Kurze Mitteilungen

Spectrophotometric Evaluation of Formation Constants. 1:2 Metal-Ligand System: Iron(II)-Quinolinic Acid Complex

Spektralphotometrische Auswertung von Bildungskonstanten. 1:2-Metall-Liganden-System: Eisen(II)-Chinolinsäure-Komplex

Bildungskonstanten des Komplexes Eisen(II)/Chinolinsäure; Spektralphotometrie

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The stepwise formation constants (k_1 and k_2) of a metal chelate have been investigated by spectrophotometric method. Photometric titration data were collected and utilized for calculation of the said constants for iron(II)-quinolinic acid [3] complex system. Iron(II) forms a yellow complex in aqueous solution. The absorption was measured at wavelength maximum 420 nm between pH 5.6—6.2. The Job's and molar ratio method for determining the metal to ligand ratio indicated the ratio to be 1:2. Both Yatsimirskii's [4] and Leden's method [2] of graphical extrapolation were applied to evaluate the formation constants.

Stepwise and successive formation constants of the system were found by constructing suitable functions in terms of intercepts obtained at zero-ligand concentrations. The equilibrium ligand concentration were calculated from Beer's law and based on the assumption that the ligand is tied up with the metal in ratio 2:1 even at the low concentration of the ligand. The calculations were made with the help of following equations:

Yatsimirskii's method:

$$\lim_{[L]\to 0} F(L)\ i = a_i = \Delta e_i \beta_i - \Delta e_1 \beta_1^i\ ;$$

$$\lim_{Y\to 0} \bar{e} = b_1; \lim_{Y\to 0} g = \frac{\bar{e} - b_1}{Y} = b_2\ ;$$

Table 1. Stepwise formation constants for iron(II)-quinolinic acid complex at 25°C

Method	log k_1	log k_2	log k	log k_{av}
Yatsimirskii's	3.72	3.30	7.02	
Harvey and Manning's	—	—	7.67	7.34
Molar ratio	—	—	7.67	
Leden's	3.56	3.43	6.99	

where

$F(L), g$ = Subsidiary functions;
a, b = Intercept values;
$Y = \frac{1}{[L]}$, e = Extinction (Molar);
and β_i = Successive Stability Constants for ith species.

Leden's method:

$$\lim_{[L]\to 0} \psi_1 = \lim_{[L]\to 0} \frac{\varphi - 1}{[L]} = k_1\ ;$$

$$\lim_{[L]\to 0} \psi_2 = \lim_{[L]\to 0} \frac{\psi_1 - \beta_1}{[L]} = \beta_2 = k_1 k_2\ ;$$

where

φ = Degree of complex function;
ψ_1, ψ_2 = Subsidiary functions;
β_1, β_2 = Successive Stability Constants;
and
k_1, k_2 = Stepwise Stability Constants.

The log k_1 and log k_2 values of the system were found to be 3.72 and 3.30 by Yatsimirskii's method and those by Leden's method are 3.56 and 3.43, respectively. The over-all stability constants were compared with those obtained by other methods and the values agree fairly well within the experimental error involved in molar ratio and Harvey and Manning's methods [1].

The overall formation constants of iron-quinolinic acid complexes are recorded in Table 1. The overall constant compares well with that calculated following Harvey and Manning's method. The reported value [3] is slightly different, as necessary dilution factor was inadvertently not incorporated. After proper correction the value is given in Table 1. The same was also calculated from extrapolated absorbance value obtained from molar ratio data.

References

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2. Leden, I.: Z. Phys. Chem. A **188**, 160 (1941).
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4. Yatsimirskii, K. B., Vasilev, V. P.: Instability constants of complex compounds, pp. 47—52. New York: Pergamon Press 1960.

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