J. Res. Inst. Catalysis, Hokkaido Univ., Vol. 30, No. 3, pp. 191 to 194 (1982)

— Note —

NUMERICAL REPRESENTATION OF ELECTRON DONOR AND ACCEPTOR ABILITIES OF MONOATOMIC CATIONS AND SOLVENTS IN THE SOLVATION PROCESS

By

A. MATSUDA*) and R. NOTOYA*)

(Received December 17, 1982)

The standard chemical free energy of solvation $\alpha^{\circ}_{i,s}$ of monoatomic cation i of valency z_i in solvent s can be expressed by eq. (1)

$$\frac{\alpha^{\circ}_{i,s}}{z_i} = \varepsilon_i \rho_s , \qquad (1)$$

indicating the electron donor-acceptor nature of the solvation bonding, as reported in a previous work[1], where ρ_s is a measure of the electron donor ability of solvent s which is defined as the gradient of a linear relation between $\alpha^{\circ}_{i,s}/z_i$ and the ionization energy I_i/z_i of ion i in the gas phase and ε_i is a measure of the electron acceptability of ion i which is defined as the gradient of the proportionality relation between $\alpha^{\circ}_{i,s}/z_i$ and ρ_s.

It will be useful for us to estimate the numerical values of ρ_s and ε_i as the characteristic quantities for a solvent and an ion, respectively, in the solvation process. The ρ_s in eq. (1) is identified with $\rho_s^{(a)}$ in the previous work and the values for ρ_s are listed in Table 1 for 15 solvents.

Table 2 shows the values of ε_i calculated by eq. (1) using the values of $\alpha^{\circ}_{i,s}/z_i$ in

TABLE 1. The electron donor ability ρ_s of solvents

Solvent	ρ_s	Solvent	ρ_s
1 Nitromethane	0.868	9 Ethanol	0.948
2 Propylene carbonate	0.902	10 Formamide	0.958
3 Formic acid	0.909	11 Dimethylformamide	0.963
4 Pyridine	0.909	12 N-methylformamide	0.989
5 Acetonitrile	0.922	13 Quinoline	0.997
6 Dimethylsulfoxide	0.943	14 Hydrazine	1.051
7 Methanol	0.942	15 Ammonia	1.062
8 Water	0.947		

*) The Research Institute for Calalysis, Hokkaido University, Sapporo, 060 Japan.

TABLE 2. The electron acceptability ε_i of monoatomic cations in eV. No. denotes the atomic number

No.	Ion	ε_i	S. D.	Group	No.	Ion	ε_i	S. D.	Group
1	H^+	12.36	0.09		30	Zn^{2+}	11.50	0.07	(b)
3	Li^+	6.01	0.06	(a)					
4	Be^{2+}	13.63	0.13	(a)	31	Ga^{2+}	11.52	0.04	(b)
5	$*B^{3+}$	23.79		(a)		Ga^{3+}	17.32	0.06	
					32	$*Ge^{2+}$	10.27		(b)
7	$*N^{3+}$	30.52		(a)		$*Ge^{4+}$	23.40		
					33	$*As^{2+}$	12.47		(b)
11	Na^+	4.95	0.07	(a)		As^{3+}	16.65	0.06	
12	Ma^{2+}	10.87	0.04	(a)	34	$*Se^{2+}$	13.75		(b)
13	Al^{3+}	17.27	0.06	(a)		$*Se^{4+}$	23.97		
14	$*Si^{2+}$	12.24		(a)		$*Se^{6+}$	39.15		
	$*Si^{4+}$	25.77							
15	$*P^{5+}$	35.34		(a)	37	Rb^+	3.86	0.04	(a)
					38	Sr^{2+}	8.38	0.03	(a)
16	$*S^{6+}$	46.06		(a)	39	$*Y^+$	6.38		(a)
19	K^+	4.14	0.05	(a)		$*Y^{2+}$	9.31		
20	Ca^{2+}	9.06	0.23	(a)		Y^{3+}	13.43	0.05	
					40	$*Zr^{2+}$	9.88		(a)
21	$*Sc^{2+}$	9.73		(a)		Zr^{4+}	19.59	0.07	
	Sc^{3+}	14.75	0.05						
22	Ti^{2+}	10.76	0.04	(a)	41	$*Nb^{2+}$	10.39		(a)
	$*Ti^{4+}$	22.95				Nb^{3+}	16.60	0.06	
23	V^{2+}	10.56	0.04	(a)		$*Nb^{4+}$	21.80		
	$*V^{3+}$	16.88				$*Nb^{5+}$	27.44		
	$*V^{5+}$	32.77			42	$*Mo^{2+}$	9.83		(b)
24	$*Cr^+$	5.46		(b)		Mo^{3+}	15.60	0.01	
	Cr^{2+}	10.65	0.04			$*Mo^{4+}$	22.26		
	Cr^{3+}	16.29	0.06			$*Mo^{6+}$	34.55		
	$*Cr^{4+}$	23.76			43	$*Tc^{4+}$	21.83		(b)
	$*Cr^{5+}$	32.31			44	Ru^{2+}	11.05	0.04	(b)
	$*Cr^{6+}$	40.91				$*Ru^{4+}$	22.83		
25	Mn^{2+}	10.45	0.04	(b)		$*Ru^{6+}$	37.39		
	$*Mn^{4+}$	24.81			45	$*Rh^{2+}$	10.07		(b)
26	Fe^{2+}	10.82	0.04	(b)		Rh^{3+}	16.62	0.06	
	Fe^{3+}	16.24	0.06			$*Rh^{4+}$	23.04		
27	Co^{2+}	11.51	0.04	(b)					
	Co^{3+}	17.59	0.06		46	Pd^{2+}	11.27	0.04	(b)
28	Ni^{2+}	11.77	0.04	(b)		$*Pd^{4+}$	24.81		
29	Cu^+	7.03	0.81	(b)	47	Ag^+	5.84	0.25	(b)
	Cu^{2+}	11.83	0.05			$*Ag^{2+}$	12.73		

