and (c) groups are shown in table 1 for 15 solvents which are available at present, the hydrogen ion being taken as the reference ion for the estimation of the value of $a_{ij,s}$. The standard deviations of $a_{1j,s}$ from the straight lines, eq. (5), obtained by the least square method are less than 0.35 eV, 0.47 eV and 0.44 eV for the (a), (b) and (c) group cations, respectively.

The graphical representation for the relationships between ρ_s and β_s, and k_s and β_s for (a), (b) and (c) groups is given in figs. 1 and 2. The β_s and

TABLE 1. The values of β_s for 15 solvents and those of ρ_s and k_s for the cations of (a), (b) and (c) groups at 25°C, except for ammonia at −35°C

	Solvent	β_s	ρ_s			k_s, eV		
			(a)	(b)	(c)	(a)	(b)	(c)
1	Nitromethane (NM)	0.916	0.868	0.810	0.749	10.68	11.41	11.73
2	Propylene carbonate (PC)	0.953	0.902	0.844	0.776	11.17	11.95	12.23
3	Formic acid (FAc)	0.956	0.909	0.845	0.778	11.04	11.74	12.02
4	Pyridine (Py)	0.961	0.909	0.852	0.785	11.28	12.07	12.38
5	Acetonitrile (AN)	0.974	0.922	0.856	0.797	11.44	12.12	12.59
6	Dimethylsulfoxide (DMSO)	0.994	0.943	0.878	0.814	11.64	12.39	12.78
7	Methanol (MeOH)	0.994	0.942	0.881	0.812	11.65	12.47	12.78
8	Water (W)	1.000	0.947	0.886	0.816	11.72	12.54	12.88
9	Ethanol (EtOH)	1.000	0.948	0.886	0.816	11.73	12.54	12.85
10	Formamide (FA)	1.011	0.958	0.896	0.823	11.84	12.65	12.93
11	Dimethylformamide (DMF)	1.016	0.963	0.894	0.826	11.94	12.65	13.02
12	N-methylformamide (N-MF)	1.044	0.989	0.925	0.853	12.24	13.10	13.43
13	Quinoline (Q)	1.066	0.997	0.944	0.870	12.35	13.40	13.74
14	Hydrazine (Hz)	1.107	1.051	0.977	0.904	13.14	13.95	14.36
15	Ammonia (A)	1.117	1.062	0.985	0.912	13.20	13.97	14.41

k_s for different group will be distinguished from each other with superscript (a), (b) or (c) at need.

It is surprising that β_s can be correlated to ρ_s and k_s for each of the three groups by the simple relations

$$\beta_s = \frac{\rho_s^{(a)}}{\rho_w^{(a)}} = \frac{\rho_s^{(b)}}{\rho_w^{(b)}} = \frac{\rho_s^{(c)}}{\rho_w^{(c)}}, \tag{6}$$

$$\beta_s = \frac{k_s^{(a)}}{k_w^{(a)}} = \frac{k_s^{(b)}}{k_w^{(b)}} = \frac{k_s^{(c)}}{k_w^{(c)}}, \tag{7}$$

as seen from figs. 1 and 2, where subscript w means water.

If we can find an ideal ion for which $\alpha_{i,s}^0$ equals zero, then $-\alpha_{ij,s}$ for the ion can be identified with $\alpha_{j,s}^0/z_j$ as seen from eq. (1). In order to

