Kurze Mitteilungen

Note on the Complexation of Iron(III) with Quinizarin-2-sulphonic Acid

Bemerkungen zur Komplexierung von Eisen(III) mit Chinizarin-2-sulfonsäure

Komplexierung von Eisen(III) mit Chinizarin-2-sulfonsäure

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Recently [4] the complexation of iron(III) with quinizarin-2-sulphonic acid (H_3L) was described. The authors assumed the equilibria

and calculated the corresponding equilibrium constants (they call them overall formation or stability constants, β , which could be misleading because they do not conform to the standard definition of these terms). However, if we have a complex of $M_mH_jL_n$, the determination of the value of j must be performed by means of eq. (1)

$$\log K_{mn} \alpha_{M(Y)}^m \alpha_{L(H)}^n = \log \beta - j \text{ pH} \quad (3)$$

where K_{mn} is the effective stability constant, β is the overall stability constant and $\alpha_{M(Y)}$ and $\alpha_{L(H)}$ are the coefficients of side reactions of the metal M with a ligand of Y (from buffer, masking reagent or solvent) and ligand L with hydrogen ions, respectively. Since the experiments in the paper discussed were performed only in 0.1 M perchloric acid, it is obvious that the authors did not estimate the number of hydrogens in the complex and there is no reason to write the eq. (1) and (2). The assumption that only

the particles H_2L^- are present in the solution and only the complex of $FeHL$ can be formed is unfounded and in contrast to the sophisticated method used. Many arylsulphonic acids dissociate just near the pH 1.0 [2]. The authors missed that fact since they used visible spectrophotometry which is not proper method for estimation of dissociation of sulphonic acids. Moreover, the proper application of the method confirms that many other values of j can be obtained because the whole system is unsettled just at one pH.

The only rigorous solution is to calculate the effective stability constant

$$K_{mn} = c_{mn} c'_M{}^{-m} c'_L{}^{-n}$$

where c_{mn} is the actual concentration of the complex (with molar ratio metal/ligand $m:n$) and c'_M and c'_L are the total concentrations of the metal and ligand, respectively, that are not complexed with each other. In this way we computed the values 2.49 ± 0.02 and 17.22 ± 0.07 for logarithmic constants of complexes 1:1 and 4:3, respectively, employing the experimental data of Table 2 of the paper [4]. The concept of effective stability constant was introduced by Schwarzenbach [3] just to describe the equilibria where the side reactions cannot be taken into account.

References

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