# Chelate Extraction Constant Based on HSAB Rule

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Extraction constants for metal chelate were rationalized by HSAB rule, into which a new dual parameter scale for strength and hard-soft factors of a metal ion was introduced. The applicability of this scale was confirmed with several chelating agents of analytical use.

Since the concept "Hard and Soft Acids and Bases (HSAB)" was introduced by Pearson,[1-3] several kinds of a dual parameter scale have been proposed for evaluating hard-soft nature of a metal ion as a Lewis acid and/or a monodentate ligand as a Lewis base.[4-5] However, as far as a polydentate ligand is concerned, little information based on HSAB rule has so far been reported. In the present work, a new dual parameter scale is proposed and applied to Pearson's equation;[2]

$$\log K = S_A S_B + \sigma_A \sigma_B \tag{1}$$

where K is an equilibrium constant for the formation of a complex AB and the subscript A and B denote Lewis acid and base, respectively. The S represents a strength factor, and the $\sigma$ represents a soft factor.[2] By using the above equation, the extraction constant $(K_{ex})$ for metal chelate can be explained quantitatively, and softness of a chelating agent can be evaluated.

The K value: Extraction reaction of a metal ion($M^{z+}$) with a chelating agent (HR) is expressed as follows;

$$M^{z+} + zHR_{org} \rightleftharpoons MR_{z,org} + zH^+ \tag{2}$$
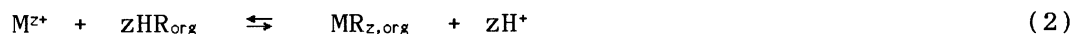
where the subscript org denotes the organic phase. The extraction constant for a particular extraction system is defined as the equilibrium constant for reaction 2. On the other hand, Eq. 3 is obtained from regular solution theory;[6]

$$\log K_{dm} = z \log K_{dr} \tag{3}$$

where $K_{dm}$ and $K_{dr}$ are distribution coefficients for $MR_z$ and HR, respectively. If Eq. 3 is valid, Eq. 4 can be derived;

$$\log \beta = \log K_{ex} + z\, pK_a \tag{4}$$

where $\beta$ and $pK_a$ are the stability constant for $MR_z$ in the aqueous phase and acid dissociation exponent of the HR, respectively. In this work, the value of right hand side of Eq. 4 is applied to Eq. 1, namely, $\beta$ = K is assumed.

Dual parameter scale: While various arbitrary scale for strength and softness have been proposed,[2] we defined the $S_A$ scale on the basis of the electrostatic affinity of a metal ion toward chelating anion. The formation of an extractable chelate $MR_z$ proceeds according to Eq. 5. In the case of a purely ionic chelate, the

$$M(H_2O)_6^{z+} + zR^- = MR_z + 6H_2O \tag{5}$$

forward reaction accompanies dehydration of an aqueous metal ion and the resulting ion $M^{z+}$ forms a metal chelate with $zR^-$. This corresponds to the inverse process of hydration of a bare metal ion, in which the hydration entropy $\Delta S_h^\circ$ plays an important role, when the electrostatic bonding ability of $6H_2O$ toward a bare metal ion equals to that of $zR^-$. In this case, the driving force of the forward reaction of Eq. 5 is attributable to an entropy change caused by an increase in the number of molecules and a decrease in the charge of reactants. Assuming that the loss of 2z charges during the formation of $MR_z$ causes an increase of entropy by $2\Delta S_h^\circ$, Eq. 6 is obtained:

$$\Delta G^\circ = 2T\Delta S_h^\circ \tag{6}$$

where $\Delta G^\circ$ and T represent free energy change of reaction 5 and absolute temperature, respectively. Since $\Delta G^\circ = -2.30RT\log\beta$, the $S_A$ scale is defined as
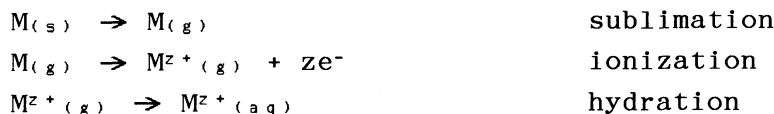
$$S_A = - \frac{2\Delta S_h^\circ}{2.30R} \tag{7}$$

where R denotes the gas constant. A positive relationship between $\Delta S_h^\circ$ and $z^2/r$ (r = ionic radius of a metal ion) suggests that $S_A$ parameter reflects an electrostatic factor. On the other hand, in the case of a purely covalent bonded chelate, the central metal having no charge forms an aqueous metal ion $M^{z+}_{(aq)}$:

$$M_{(s)} \rightarrow M^{z+}_{(aq)} + ze^-$$
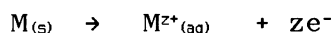
where the subscript s denotes solid phase and the heat of formation of $M^{z+}_{(aq)}$ is defined as $\Delta H_f^\circ$. The formation of an aqueous metal ion can be divided into three

hypothetical parts:

