



Title	NUMERICAL REPRESENTATION OF ELECTRON DONOR AND ACCEPTOR ABILITIES OF MONOATOMIC CATIONS AND SOLVENTS IN THE SOLVATION PROCESS
Author(s)	MATSUDA, A.; NOTOYA, R.
Citation	JOURNAL OF THE RESEARCH INSTITUTE FOR CATALYSIS HOKKAIDO UNIVERSITY, 30(3), 191-194
Issue Date	1983-03
Doc URL	<a href="http://hdl.handle.net/2115/25140">http://hdl.handle.net/2115/25140</a>
Type	bulletin (article)
File Information	30(3)_P191-194.pdf



[Instructions for use](#)

— 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  $\alpha_{i,s}^0$  of monoatomic cation  $i$  of valency  $z_i$  in solvent  $s$  can be expressed by eq. (1)

$$\frac{\alpha_{i,s}^0}{z_i} = \varepsilon_i \rho_s, \quad (1)$$

indicating the electron donor-acceptor nature of the solvation bonding, as reported in a previous work<sup>1)</sup>, where  $\rho_s$  is a measure of the electron donor ability of solvent  $s$  which is defined as the gradient of a linear relation between  $\alpha_{i,s}^0/z_i$  and the ionization energy  $I_i/z_i$  of ion  $i$  in the gas phase and  $\varepsilon_i$  is a measure of the electron acceptability of ion  $i$  which is defined as the gradient of the proportionality relation between  $\alpha_{i,s}^0/z_i$  and  $\rho_s$ .

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

Table 2 shows the values of  $\varepsilon_i$  calculated by eq. (1) using the values of  $\alpha_{i,s}^0/z_i$  in

TABLE 1. The electron donor ability  $\rho_s$  of solvents

Solvent	$\rho_s$	Solvent	$\rho_s$
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 Catalysis, Hokkaido University, Sapporo, 060 Japan.

A. MATSUDA and R. NOTOYA

TABLE 2. The electron acceptability  $\varepsilon_1$  of monoatomic cations  
in eV. No. denotes the atomic number