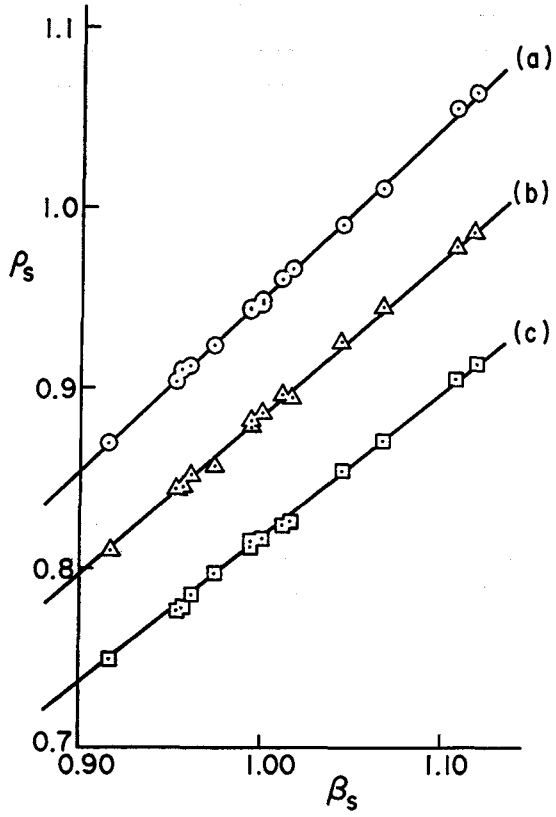

Fig. 1. The relationship between ρ_s and β_s for the cations of (a), (b) and (c) groups for 15 solvents in table 1. The straight lines are those given by the least square method.

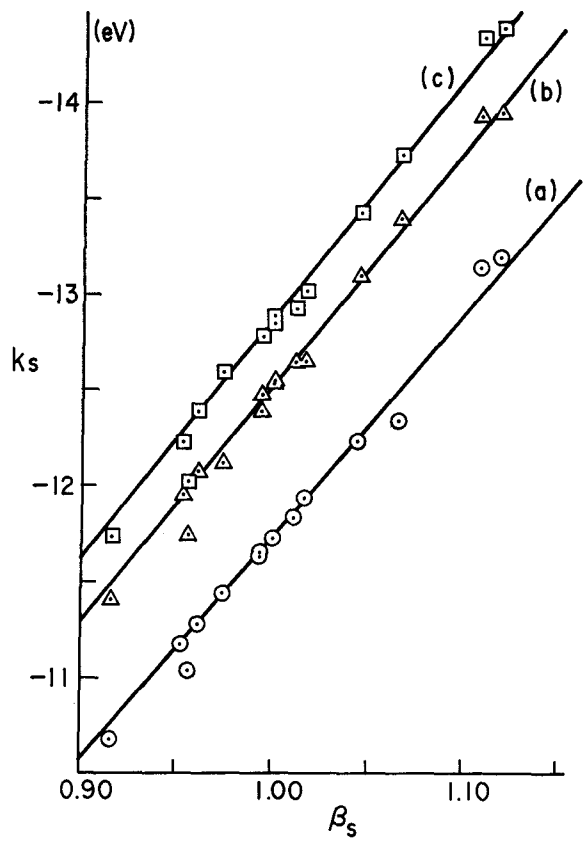

Fig. 2. The relationship between k_s and β_s for the cations of (a), (b) and (c) groups for 15 solvents in table 1. The straight lines (a), (b) and (c) represent the proportionality $k_s = \beta_s k_w$ with the values of k_w in table 1.

find the value of $\alpha^0_{j,s}/z_j$ we introduce here an extrathermodynamic assumption into the empirical rule II for the (a) group cations that an ion whose ionization energy is zero has no chemical interaction with any solvent. Such an ion may be regarded as the ideal ion whose chemical free energy of solvation also equals zero, *i. e.*,

$$k_s^{(a)} = \frac{\alpha^0_{j,s}}{z_j}, \tag{8}$$

since $k_s^{(a)}$ equals $-a_{ij,s}$ for the ideal ion.

Putting eq. (8) into eq. (7), we obtain

$$\alpha^0_{j,s} = \beta_s \alpha^0_{j,w}. \tag{9}$$

TABLE 2. The values of $\alpha^0_{i,s}/z_i$ of monoatomic cations in 15 solvents at 25°C, but for ammonia at −35°C. The figures with # are those calculated from the values of $a_{ij,w}$ on the basis of the empirical rule I for ion-solvent pairs for which we have no information on the experimental values for $E^0_{ij,s}$. The figures without # are those calculated from the values of $a^0_{ij,s}$ obtained from the experimental values for $E^0_{ij,s}$. Hydrogen ion is taken as the reference ion in the estimation of $a_{ij,w}$ and $a_{ij,s}$

