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The Volume Change for the Dissociation of Telluric Acid

Short Communication

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The hydrolysis constants of telluric acid were determined by potentiometric titrations at 25 °C and $I = 1.0\,\mathrm{mol\,kg^{-1}}$ $NaClO_4$. Using these results the partial molar volume change according to the dissociation reaction $Te(OH)_{6(aq)} \rightleftharpoons TeO(OH)^-_{5(aq)} + H^+_{(aq)}$ was measured densitymetrically.

[Keywords: Hydrolysis constants; Molar volume; Telluric acid(VI)]

Das Dissoziationsvolumen der Tellursäure (Kurze Mitteilung)

Die Hydrolysekonstanten der Tellursäure wurden bei 25 °C und $I = 1.0\,\mathrm{mol\,kg^{-1}}$ $NaClO_4$ durch potentiometrische Titrationen bestimmt. Diese Ergebnisse wurden verwendet, um die Volumsänderung zufolge der Dissoziationsreaktion $Te(OH)_{6(aq)} \rightleftharpoons TeO(OH)^-_{5(aq)} + H^+_{(aq)}$ durch Dichtemessungen zu ermitteln.

The partial molar change of volume $\Delta \bar{V}_1$ according to the dissociation reaction (1) is thermodynamically relevant because it governs the pressure

$$Te(OH)_{6(aq)} \rightleftharpoons TeO(OH)^-_{5(aq)} + H^+_{(aq)} \qquad (1)$$

dependence of the corresponding acidity constant by Eq. (2). However, $\Delta \bar{V}_1$ also provides mechanistic information, since for rate constants involving a $TeO(OH)_5^-$ catalyzed path of the form of Eq. (3) the respective activation volume, Eq. (4), can be separated into contributions of the pressure effect on k and K_1 as in Eq. (5).

$$(\partial \ln K_1/\partial P)_T = -\Delta \bar{V}_1/RT \tag{2}$$

$$k_{obsd} = k \times K_1/[\mathrm{H}^+] \tag{3}$$

$$\Delta^{\ddagger} V_{obsd} = -RT(\partial \ln k_{obsd}/\partial P)_T \tag{4}$$

$$\Delta^{\ddagger} V_{obsd} = \Delta^{\ddagger} V(k) + \Delta \bar{V}_1(K_1) \tag{5}$$

Efforts to measure $\Delta \bar{V}_1$ are impeded by the complicated hydrolysis scheme of telluric acid [1]. An attempt was made first to establish composition and stability constants of the various hydrolysis species at 25 °C and constant ionic strength ($I = 1.0\,\mathrm{mol\,kg^{-1}}$ $NaClO_4$) by potentiometric titrations and then to measure $\Delta \bar{V}_1^{\infty}$ for the same conditions from the individual $\bar{V}^{\infty}$ contributions as shown in Eq. (6).

$$\begin{aligned}\Delta \bar{V}_1^{\infty} = {} & \bar{V}^{\infty}(\mathrm{HClO_4}, I) + \bar{V}^{\infty}(\mathrm{TeO(OH)_5Na}, I) - \\ & - \bar{V}^{\infty}(\mathrm{Te(OH)_6}, I) - \bar{V}^{\infty}(\mathrm{NaClO_4}, I)\end{aligned} \tag{6}$$

Since potentiometric studies revealed the presence of dimeric species the density measurements were restricted to solutions of low tellurium molality ($m_{\mathrm{Te}} \leqslant 0.01\,\mathrm{mol\,kg^{-1}}$) so as to make sure that the monomeric species $TeO(OH)_5^-$ predominates. Moreover only dilute acidic solutions of $Te(OH)_6$ remain stable during the period of observation.

Potentiometric titrations were carried out with m_{Te} kept constant throughout each run. Increasing m_{Te} and *pH* favour the precipitation of unknown compounds, probably polymeric alkali tellurates. The ranges of m_{Te} and *pH*, where the hydrolysis reaction proceeded reversibly and stability constants can be evaluated, were checked by the agreement of forward and backward titrations. The ranges of m_{Te} and *pH*, together with that of $\bar{n}$, the average number of protons removed per $Te(OH)_6$, are summarized in Table 1. The experimental data obtained were treated as described elsewhere [2] and the resulting set of m_{Te}, *pH* and $\bar{n}$ values was

Table 1. *Experimental range of titration data*

$m_{\mathrm{Te}}/\mathrm{mol\,kg^{-1}}$	*pH*	$\bar{n}$	No. of data
0.005	5.90–10.40	$\leqslant 1.7$	102
0.010	5.40– 9.14	$\leqslant 1.1$	30
0.025	5.30– 9.00	$\leqslant 1.0$	28
0.050	5.30– 8.70	$\leqslant 1.0$	28
0.100	5.70– 8.40	$\leqslant 1.0$	28

used to calculate the stability constants by a nonlinear least squares procedure which evaluates all data triples simultaneously. The resulting constants for the hydrolysis reactions of telluric acid are compiled in Table 2, along with the simplified model on which the calculation is based.

