The Effect of Electrolytes on the Formation of Polyacids

Telluric Acid in Aqueous Sodium Perchlorate Solutions

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The equilibria in 3 and 0.1 molar sodium perchlorate solutions containing different concentrations of telluric acid have been studied potentiometrically. The data indicate that singly-charged di- and trinuclear species are present in concentrated telluric acid solutions. The results are compared with earlier results relating to the formation of polynuclear complexes of telluric acid in potassium chloride solutions[3] and those of boric acid in potassium chloride and sodium perchlorate solutions[1]. In contrast to the results obtained with boric acid, it appears that a change in the neutral electrolyte does not appreciably alter the concentration ratio of di- and trinuclear species of telluric acid.

It was found in a previous investigation[1] that very interesting details characterize the effects of electrolytes on the formation of polynuclear oxyacids of boron. The present paper reports the results of a study of the polynuclear tellurium complexes in electrolytic solutions.

According to previous investigations[2-5] on the polymerization of telluric acid, mainly singly-charged di-and trinuclear species of tellurium are present in addition to the monomeric species in aqueous solutions of telluric acid.

In a previous study Antikainen[3] found that the relationship between the first apparent ionization constant (K^*) of telluric acid and its concentration (C) (in 0—1.5 M KCl solutions) can be expressed by the following equation:

$$K^* = k_2C + k_3C^2 + K_1, \qquad (1)$$

where k_2 and k_3 are the equilibrium constants for the formation of di-and trinuclear species of telluric acid (HT):

$$k_2 = [H^+] [T_2^-] / [HT]^2$$
$$k_3 = [H^+] [T_3^-] / [HT]^3 \qquad (2)$$

The results given in Table 1 and in Figs. 1 and 2 show that mainly di- and trinuclear species are present also in aqueous sodium perchlorate solutions. It should be noted further that these data indicate that a change in the electrolyte does not influence the concentration ratio of the di- and trinuclear species in the solutions. (The slopes of the curves in Fig. 2 are almost equal in solutions of various electrolytes *e.g.* 1.31 in 0.1 M KCl, 1.38 in 0.1 M NaClO$_4$ and 1.40 in 3.0 M NaClO$_4$ solutions.) In contrast the effect of a change in the electrolyte seems according to Antikainen[1] to explain some differences

Table 1. The influence of the telluric acid concentration (C) on the apparent ionization constant of the acid in approximately I 0.1 and II 3.0 molar sodium perchlorate solutions at 25°C[x]

I			II		
C	$P_m \cdot 10^3$	pK^*	C	$P_m \cdot 10^3$	pK^*
0.009962	0.08253	7.491	0.004997	0.08966	7.120
0.009985	0.07743	7.548	0.009994	0.1281	7.112
0.09938	0.3083	7.342	0.09864	0.5004	6.922
0.2983	0.8070	6.988	0.1385	0.6217	6.881
0.3987	1.055	6.881	0.1988	0.8899	6.726
0.4964	1.272	6.814	0.2941	1.266	6.590
0.5944	1.582	6.708	0.3925	1.635	6.494
			0.4839	2.223	6.318
			0.5879	2.706	6.231
			0.6909	3.234	6.146
			0.7927	3.731	6.082

[x]) For the experimental details and the buffer capacity method used, the reader is referred to earlier papers.[6,3]
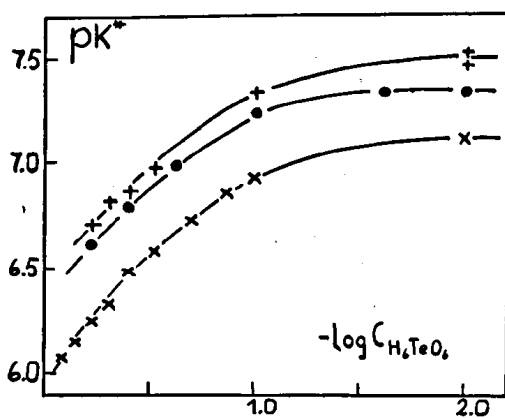
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Fig. 1.

Fig. 2.

Fig. 1. The influence of the concentration of telluric acid on its ionization in aqueous electrolyte solutions. + 0.1 M NaClO₄, ● 0.1 M KCl and × 3.0 M NaClO₄ (cf. Table 1.)
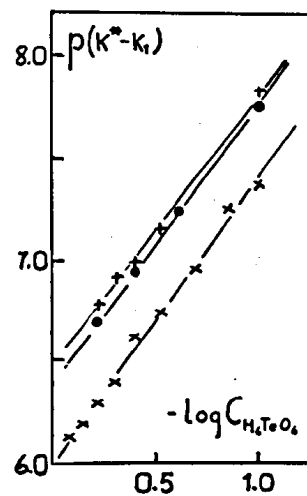
Fig. 2. Plot of the term $p(K-K_1^*)$ against the value of $-\log C_{H_6TeO_6}$ showing the formation of di- and trinuclear species (slopes 1.31—1.40). + 0.1 M NaClO₄, ● 0.1 M KCl³ and × 3.0 M NaClO₄.

Table 2. Values of the first ionization constant (K_1) and the formation constants of the di- and trinuclear telluric acids in aqueous electrolyte solutions at 25°C (cf. Table 1. eqns. 2 and 3 ref. 3.).

$\sqrt{I}$		pK_1	pk_2	pk_3	$\log k_2'$	$\log k_3'$
0.00³		7.611	6.838	6.910	0.773	0.702
0.315	(KCl)³	7.356	—	—	—	—
0.315	(NaClO₄)	7.522	6.796	6.764	0.716	0.748
1.725	(NaClO₄)	7.116	6.409	6.168	0.706	0.948

between the data relating to the polymerization of boric acid obtained by Antikainen[6] and Ingri et al.[7,8].

Fig. 1 clearly indicates that only mononuclear species are present in solutions below 0.01 molar in telluric acid. Thus it is obvious that in these solutions $pK^* = pK_1$. In the calculation of the complex formation constants the values of the first ionization constant K_1 based on data obtained in this concentration range have been used. The calculated complex formation constants are given in Table 2. The constants k_2' and k_3' are defined as follows (cf. ref. 3):

$$k_2' = k_2/K_1 = [T_2^-] / [HT] [T^-]$$
$$k_3' = k_3/K_1 = [T_3^-] / [HT]^2 [T^-] \tag{3}$$

References

1. Antikainen, P. J. *Suomen Kemistilehti* B 30 (1957) 74.
2. Lourijsen-Teyssédre *Bull. soc. chim. France* 22 (1955) 1196.
3. Antikainen, P. J. *Suomen Kemistilehti* B 28 (1955) 135, B 30 (1957) 22.
4. Earley, J. E., Fortnum, D., Wojcicki, A., and Edwards, J. O. *J. Am Chem. Soc.* 81 (1959) 1295.
5. Everest, D. A. and Popiel, W. J. *J. Inorg. Nucl. Chem.* 6 (1958) 153.
6. Antikainen, P. J. *Ann. Acad. Sci. Fennicae, ser. A* 56 (1954).
7. Ingri, N., Lagerström, G., Frydman, M., and Sillén, L. G. *Acta Chem. Scand.* 11 (1957) 1034.
8. Ingri, N. *Tenth Meeting of Scandinavian Chemists*, Stockholm, August 17—22, 1959.