	Ion	NM	CH_3CN	PC	H_2O	CH_3OH	C_2H_5OH	$HCONH_2$	DMF	N_2H_4	DMSO	Pyridine	NH_3	HCOOH	N-MF	Quinol
1	H^+	10.67	11.43	11.15#	11.71	11.64	11.71	11.81	11.92	13.09	11.61	11.27	13.13	10.99	12.23	12.51
2	Li^+	5.15	5.63	5.39	5.71	5.70	5.72	5.77#	5.79	6.26	5.56	5.49#	6.34	5.44	5.94	6.08#
3	Na^+	4.33	4.55	4.44	4.67	4.61	4.61	4.72#	4.73	5.16	4.64#	4.49#	5.39	4.66	4.90	4.98#
4	K^+	3.58#	3.87	3.77	3.91	3.89#	3.91#	3.96	4.00	4.39	3.89#	3.76#	4.39	3.63	4.14	4.17#
5	Rb^+	3.37#	3.58	3.50	3.68	3.66#	3.68#	3.64	3.67	4.08	3.66#	3.54#	4.05	3.42	3.84#	3.92
6	Cs^+	3.07#	3.21	3.16	3.35	3.33#	3.35#	3.39#	3.40#	3.71#	3.33#	3.22#	3.70	3.05	3.45	3.57#
7	Cu^+	5.78	6.18	6.02#	6.32	6.28#	6.32	6.39#	6.78	8.00	6.42	6.07#	7.85	6.04#	6.60#	6.73#
8	Cu^{2+}	10.25#	10.98	10.66#	11.19	11.13	11.33	11.36	11.37#	12.39#	11.11	10.73	12.53	10.68	11.68#	11.88
9	Ag^+	5.04	5.66	5.10	5.37	5.34#	5.42	5.43#	5.57	6.78	5.39	5.16#	6.76	5.28	5.61#	5.72#
10	Au^+	6.14#	6.52#	6.38#	6.70	6.66#	6.70#	6.77#	6.81#	7.42#	6.66#	6.44#	7.49#	6.41#	7.00#	7.14#
11	Au^{3+}	13.96#	14.84#	14.52#	15.24	15.15#	15.25#	15.41#	15.49#	16.87#	15.15#	14.64#	17.03#	14.58#	15.91#	16.24#
12	Be^{2+}	11.86#	12.60#	12.33#	12.94	12.87#	12.94#	13.08#	13.15#	14.32#	12.86#	11.97	14.46#	12.38#	13.51#	13.79#
13	Mg^{2+}	9.51	10.02#	9.80#	10.29	10.23#	10.29#	10.40#	10.46#	11.39#	10.23#	9.89#	11.50#	9.84#	10.74#	10.96#
14	Ca^{2+}	7.94#	8.27	8.28	8.67	8.62#	8.67#	8.76#	8.79	9.09	8.62#	8.33#	8.86	8.28	9.05#	9.24#
15	Sr^{2+}	7.27#	7.73#	7.56#	7.94	7.89#	7.94#	8.03#	8.07#	8.79#	7.89#	7.63#	8.88#	7.59#	8.29#	8.46#
16	Ba^{2+}	6.65#	7.07#	6.92#	7.26	7.22#	7.26#	7.34#	7.38#	8.04#	7.22#	6.98#	8.12#	6.94#	7.58#	7.74#
17	Ra^{2+}	6.52#	6.93#	6.78#	7.12	7.08#	7.12#	7.20#	7.23#	7.88#	7.08#	6.84#	7.96#	6.81#	7.43#	7.59#
18	Zn^{2+}	10.00#	10.61	10.40#	10.92	10.82	10.79	11.01	11.10#	11.94	10.86#	10.49#	12.10	10.48	11.40#	11.64#
19	Cd^{2+}	8.93#	9.53	9.29#	9.75	9.70	9.72	9.85	9.91#	10.82	9.70	9.37#	10.96	9.37	10.18#	10.39#
20	Hg^{2+}	9.06#	9.63#	9.42#	9.89	9.83#	9.89#	10.00#	10.05#	10.95#	9.83#	9.50#	11.05#	9.46#	10.33#	10.54#
21	Al^{3+}	14.99#	15.93#	15.58#	16.36	16.27#	16.37#	16.54#	16.62#	18.11#	16.26#	15.72#	18.29#	15.65#	17.08#	17.43#
22	Ga^{2+}	10.00#	10.62#	10.39#	10.91	10.85#	10.91#	11.03#	11.09#	12.08#	10.85#	10.48#	12.19#	10.43#	11.39#	11.62#
23	Ga^{3+}	15.03#	15.97#	15.62#	16.40	16.31#	16.41#	16.58#	16.66#	18.16#	16.30#	15.76#	18.33#	15.68#	17.12#	17.47#
24	In^+	3.77#	4.01#	3.92#	4.12	4.10#	4.12#	4.16#	4.19#	4.56#	4.10#	3.96#	4.61#	3.94#	4.30#	4.39#
25	In^{3+}	13.28#	14.11#	13.80#	14.49	14.41#	14.49#	14.65#	14.72#	16.04#	14.40#	13.92#	16.20#	13.86#	15.13#	15.44#

