

SHORT COMMUNICATIONS

A METHOD FOR INVESTIGATING POLYNUCLEAR COMPLEX FORMATION IN SOLUTION*

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Stability constants for complex formation between any cation, M, and any ligand, L, can be determined by the theoretical treatment due to Bjerrum (1941). When some or all of the complexes, M_xL_y (where x and y have the values : $m \geq x \geq 1$; $n \geq y \geq 1$ and m and n are the greatest number of metal ions and ligand molecules found in any complex), are present in the solution, Bjerrum's *formation function* becomes :

$$\bar{n} = \frac{\sum_{x=1}^m \sum_{y=1}^n y \beta_{xy} [M]^{x-1} [L]^y}{1 + \sum_{x=1}^m \sum_{y=1}^n x \beta_{xy} [M]^{x-1} [L]^y}, \quad \dots \dots \dots (1)$$

where β_{xy} is the overall stability constant of the complex M_xL_y . As the number of unknowns in the numerator and in the denominator depends on the product, mn , it is experimentally difficult to evaluate stability constants by this method when polynuclear complexes are present. Use of oxidation-reduction potentials (Perrin 1958) to calculate $[M]$ makes some simplification possible, because it may readily be shown that

$$[M]_T/[M] = 1 + \sum_{x=1}^m \sum_{y=1}^n x \beta_{xy} [M]^{x-1} [L]^y, \quad \dots \dots \dots (2)$$

where $[M]_T$ is the total concentration of M in the solution. However, this equation still contains mn unknown constants.

In general, if polynuclear complexes are present, and especially where hydroxyl groups may also be bound to the metal ion, equations (1) and (2) become too complex for reliable constants to be obtained, and a simpler approach is necessary.

For solutions of varying total ferric iron concentration, at constant pH, ferrous ion and ligand concentration, the oxidation-reduction potentials vary according to the equation (Perrin 1959) :

$$\frac{2 \cdot 3026 RT}{F \cdot \partial E / \partial \log [Fe^{+++}]_T} = \frac{\sum_x \sum_y \sum_z x^2 \beta_{xyz} [Fe^{+++}]^x [H^+]^{-y} [L]^z}{\sum_x \sum_y \sum_z x \beta_{xyz} [Fe^{+++}]^x [H^+]^{-y} [L]^z}, \quad \dots \dots (3)$$

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where x, y, z refer to any complex, $\text{Fe}_x(\text{OH})_y\text{L}_z$. Hence, the plot of $2.3026 RT \log [\text{Fe}^{+++}]_T/F$ against E will be a straight line of unit slope if only mononuclear complexes are present. When polynuclear complexes are also present, greater slopes should be found, the tangent to the curve at any selected value of $[\text{Fe}^{+++}]_T$ being the weighted mean value of x . It may readily be shown, by setting equation (3) equal to a constant and then differentiating with respect to $[\text{Fe}^{+++}]$, that if x remains constant ($=c$, say) over a range of $[\text{Fe}^{+++}]_T$, only complexes containing c ferric ions per molecule are present in significant amounts. If conditions are chosen such that this requirement is fulfilled over a range of pH and ligand concentrations, evaluation of the appropriate stability constants is considerably simplified, because one of the variables is eliminated. This treatment has recently been successfully applied to the ferric acetate system in which the complexes $\text{Fe}(\text{CH}_3\text{COO})^{++}$ and $\text{Fe}_3(\text{OH})_2(\text{CH}_3\text{COO})_6^+$ are the main species present (Perrin 1959).

The procedure described above, and equation (3), should be applicable directly to any system in which metal ions are in equilibrium with electrodes of the same metal, including silver, cupric ion (with copper amalgam), and cadmium.

References

- BJERRUM, J. (1941).—"Metal Ammine Formation in Aqueous Solution." (P. Haase & Son: Copenhagen.)
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