Table 2 (Continued)

No.	Ion	ε_i	S. D.	Group	No.	Ion	ε_i	S. D.	Group
48	Cd^{2+}	10.31	0.04	(b)		$*Ta^{4+}$	19.73		
49	In^{+}	4.35	0.02	(b)		$*Ta^{5+}$	24.78		
	$*In^{2+}$	10.66			74	$*W^{2+}$	11.15		(b)
	In^{3+}	15.30	0.05			$*W^{4+}$	18.94		
50	Sn^{2+}	8.99	0.03	(b)		$*W^{6+}$	29.34		
					75	$*Re^{4+}$	19.83		(b)
51	$*Sb^{2+}$	9.36		(b)		$*Re^{7+}$	37.04		
	Sb^{3+}	14.38	0.05						
52	Te^{4+}	21.75	0.08	(b)	76	Os^{2+}	11.25	0.04	(b)
55	Cs^{+}	3.51	0.05	(a)		$*Os^{4+}$	20.35		
						$*Os^{8+}$	46.01		
56	$*Ba^{+}$	5.21		(a)	77	$*Ir^{2+}$	11.39		(b)
	Ba^{2+}	7.67	0.03			Ir^{3+}	15.70	0.01	
57	$*La^{+}$	5.61		(a)		$*Ir^{4+}$	20.70		
	$*La^{2+}$	8.52			78	Pt^{2+}	11.48	0.04	(b)
	La^{3+}	12.20	0.04			$*Pt^{4+}$	21.95		
58	$*Ce^{+}$	6.54		(a)	79	Au^{+}	7.07	0.02	(c)
	$*Ce^{2+}$	9.43				Au^{3+}	16.09	0.06	
	Ce^{3+}	13.34	0.05		80	$*Hg^{+}$	7.77		(c)
	Ce^{4+}	18.26	0.06			Hg^{2+}	10.44	0.04	
59	$*Pr^{2+}$	8.65		(a)	81	Tl^{+}	4.20	0.04	(c)
60	$*Nd^{2+}$	9.20		(a)		Tl^{3+}	15.39	0.05	
	Nd^{3+}	13.11	0.05		82	Pb^{2+}	8.65	0.06	(c)
62	$*Sm^{2+}$	8.50		(a)		$*Pb^{4+}$	18.90		
	Sm^{3+}	13.37	0.05		83	$*Bi^{2+}$	10.21		(c)
63	$*Eu^{2+}$	8.46		(a)		Bi^{3+}	13.62	0.05	
64	$*Gd^{2+}$	9.08		(a)	84	Po^{2+}	10.23	0.03	(c)
	Gd^{3+}	13.51	0.05			Po^{3+}	14.89	0.05	
65	$*Tb^{2+}$	9.63		(a)					
	$*Tb^{3+}$	13.43			88	Ra^{2+}	7.52	0.03	(a)
					90	$*Th^{2+}$	9.40		(a)
66	$*Dy^{2+}$	9.71		(a)		Th^{4+}	18.07	0.06	
67	$*Ho^{2+}$	9.80		(a)					
68	$*Er^{2+}$	9.60		(a)	91	$*Pa^{4+}$	18.45		(a)
70	$*Yb^{2+}$	9.16		(a)	92	$*U^{2+}$	9.10		(a)
						U^{3+}	13.05	0.05	
71	$*Lu^{2+}$	9.08		(a)		U^{4+}	18.63	0.07	
	Lu^{3+}	14.27	0.05		93	Np^{3+}	12.97	0.01	(a)
72	$*Hf^{2+}$	10.95		(a)	94	Pu^{3+}	13.21	0.01	(a)
	Hf^{4+}	18.66	0.07		95	Am^{3+}	13.18	0.01	(a)
73	$*Ta^{2+}$	11.95		(a)					

the previous work[1]. The standard deviation (S. D.) of ε_i from the regression line eq. (1) obtained by the least square method are found to be less than 3%, except Ag^+, Cu^+, Ca^{2+} and Be^{2+} ions.

It may also be possible to estimate the values of ε_i from I_i/z_i for the cations of valence states for which we have no information on the values of $\alpha^0_{i,s}/z_i$ by the following equations deduced in the previous work[1]

$$\varepsilon_i = \frac{I_i}{z_i}, \tag{2}$$

for the cations of the rare gas type, the lanthanides and the actinides classified as (a) group previously, and

$$\varepsilon_i = 0.936\left(\frac{I_i}{z_i} - 0.93\right), \quad \text{eV} \tag{3}$$

for the cations classified as (b) group previously which have more than 3 d-electrons in the outer shell, and

$$\varepsilon_i = 0.862\left(\frac{I_i}{z_i} - 1.42\right), \quad \text{eV} \tag{4}$$

for the cations of the electronic configuration of $5d^{10}+4f^{14}$ type classified as (c) group in the previous work. The values of ε_i calculated by eqs. (2)-(4) using the values of I_i/z_i in ref. 2 are listed also in Table 2 for a series of cationic species with symbol (*).

References

1) R. Notoya and A. Matsuda, J. Res. Inst. Catalysis, Hokkaido Univ., **30**, **61** (1982).
2) *Properties of Elements*, Part I, edited by G. V. Samsonov, Moscow, Metallurgia, 1976, Translated by Nissotsushinsha in Japanese.