26	Tl^{+}	3.64#	3.87#	3.83	3.97	3.94	3.98	4.08	4.13	4.39#	3.89	3.81#	4.44#	3.80#	4.15#	4.23#
27	Tl^{3+}	13.36#	14.20#	13.89#	14.58	14.50#	14.58#	14.74#	14.82#	16.14#	14.49#	14.01#	16.30#	13.94#	15.22#	15.53#
28	Sc^{3+}	12.80#	13.60#	13.31#	13.97	13.89#	13.97#	14.12#	14.20#	15.47#	13.89#	13.42#	15.62#	13.36#	14.59#	14.88#
29	Y^{3+}	11.65#	12.39#	12.12#	12.72	12.65#	12.72#	12.86#	12.93#	14.08#	12.64#	12.22#	14.22#	12.17#	13.28#	13.55#
30	La^{3+}	10.58#	11.25#	11.00#	11.55	11.48#	11.55#	11.68#	11.74#	12.79#	11.48#	11.10#	12.91#	11.05#	12.06#	12.31#
31	Ce^{3+}	11.57#	12.30#	12.03#	12.63	12.56#	12.63#	12.77#	12.83#	13.98#	12.56#	12.14#	14.12#	12.08#	13.19#	13.46#
32	Ce^{4+}	15.84#	16.84#	16.47#	17.29	17.19#	17.30#	17.48#	17.57#	19.14#	17.19#	16.61#	19.33#	16.54#	18.05#	18.42#
33	Nd^{3+}	11.37#	12.09#	11.82#	12.41	12.34#	12.41#	12.55#	12.61#	13.74#	12.34#	11.93#	13.87#	11.87#	12.96#	13.22#
34	Sm^{3+}	11.60#	12.33#	12.06#	12.66	12.59#	12.66#	12.80#	12.86#	14.01#	12.59#	12.17#	14.15#	12.11#	13.22#	13.49#
35	Gd^{3+}	11.72#	12.46#	12.18#	12.79	12.72#	12.79#	12.93#	13.00#	14.16#	12.71#	12.29#	14.30#	12.23#	13.35#	13.62#
36	Lu^{3+}	12.38#	13.16#	12.87#	13.51	13.43#	13.51#	13.66#	13.73#	14.96#	13.43#	12.98#	15.10#	12.92#	14.11#	14.39#
37	Th^{4+}	15.68#	16.66#	16.30#	17.11	17.01#	17.12#	17.30#	17.39#	18.94#	17.01#	16.44#	19.13#	16.36#	17.87#	18.23#
38	U^{3+}	11.32#	12.04#	11.77#	12.36	12.29#	12.36#	12.49#	12.56#	13.68#	12.29#	11.88#	13.82#	11.82#	12.91#	13.17#
39	U^{4+}	16.16#	17.18#	16.80#	17.64	17.54#	17.65#	17.83#	17.92#	19.53#	17.54#	16.95#	19.72#	16.87#	18.42#	18.80#
40	Sn^{2+}	7.80#	8.29#	8.11#	8.51	8.46#	8.51#	8.60#	8.65#	9.42#	8.46#	8.18#	9.51#	8.14#	8.89#	9.07#
41	Pb^{2+}	7.49#	7.88	7.78#	8.17	8.17	8.19	8.26#	8.30#	9.07	8.18	7.85#	9.14	8.04	8.53#	8.70#
42	Ti^{2+}	9.34#	9.92#	9.71#	10.19	10.13#	10.19#	10.30#	10.35#	11.28#	10.13#	9.79#	11.39#	9.75#	10.64#	10.86#
43	Zr^{4+}	17.00#	18.06#	17.67#	18.55	18.44#	18.56#	18.75#	18.85#	20.54#	18.44#	17.83#	20.73#	17.74#	19.37#	19.76#
44	Hf^{4+}	16.19#	17.21#	16.83#	17.67	17.57#	17.68#	17.86#	17.96#	19.56#	17.57#	16.98#	19.75#	16.90#	18.45#	18.83#
45	As^{3+}	14.45#	15.36#	15.02#	15.77	15.68#	15.78#	15.94#	16.02#	17.46#	15.68#	15.15#	17.63#	15.08#	16.47#	16.80#
46	Sb^{3+}	12.48#	13.26#	12.97#	13.62	13.54#	13.62#	13.77#	13.84#	15.08#	13.54#	13.09#	15.22#	13.03#	14.22#	14.51#
47	Bi^{3+}	11.82#	12.56#	12.29#	12.90	12.83#	12.90#	13.04#	13.11#	14.28#	12.82#	12.40#	14.42#	12.34#	13.47#	13.74#
48	V^{2+}	9.16#	9.74#	9.53#	10.00	9.94#	10.00#	10.11#	10.16#	11.07#	9.94#	9.61#	11.18#	9.56#	10.44#	10.65#
