# Notes on the Formation of Polyacids in Concentrated Telluric Acid Solutions

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According to earlier investigations [1–6], it is obvious that an increase in temperature and in concentration of telluric acid solutions favours the formation of different polytelluric acids. However, it should be noted that according to recent cryoscopic[7] and diffusion[8] measurements the polyacids are present in only minute concentrations at low temperatures.

The aim of the present study was to investigate the formation of polytelluric acids in aqueous telluric acid solutions of different concentrations. According to Fouasson[3] some polyacids are present in concentrated telluric acid solutions. In a recent paper[4] the present author showed that these polyacids seems to be mainly a dimer, although higher polymers are also present. The existence of a dimer has also been reported by Lourijsen-Teyssédre[5]. On the other hand, Earley and Edwards[6] have noted that mainly a trimer and a dimer are formed in concentrated telluric acid solutions, but suspect that higher polymers may also be present in telluric acid solutions more concentrated than 1.0 M.

According to above-mentioned studies of Earley and Edwards and the present author it is obvious that the polyacids formed as the concentration of telluric acid is increased are mainly a dimer and a trimer, although it is difficult to explain some deviations found to occur in other details of these investigations. It should be noted, however, that in their investigation Earley and Edwards used concentrations instead of activities while the present author determined the true concentration conetants. These can be obtained by using data either for the inflection point at the beginning of the titration or for the equivalence point on the titration curve[9]. The present author has used only data for the inflection point at the beginning of the titration in his investigations[4,10] since it is then possible to neglect the influence of added alkali on the polymerization of telluric and boric acids. Thus the results of these investigations can be interpreted as relating to reactions in acid solutions where the complex formation reactions are different from those in alkaline solutions.

In a previous study[4] the author found that the relationship between the first apparent ionization constant $K^*$ of telluric acid and its concentration $C_1$ can be expressed in the following form (for 25° C.)

$$K^* = K_m \cdot C_1^{(m-1)} + K_1 = 2.680 \cdot 10^{-7} \cdot C_1^{1.378} + 2.448 \cdot 10^{-8}, \qquad (1)$$

where m is the average polymerization number (= 2.378), $K_1$ the first thermodynamic ionization constant of telluric acid determined in very dilute acid solutions and $K_m$ the equilibrium constant of the polymerization reaction:

$$\text{m HT} \rightleftarrows H^+ + T_m^-, \qquad (2)$$

where HT designates telluric acid and $T_m^-$ the polyacid anion formed.

The deviation of the average polymerization number m from a whole number can now be explained on the basis of the results of the above-mentioned investigations. Thus equation (1) can be rewritten in the following form (cf. ref. 11.):

$$K^* = k_2 C_1 + k_3 C_1^2 + K_1 \qquad (3)$$

when a dimer and a trimer of telluric acid are simultaneously present[4–6]. Here $k_2$ and $k_3$ are the equilibrium constants of the reactions:

$$2\,HT \rightleftarrows H^+ + T_2^- \qquad (4)$$
$$3\,HT \rightleftarrows H^+ + T_3^-,$$

respectively.

The constants $k_2$ and $k_3$ can be calculated with the aid of equation (3) using previously measured values of $K^*$ (cf. refs. 4 and 11). When these calculations are carried out, the values of constants $k_2$ and $k_3$ are found to be $1.45 \cdot 10^{-7}$ and $1.23 \cdot 10^{-7}$, respectively. Using these values, values of the apparent ionization constant $K^*$ for different concentrations $C_1$ can be calculated. The results are given in Fig. 1. In general the calculated values are in good agreement with those measured previously[4], and thus it is apparent that in concentrated solutions mainly a dimer and a trimer of telluric acid are present.

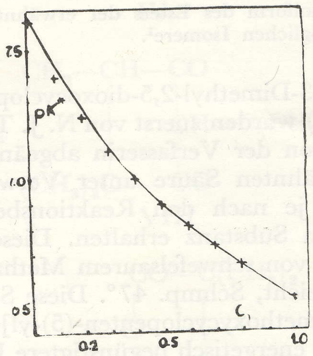


Fig. 1. The influence of the concentration of telluric acid on its apparent ionization constant at ionic strength $I = 0$. The points × correspond to the values calculated using equation (3) and the calculated values of $k_2$ and $k_3$. The curve plots previously reported experimental values[4].

Using the calculated values for $K_1$, $k_2$ and $k_3$, the complex formation constants $k_2'$ and $k_3'$ can be calculated as follows:

$$k_2' = \frac{c_{T_2^-}}{c_{T^-} \cdot c_{HT}} = k_2/K_1 = 5.93$$

$$k_3' = \frac{c_{T_3^-}}{c_{T^-} \cdot (c_{HT})^2} = k_3/K_1 = 5.03$$

References

1. Patry, M. *Bull. soc. chim. France* [5] **3** (1930) 845.
2. Myllius, F. *Ber.* **34** (1901) 2214.
3. Fouasson, F. *Ann. chim.* **12** (1948) 3, 594.
4. Antikainen, P. J. *Suomen Kemistilehti B* **28** (1955) 135.
5. Lourijsen-Teyssédre *Bull. soc. chim. France* **22** (1955) 1196.
6. Earley, J. E. and Edwards, J. O. *Third Interim Technical Report.* Department of the Army Project No. 5B99—01—004. Ordnance R. and D. Project No. TB2—0001. Office of Ordnance Research Project No. 1349. Office of Ordnance Research Contract No. DA—19—020—ORD—3504 with Brown University, Providence, Rhode Island.
7. Heberlein, A. and Jander, G. *Kolloid-Z.* **22** (1918) 38.
8. Stüber, C., Braida, A., and Jander, G. *Z. physik. Chem. A* **171** (1934) 327.
9. Kilpi, S. *J. Amer. Chem. Soc.* **74** (1952) 5296.
10. Antikainen, P. J. *Ann. Acad. Sci. Fennicae, Ser. A II* **56** (1954), *Suomen Kemistilehti B* **29** (1956) 14, 135, 179, *Acta Chem. Scand.* **10** (1956) 756.
11. Antikainen, P. J. *Acta Chem. Scand.* **9** (1955) 1008.

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