No. Ion	$\varepsilon_1$	S. D.	Group	No. Ion	$\varepsilon_1$	S. D.	Group
1 H <sup>+</sup>	12.36	0.09		30 Zn <sup>2+</sup>	11.50	0.07	(b)
3 Li <sup>+</sup>	6.01	0.06	(a)	31 Ga <sup>2+</sup>	11.52	0.04	(b)
4 Be <sup>2+</sup>	13.63	0.13	(a)	Ga <sup>3+</sup>	17.32	0.06	
5 *B <sup>3+</sup>	23.79		(a)	32 *Ge <sup>2+</sup>	10.27		(b)
7 *N <sup>3+</sup>	30.52		(a)	*Ge <sup>4+</sup>	23.40		
				33 *As <sup>2+</sup>	12.47		(b)
11 Na <sup>+</sup>	4.95	0.07	(a)	As <sup>3+</sup>	16.65	0.06	
12 Ma <sup>2+</sup>	10.87	0.04	(a)	34 *Se <sup>2+</sup>	13.75		(b)
13 Al <sup>3+</sup>	17.27	0.06	(a)	*Se <sup>4+</sup>	23.97		
14 *Si <sup>2+</sup>	12.24		(a)	*Se <sup>6+</sup>	39.15		
*Si <sup>4+</sup>	25.77						
15 *P <sup>5+</sup>	35.34		(a)	37 Rb <sup>+</sup>	3.86	0.04	(a)
				38 Sr <sup>2+</sup>	8.38	0.03	(a)
16 *S <sup>6+</sup>	46.06		(a)	39 *Y <sup>+</sup>	6.38		(a)
19 K <sup>+</sup>	4.14	0.05	(a)	*Y <sup>2+</sup>	9.31		
20 Ca <sup>2+</sup>	9.06	0.23	(a)	Y <sup>3+</sup>	13.43	0.05	
				40 *Zr <sup>2+</sup>	9.88		(a)
21 *Sc <sup>2+</sup>	9.73		(a)	Zr <sup>4+</sup>	19.59	0.07	
Sc <sup>3+</sup>	14.75	0.05					
22 Ti <sup>2+</sup>	10.76	0.04	(a)	41 *Nb <sup>2+</sup>	10.39		(a)
*Ti <sup>4+</sup>	22.95			Nb <sup>3+</sup>	16.60	0.06	
23 V <sup>2+</sup>	10.56	0.04	(a)	*Nb <sup>4+</sup>	21.80		
*V <sup>3+</sup>	16.88			*Nb <sup>5+</sup>	27.44		
*V <sup>5+</sup>	32.77			42 *Mo <sup>2+</sup>	9.83		(b)
24 *Cr <sup>+</sup>	5.46		(b)	Mo <sup>3+</sup>	15.60	0.01	
Cr <sup>2+</sup>	10.65	0.04		*Mo <sup>4+</sup>	22.26		
Cr <sup>3+</sup>	16.29	0.06		*Mo <sup>6+</sup>	34.55		
*Cr <sup>4+</sup>	23.76			43 *Tc <sup>4+</sup>	21.83		(b)
*Cr <sup>5+</sup>	32.31			44 Ru <sup>2+</sup>	11.05	0.04	(b)
*Cr <sup>6+</sup>	40.91			*Ru <sup>4+</sup>	22.83		
25 Mn <sup>2+</sup>	10.45	0.04	(b)	*Ru <sup>6+</sup>	37.39		
*Mn <sup>4+</sup>	24.81			45 *Rh <sup>2+</sup>	10.07		(b)
26 Fe <sup>2+</sup>	10.82	0.04	(b)	Rh <sup>3+</sup>	16.62	0.06	
Fe <sup>3+</sup>	16.24	0.06		*Rh <sup>4+</sup>	23.04		
27 Co <sup>2+</sup>	11.51	0.04	(b)	46 Pd <sup>2+</sup>	11.27	0.04	(b)
Co <sup>3+</sup>	17.59	0.06		*Pd <sup>4+</sup>	24.81		
28 Ni <sup>2+</sup>	11.77	0.04	(b)	47 Ag <sup>+</sup>	5.84	0.25	(b)
Cu <sup>+</sup>	7.03	0.81	(b)	*Ag <sup>2+</sup>	12.73		
Cu <sup>2+</sup>	11.83	0.05					

*Numerical Representation of Electron Donor and Acceptor Abilities*

Table 2 (Continued)