49	Nb^{3+}	14.40#	15.31#	14.97#	15.72	15.63#	15.73#	15.89#	15.97#	17.40#	15.63#	15.11#	17.57#	15.03#	16.41#	16.75#
50	Te^{4+}	18.87#	20.06#	19.62#	20.60	20.48#	20.61#	20.82#	20.93#	22.80#	20.48#	19.80#	23.03#	19.70#	21.51#	21.95#
51	Po^{2+}	8.88#	9.44#	9.23#	9.69	9.63#	9.69#	9.80#	9.85#	10.73#	9.63#	9.31#	10.83#	9.27#	10.12#	10.32#
52	Po^{3+}	12.92#	13.73#	13.43#	14.10	14.02#	14.10#	14.25#	14.33#	15.61#	14.02#	13.55#	15.76#	13.49#	14.72#	15.02#
53	Cr^{2+}	9.24#	9.83#	9.61#	10.09	10.03#	10.09#	10.20#	10.25#	11.17#	10.03#	9.70#	11.28#	9.65#	10.54#	10.75#
54	Cr^{3+}	14.14#	15.03#	14.70#	15.43	15.34#	15.44#	15.60#	15.68#	17.08#	15.34#	14.83#	17.25#	14.76#	16.11#	16.44#
55	Mn^{2+}	9.07#	9.64#	9.43#	9.90	9.84#	9.90#	10.01#	10.06#	10.96#	9.84#	9.51#	11.07#	9.47#	10.34#	10.55#
56	Fe^{2+}	9.39#	9.98#	9.76#	10.25	10.19#	10.25#	10.36#	10.42#	11.35#	10.19#	9.85#	11.46#	9.80#	10.70#	10.92#
57	Fe^{3+}	14.09#	14.98#	14.65#	15.38	15.29#	15.39#	15.55#	15.63#	17.03#	15.29#	14.78#	17.19#	14.71#	16.06#	16.39#
58	Ru^{2+}	9.59#	10.20#	9.97#	10.47	10.41#	10.47#	10.58#	10.64#	11.59#	10.41#	10.06#	11.70#	10.01#	10.93#	11.16#
59	Os^{2+}	9.76#	10.37#	10.14#	10.65	10.59#	10.65#	10.77#	10.82#	11.79#	10.59#	10.23#	11.90#	10.19#	11.12#	11.35#
60	Co^{2+}	9.99#	10.61#	10.38#	10.90	10.84#	10.90#	11.02#	11.08#	12.07#	10.84#	10.47#	12.18#	10.42#	11.38#	11.61#
61	Co^{3+}	15.26#	16.22#	15.87#	16.66	16.56#	16.67#	16.84#	16.93#	18.44#	16.56#	16.01#	18.62#	15.93#	17.40#	17.75#
62	Rh^{3+}	14.42#	15.33#	14.99#	15.74	15.65#	15.75#	15.91#	15.99#	17.42#	15.65#	15.13#	17.59#	15.05#	16.44#	16.77#
63	Ni^{2+}	10.22#	10.86#	10.62#	11.15	11.09#	11.15#	11.27#	11.33#	12.34#	11.08#	10.71#	12.46#	10.66#	11.64#	11.88#
64	Pd^{2+}	9.78#	10.39#	10.16#	10.67	10.61#	10.67#	10.79#	10.84#	11.81#	10.61#	10.25#	11.93#	10.20#	11.14#	11.37#
65	Pt^{2+}	9.96#	10.59#	10.35#	10.87	10.81#	10.87#	10.99#	11.05#	12.03#	10.81#	10.45#	12.15#	10.40#	11.35#	11.58#
66	Mo^{3+}	13.53#	14.38#	14.07#	14.77	14.69#	14.78#	14.95#	15.02#	16.39#	14.71#	14.19#	16.57#	14.17#	15.42#	15.56#
67	Ir^{3+}	13.62#	14.48#	14.17#	14.87	14.78#	14.88#	15.05#	15.12#	16.50#	14.81#	14.29#	16.68#	14.26#	15.53#	15.67#
68	Np^{3+}	11.25#	11.96#	11.70#	12.28	12.21#	12.29#	12.43#	12.49#	13.64#	12.23#	11.80#	13.79#	11.79#	12.82#	12.91#
69	Pu^{3+}	11.46#	12.18#	11.92#	12.51	12.44#	12.52#	12.66#	12.73#	13.89#	12.46#	12.02#	14.05#	12.01#	13.06#	13.16#
70	Am^{3+}	11.43#	12.15#	11.89#	12.48	12.41#	12.49#	12.63#	12.70#	13.86#	12.43#	11.99#	14.01#	11.98#	13.03#	13.12#