$$M_{(s)} \rightarrow M_{(g)}$$ sublimation

$$M_{(g)} \rightarrow M^{z+}_{(g)} + ze^-$$ ionization

$$M^{z+}_{(g)} \rightarrow M^{z+}_{(aq)}$$ hydration

An inverse process of the above corresponds to the formation of $MR_z$. That is, a metal ion formed by dehydration of $M^{z+}_{(aq)}$ accepts electrons from $zR^-$ and an elementary metal M is formed. Although Ahrland defined a softness parameter based on $\Delta H_f$ of the reaction $M_{(g)} \rightarrow M^{z+}_{(aq)} + ze^-$,[7] an application of his parameter to the present work did not give a satisfactory result. Since the existence of $M_{(g)}$ at room temperature is not plausible, $\Delta H_f^\circ$ instead of $\Delta H_f$ is adopted to define $\sigma_A$ parameter:

$$\sigma_A = \frac{\Delta H_f^\circ}{2.30RT} \qquad (8)$$

The values of $S_A$ and $\sigma_A$ were calculated by using $\Delta S_h^\circ$ and $\Delta H_f^\circ$ cited in Refs. 8 and 9, respectively.

Evaluation of the extraction constant: Combination of Eqs. 1 and 3 gives Eq. 9:

$$\frac{\log K_{ex} + zpK_a}{\sigma_A} = \frac{S_A S_B}{\sigma_A} + \sigma_B \qquad (9)$$

If Eq. 9 is valid, a plot of the left hand side term against $S_A/\sigma_A$ should give a straight line having a slope of $S_B$. An illustration is given in Fig. 1, where plots fall on a straight line excepting cobalt (II) and extraction constants can be expressed using Eq. 9. The $S_B$ and $\sigma_B$ values for common chelating agents are given in Table 1, which were obtained by using extraction data summarized in Refs. 10 and 11. As is seen in Table 1, the $\sigma_B$ value increases in the order, cupferron < DBM < BA $\simeq$ AA < TTA < 8-quinolinol < IPT << STTA < DDTC < dithizone, in which the last three contains sulfur as a donor atom having softness in qualitative sense. On the contrary, cupferron, $\beta$-diketones, 8-quinolinol and IPT which are rather hard bases, have smaller $\sigma_B$ values. Strength parameter($\sigma_B$) given in Table 1 is closely
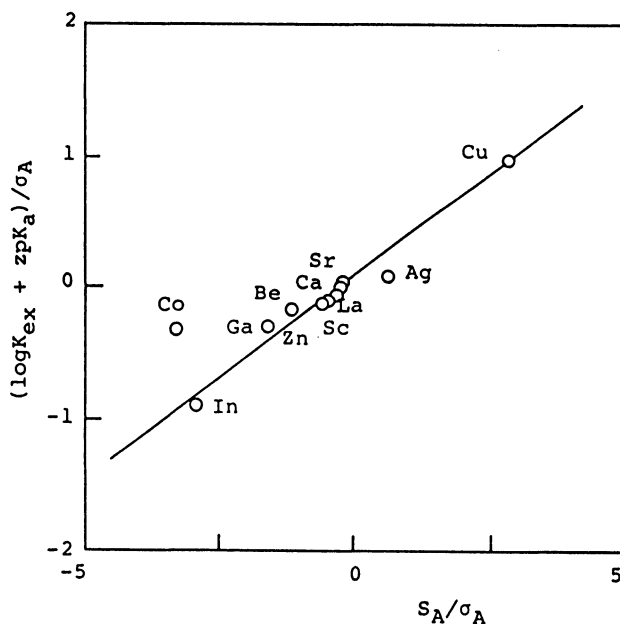


Fig. 1.  $(\log K_{ex} + zpK_a)/\sigma_A$ vs. $S_A/\sigma_A$ (TTA system)

related with $pK_a$, which may mainly be affected by electrostatic force. The above situation indicates that $S_B$ and $\sigma_B$ given in Table 1 are effective parameters to express strength and softness of a chelating agent. And the results obtained from the present work will be useful for the design of mutual separation schemes of metal ions.

Table 1.   The $S_B$ and $\sigma_B$ values for chelating agents

| Chelating agents | $S_B$ | $\sigma_B$ | $pK_a$ | Remarks |
|---|---|---|---|---|
| DBM | 0.466 | 0.043 | 9.35 | 1,3-diphenyl-1,3-propanedione |
| AA | 0.441 | 0.093 | 8.67 | 2,4-pentanedione |
| BA | 0.420 | 0.092 | 8.39 | 1-phenyl-1,3-butanedione |
| TTA | 0.312 | 0.101 | 6.23 | 4,4,4-trifluoro-1-(2-thienyl)-1,3-butane-dione |
| STTA | 0.260 | 0.287 | 4.10 | 1,1,1-trifluoro-4-mercapto-4-(2-thienyl)-3-butene-2-one |
| 8-Quinolinol | 0.623 | 0.133 | 9.66 | |
| IPT | 0.578 | 0.197 | 7.04 | 2-hydroxy-4-(2-propyl)-2,4,6-cyclohepta-trien-1-one |
| Dithizone | 0.459 | 0.440 | 4.47 | 3-mercapto-1,5-diphenyformazan |
| Cupferron | 0.379 | 0.020 | 4.16 | N-nitroso-N-phenylhydroxyammonium salt |
| DDTC | 0.569 | 0.433 | 3.35 | N,N-diethyidithiocarbamic acid |

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