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NOTA TÉCNICA

LEND'S FUNCTION: A PRACTICAL APPROACH FOR COMPARING COMPLEX IONS STABILITY

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Agtenderbos (1) and Beech (2) pointed out the deceiving manner in which textbooks frequently compare equilibrium constant data for reactions of the type:

$$Cu^{2+} + 4NH_3 \rightleftharpoons Cu(NH_3)_4^{2+}$$

$$Cu^{2+} + tren \rightleftharpoons Cu(tren)^{2+}$$

where tren is tri-(2-aminoethyl) amine and whose overall stability constants are:

$$\beta_4 = \frac{[Cu(NH_3)_4^{2+}]}{[Cu^{2+}]\,[NH_3]^4} = 10^{12.7} mol^{-4}\ l^4$$

and

$$\beta_1 = \frac{[Cu(tren)^{2+}]}{[Cu^{2+}]\,[tren]} = 10^{18.8} mol^{-1}\ l$$

respectively.

Comparison between these numerical values leads to results lacking physical meaning since ligands of different denticity are involved, (1 for NH_3 and 4 for tren). If stability constant data are expressed in mol/ml units, the new values for β_4 and β_1 will be $10^{24.7}$ mol^{-4} ml^4 and $10^{21.8}$ mol^{-1} ml, respectively, showing an inversion of magnitude (1,2). This inconvenience due to the equilibrium constants dimensional asimmetry could be eliminated if they were expressed in more convenient units, i.e., mol fractions (3,4) rather than in mol/l units (5-8).

A function quite useful for comparing equilibrium data is LEDEN'S function, $F_O(X)$, also know as "Complexity" (9-11).

This function for a mononuclear species in an equilibrium of the type

$$M \underset{-X}{\overset{+X}{\rightleftarrows}} MX \underset{-X}{\overset{+X}{\rightleftarrows}} MX_2 \dots\dots\dots \underset{-X}{\overset{+X}{\rightleftarrows}} MX_n$$

is defined as bring the relation between the metal analytical concentration, C_M, and it equilibrium concentration, [M]:

$$F_O(X) = \frac{C_M}{[M]} \qquad (1)$$

The analytical concentration, C_M, is given by

$$C_M = [M] + [MX) + [MX_2] + \dots [MX_n] \qquad (2)$$

Remembering that β_1 are the corresponding overall stability constants for the involved equilibria:

$$C_M = [M] + \beta_1[M]\,[X] + \beta_2[M]\,[X]^2 + \dots \beta_n[M]\,[X]^n \qquad (3)$$

wich for eqn (1) gives

$$F_O(X) = 1 + \beta_1[X] + \beta_2[X]^{27} \cdots \beta_n[X]^n =$$

$$= \sum_{i=1}^{n} \beta_i[X]^i;$$

the result of the products $\beta_1[X)^i\ mol^{-i}$, of course will be adimensional numbers.

Considering the examples given,

$$F_O(X) = 1 + 10^{18.8}[tren]$$

$$F_O(X) = 1 + 1.4 \times 10^4[NH_3] + 4.3 \times 10^7[NH_3]^2 +$$

$$+ 3.3 \times 10^{10}[NH_3]^3 + 4.6 \times 10^{12}[NH_3]^4$$

it is obvious that the tren affinity toward Cu^{2+} is greater than that of NH_3 when the analytical concentrations of both ligands are equal. A similar comparison may be performed for several metal ions confronted to the same ligand.

The $F_O(X)$ function also allows the experimental comparison, without a previous knowledge of the equilibrium constants and species dealt with, between the complexing power of ligands or media relating to metal ions. This is quite advantageous in dealing with biological and biochemical systems. If we wish to evaluate a medium affinity with respect to different metal ions it would be enough to measure the equilibrium concentrations of the cations in the same medium, using an appropriate experimental procedure.

In addition, an indication of the existence of polynuclear species is also possible, if one observes alteration in the values of $F_O(X)$ when different analytical concentrations of the metal ion are used in the same medium.

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