It follows from eqs. (4) and (9) that the empirical rule I can be expressed in terms of $\alpha^0_{i,s}$ by the equation

$$\alpha^0_{i,s} = \beta_s \alpha^0_{i,w}\,, \tag{10}$$

and from eqs. (5) and (8) that the empirical rule II for the (a) group cations can be expressed simply by the equation

$$\alpha^0_{i,s} = \rho_s^{(a)} I_i\,, \tag{11}$$

and from eqs. (5)~(8) that the empirical rule II for the (b) or (c) group cations can be expressed by the equation with a correction term $\Delta k_s/\rho_w$

$$\frac{\alpha^0_{1,s}}{z_i} = \rho_s\left(\frac{I_i}{z_i} - \frac{\Delta k_s}{\rho_w}\right), \tag{12}$$

where $\rho_s = \rho_s^{(b)}$ and $\Delta k_s/\rho_w = (k_s^{(b)} - k_s^{(a)})/\rho_w^{(b)}$ for the (b) group cations and $\rho_s = \rho_s^{(c)}$ and $\Delta k_s/\rho_w = (k_s^{(c)} - k_s^{(a)})/\rho_w^{(c)}$ for the (c) group cations, and $\Delta k_s/\rho_w$ is given from table 1 at 0.93 eV or 1.42 eV for (b) or (c) group cations.