No.	Ion	$\varepsilon_1$	S. D.	Group	No.	Ion	$\varepsilon_1$	S. D.	Group
48	Cd <sup>2+</sup>	10.31	0.04	(b)		*Ta <sup>4+</sup>	19.73		
49	In <sup>+</sup>	4.35	0.02	(b)		*Ta <sup>5+</sup>	24.78		
	*In <sup>2+</sup>	10.66			74	*W <sup>2+</sup>	11.15		(b)
	In <sup>3+</sup>	15.30	0.05			*W <sup>4+</sup>	18.94		
50	Sn <sup>2+</sup>	8.99	0.03	(b)		*W <sup>6+</sup>	29.34		
51	*Sb <sup>2+</sup>	9.36		(b)	75	*Re <sup>4+</sup>	19.83		(b)
	Sb <sup>3+</sup>	14.38	0.05			*Re <sup>7+</sup>	37.04		
52	Te <sup>4+</sup>	21.75	0.08	(b)	76	Os <sup>2+</sup>	11.25	0.04	(b)
55	Cs <sup>+</sup>	3.51	0.05	(a)		*Os <sup>4+</sup>	20.35		
						*Os <sup>8+</sup>	46.01		
56	*Ba <sup>+</sup>	5.21		(a)	77	*Ir <sup>2+</sup>	11.39		(b)
	Ba <sup>2+</sup>	7.67	0.03			Ir <sup>3+</sup>	15.70	0.01	
57	*La <sup>+</sup>	5.61		(a)		*Ir <sup>4+</sup>	20.70		
	*La <sup>2+</sup>	8.52			78	Pt <sup>2+</sup>	11.48	0.04	(b)
	La <sup>3+</sup>	12.20	0.04			*Pt <sup>4+</sup>	21.95		
58	*Ce <sup>+</sup>	6.54		(a)	79	Au <sup>+</sup>	7.07	0.02	(c)
	*Ce <sup>2+</sup>	9.43				Au <sup>3+</sup>	16.09	0.06	
	Ce <sup>3+</sup>	13.34	0.05		80	*Hg <sup>+</sup>	7.77		(c)
	Ce <sup>4+</sup>	18.26	0.06			Hg <sup>2+</sup>	10.44	0.04	
59	*Pr <sup>2+</sup>	8.65		(a)	81	Tl <sup>+</sup>	4.20	0.04	(c)
60	*Nd <sup>2+</sup>	9.20		(a)		Tl <sup>3+</sup>	15.39	0.05	
	Nd <sup>3+</sup>	13.11	0.05		82	Pb <sup>2+</sup>	8.65	0.06	(c)
62	*Sm <sup>2+</sup>	8.50		(a)		*Pb <sup>4+</sup>	18.90		
	Sm <sup>3+</sup>	13.37	0.05		83	*Bi <sup>2+</sup>	10.21		(c)
63	*Eu <sup>2+</sup>	8.46		(a)		Bi <sup>3+</sup>	13.62	0.05	
64	*Gd <sup>2+</sup>	9.08		(a)	84	Po <sup>2+</sup>	10.23	0.03	(c)
	Gd <sup>3+</sup>	13.51	0.05			Po <sup>3+</sup>	14.89	0.05	
65	*Tb <sup>2+</sup>	9.63		(a)	88	Ra <sup>2+</sup>	7.52	0.03	(a)
	*Tb <sup>3+</sup>	13.43			90	*Th <sup>2+</sup>	9.40		(a)
66	*Dy <sup>2+</sup>	9.71		(a)		Th <sup>4+</sup>	18.07	0.06	
67	*Ho <sup>2+</sup>	9.80		(a)	91	*Pa <sup>4+</sup>	18.45		(a)
68	*Er <sup>2+</sup>	9.60		(a)	92	*U <sup>2+</sup>	9.10		(a)
70	*Yb <sup>2+</sup>	9.16		(a)		U <sup>3+</sup>	13.05	0.05	
						U <sup>4+</sup>	18.63	0.07	
71	*Lu <sup>2+</sup>	9.08		(a)	93	Np <sup>3+</sup>	12.97	0.01	(a)
	Lu <sup>3+</sup>	14.27	0.05		94	Pu <sup>3+</sup>	13.21	0.01	(a)
72	*Hf <sup>2+</sup>	10.95		(a)	95	Am <sup>3+</sup>	13.18	0.01	(a)
73	*Ta <sup>2+</sup>	11.95		(a)					

A. MATSUDA and R. NOTOYA

the previous work<sup>1)</sup>. The standard deviation (S.D.) of  $\varepsilon_1$  from the regression line eq. (1) obtained by the least square method are found to be less than 3%, except Ag<sup>+</sup>, Cu<sup>+</sup>, Ca<sup>2+</sup> and Be<sup>2+</sup> ions.

It may also be possible to estimate the values of  $\varepsilon_1$  from  $I_1/z_1$  for the cations of valence states for which we have no information on the values of  $\alpha_{1,s}^0/z_1$  by the following equations deduced in the previous work<sup>1)</sup>

$$\varepsilon_1 = \frac{I_1}{z_1}, \quad (2)$$

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

$$\varepsilon_1 = 0.936 \left( \frac{I_1}{z_1} - 0.93 \right), \text{ eV} \quad (3)$$

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

$$\varepsilon_1 = 0.862 \left( \frac{I_1}{z_1} - 1.42 \right), \text{ eV} \quad (4)$$

for the cations of the electronic configuration of 5d<sup>10</sup>+4f<sup>14</sup> type classified as (c) group in the previous work. The values of  $\varepsilon_1$  calculated by eqs. (2)-(4) using the values of  $I_1/z_1$  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 Nissotushinsha in Japanese.