Polynuclear Complexes: Criticism Invited

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B. S. Jensen [1] has recently published a paper on "The determination of the composition and formation constants of polynuclear complexes", a subject to which our group in Stockholm has devoted some interest for the last ten years. He who reads and understands the various series of papers from our group [2] will find that we endeavour to start without any previous assumptions on the composition of the complexes and that our present methods — given sufficiently good "three-dimensional" data — can deal with practically any set of polynuclear complexes; they are certainly not limited to sets of the "core and links" type, which correspond to exactly parallel Z curves.

Jensen's method requires that two species predominate in the solution. If there are only two species, however, one of them can be treated as the "core" and the other as a singular "core and links" complex. Then the curves $Z(\log h)_B$ are parallel, Jensen's equation (14) or (19) is exactly valid, and the data can be treated in a much simpler way than he gives.

Let us now consider some of the chemical results that Jensen deduces from data of the Stockholm group.

Rossotti and Rossotti [3], from their data on the hydrolysis of VO^{2+}, deduced the formulas $(VO)_2(OH)_2^{2+}$ and $VOOH^+$ and the formation constants $\log^*\beta_{22} = -6.88 \pm 0.05$ and $\log^*\beta_{11} = -6.0 \pm 0.1$. Jensen finds $\log^*\beta_{22} = -6.9 \pm 0.3$; he notices the deviations that indicate another complex but fails to find its formula or formation constant.

Rossotti and Rossotti [4] from their data on the acid hydrolysis of VO_2^+ have deduced the equilibria (25°C, 1 M $(Na)ClO_4$):

$$10VO_2^+aq + 8\,H_2O \rightleftharpoons H_2V_{10}O_{28}^{4-}aq + 14H^+,$$
$$\log^*\beta_{14,10} = -6.75$$
$$H_2V_{10}O_{28}^{4-}aq \rightleftharpoons HV_{10}O_{28}^{5-}aq + H^+,$$
$$\log K = -3.6$$
$$HV_{10}O_{28}^{5-}aq \rightleftharpoons V_{10}O_{28}^{6-} + H^+,$$
$$\log K = -5.8 \qquad (1)$$

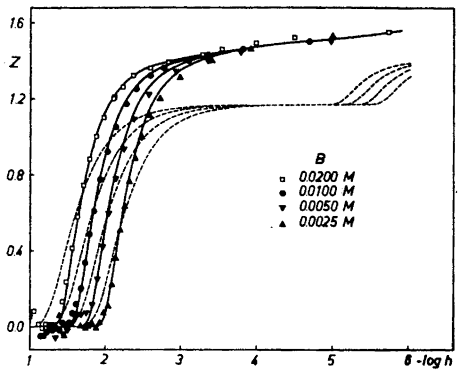

Fig. 1. Hydrolysis of VO_2^+ (1 M $(Na)ClO_4$, 25°C). Z (average number of OH^- bound per VO_2^+) as a function of log $[H^+]$ for four different values of B, the total vanadium concentration. Points: experimental data, Ref.[4] Solid curves calculated with Rossotti's theory [4] (1), dotted curves with B. S. Jensen's [1] (2).

From these same data, Jensen [1] deduces a different set of equilibria (notations below as in "Stability constants"[5])

$$6VO_2^+ + 7OH^- \rightleftharpoons (VO_2)_6(OH)_7^-,$$
$$\log \beta_{7,6} = 94.6 \pm 0.5$$
$$7(VO_2)_6(OH)_7^- + 10\,OH^- \rightleftharpoons (VO_2)_{42}(OH)_{59}^{17-},$$
$$\log K = 100 \pm 2. \qquad (2a)$$

With $\log K_w = -13.8$, which Jensen has used, this gives

$$6VO_2^+ + 7H_2O \rightleftharpoons (VO_2)_6(OH)_7 + 7H^+,$$
$$\log^*\beta_{7,6} = -2.0$$
$$7(VO_2)_6(OH)_7^- + 10\,H_2O \rightleftharpoons (VO_2)_{42}(OH)_{59}^{17-} + 10\,H^+, \log K = -38. \qquad (2b)$$

Jensen claims (p. 498) "The above conclusions are well in accord with the experimental data". Among his several diagrams, however, one does not find any comparison of the experimental data with his theory (2), and with the Rossotti's (1). Fig. 1 gives such a diagram (calculated using our computer program KUSKA) [6]. The points are the experimental data, the solid curves are calculated with Rossotti's theory (1), and the dotted curves from Jensen's (2). The reader is invited to compare the agreement.

He who is interested may then read Jensen's "general discussion" where he claims, among other things, "A distinct

advantage is that the primary polymerisation product often can be determined with certainty".

Those who would like to question (as we do ourselves sometimes) the conclusions reached by our group are cordially invited either

a) to present a better set of data (more accurate or covering a broader range of concentrations), or

b) to give another set of reactions and equilibrium constants that explain our data as well as or better than those deduced by our methods.

It is hard to see that B. S. Jensen's contribution [1] means any progress in our methodical or chemical knowledge.

1. Jensen, B. S. *Acta Chem. Scand.* **15** (1961) 487.
2. See, *e.g.*, Ingri, N. and Brito, F. *Acta Chem. Scand.* **13** (1959) 1971; Olin, Å. *Acta Chem. Scand.* **14** (1960) 126, 814; Biedermann, G. and Ciavatta, L. *Acta Chem. Scand.* **15** (1961) 1347.
3. Rossotti, F. J. C. and Rossotti, H. S. *Acta Chem. Scand.* **9** (1955) 1177.
4. Rossotti, F. J. C. and Rossotti, H. S. *Acta Chem. Scand.* **10** (1956) 957.
5. Bjerrum, J., Schwarzenbach, G. and Sillén, L. G. *Stability Constants* I—II, *Chem. Soc. Spec. Publ.* **6—7** (1957—1958).
6. Ingri, N. and Sillén, L. G. *Acta Chem. Scand. In print.*

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