Eqs. (11) and (12) show that the ionization energy of the ion plays an essential role in the ion-solvent interactions in the solvation process.

Using the value of $\alpha^0_{j,s}/z_j$ obtained from eq. (8) for the (a) group cations, the value of $\alpha^0_{i,s}$ for any cation can be estimated from the value of $a_{ij,s}$ according to eq. (1). Table 2 shows the list of the values of $\alpha^0_{i,s}/z_i$ for monoatomic cations for 15 solvents in electron volts calculated from the values of $a_{ij,s}$ reported in the previous work.[2]

The classification of cationic species by the nature of the solvation bonding and the HSAB concept

As reported by Ahrland *et al*[4] and Pearson,[5] the metal ions can be classified into three groups by the HSAB concept for the ions as the Lewis acids. It is interesting to compare the classification of cations by the empirical rule II in the present work with that by the HSAB concept. Fig. 3 shows the classifications of the cationic species in the periodic table by the two different criteria.

As seen from the comparison of these two classifications, the cationic species of the (a) group can be regarded as the hard acids*, the cations of the (b) group as the borderline acids and the cations of the (c) group as the soft acids, although some difference in the boundaries can be seen between

*) Prof. G. J. Hills (University of Strathclyde, Scotland) kindly suggested at the 32-nd ISE meeting held in Dubrovnik, Yugoslavia, 1981, that the (a) group cations belong to the hard acids.

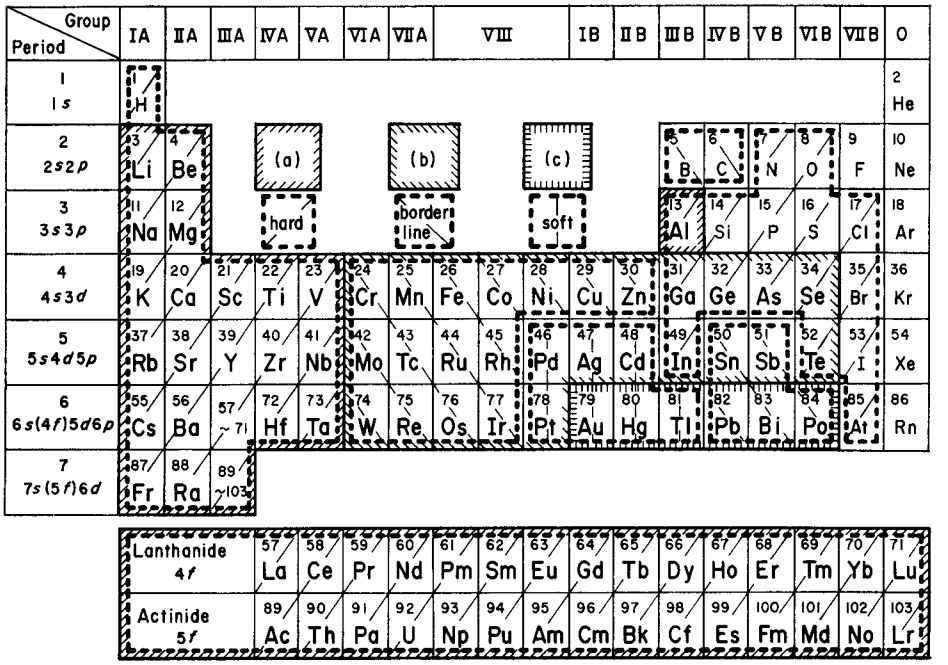

Fig. 3. The classifications of cationic species in the periodic table by the empirical rule II[3] and by the HSAB concept of the ions as the Lewis acids.[5,4]

the two classifications, which may be attributed to the qualitative nature of the classification by the HSAB concept.

The coincidence of the two classifications is a strong evidence for the formation of aqua-complexes in the solvation process of monoatomic cations. It should be emphasized, however, that the ionization energy of the ion in any group forms a substantial contribution to the ion-solvent interactions, as pointed out in eqs. (11) and (12).

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