The scheme proposed by *Kaehler* and *Brito* [3], [4] and that of the present work are in accordance, except that the former includes a third step of deprotonation for the dinuclear species. The influence of this assumption on the pK values given in Table 2 is almost negligible as was noted previously [3]. Table 2 shows that the numerical agreement between the equilibrium constants can be considered as satisfactory. The difference in pK_{12} may be due to the larger range of pH accessible in this work which led to a higher molality of $TeO_2(OH)_4^{2-}$ and consequently a more accurate calculation of the equilibrium constant.

Table 2. pK-values at 25 °C and $I = 1.0\,\mathrm{mol\,kg^{-1}}$

Reaction	pK	This work	Ref. [3], [4]^a
$Te(OH)_6 \rightleftharpoons TeO(OH)_5^- + H^+$	pK_{11}	7.166 ± 0.004	7.31 ± 0.01
$TeO(OH)_5^- \rightleftharpoons TeO_2(OH)_4^{2-} + H^+$	pK_{12}	10.090 ± 0.005	11.19 (> 9.89)
$2\,Te(OH)_6 \rightleftharpoons Te_2O(OH)_{11}^- + H^+$	pK_{21}	6.222 ± 0.036	6.25 ± 0.03
$Te_2O(OH)_{11}^- \rightleftharpoons Te_2O_2(OH)_{10}^{2-} + H^+$	pK_{22}	7.050 ± 0.020	7.04 ± 0.04

^{a} NaCl solutions ($I = 1.0\,\mathrm{mol\,kg^{-1}}$)

The partial molar volume change for reaction (1) was studied by density measurements in dilute solutions of the respective compound [up to $0.01\,\mathrm{mol\,kg^{-1}}$ $Te(OH)_6$ and $TeO(OH)_5Na$ and up to $0.1\,\mathrm{mol\,kg^{-1}}$ $HClO_4$]. But even at such low molalities the formation of dimeric tellurates cannot be completely avoided. However, it is experimentally very difficult to study the volume effect of small amounts of substances dissolved in a solvent of high ionic strength. When the apparent molal volume is calculated by Eq. (7), extremely small errors in molality and/or density result in large deviations of φ-values, as predicted by the law of error propagation. This fact was noted by *Millero* et al. [5] who used a weighting factor of ten times the molality to account for decreasing accuracy of φ with decreasing molality of the electrolyte in the solvent of constant ionic strength ($0.725\,\mathrm{mol\,kg^{-1}}$ NaCl).

$$\varphi_{solute} = \frac{1}{\rho}\left[M_{solute} - \left(\sum_{i=1}^{i=n} m_i M_i/m_{solute}\right) \times (\rho - \rho_0)/\rho_0\right] \qquad (7)$$

It turned out that the density function $(\rho - \rho_0)/\rho_0$ varies linearly with molality of the electrolyte added. This was found valid up to the highest concentrations used. The relation $(\rho - \rho_0)/\rho_0 = s \times m_{solute}$ and Eq. (7)* combine to Eq. (8) which is useful for the extrapolation of apparent molal volumes to infinite dilution.

$$\varphi^{\infty}_{solute} = \frac{1}{\rho_0}\left[M_{solute} - \left(\sum_{i=1}^{i=n} m_i M_i\right) \times s\right] \qquad (8)$$

The values of $\bar{V}^{\infty} = \varphi^{\infty}$ and s are listed in Table 3. The value of φ^{∞} for $HClO_4$ is in excellent agreement with that reported by *Wirth* and *Collier* [6]. The apparent molal volume of $NaClO_4$ in aqueous solution at $m = 1.0\,\mathrm{mol\,kg^{-1}}$ was found to be $\varphi^{\infty} = 44.795\,\mathrm{cm^3\,mol^{-1}}$ and used throughout this work. Data in Ref. [6], converted to molality and fitted to the function $\varphi = a + bm + cm^2$ gave $44.771\,\mathrm{cm^3\,mol^{-1}}$. The volume change for the first dissociation step of telluric acid was calculated by Eq. (6). The final result is

$$\Delta \bar{V}^{\infty}_1 = -16.2 \pm 2.1\,\mathrm{cm^3\,mol^{-1}}\ (25\,^{\circ}\mathrm{C}\ \text{and}\ I = 1.0\,\mathrm{mol\,kg^{-1}}).$$

Table 3. *Summary of volumes measured at 25 °C and $I = 1.0\,\mathrm{mol\,kg^{-1}}$*

Solute	$s/\mathrm{kg\,mol^{-1}}$	$\bar{V}^{\infty}/\mathrm{cm^3\,mol^{-1}}$	$m/\mathrm{mol\,kg^{-1}}$
$Te(OH)_6$	0.1497 ± 0.0005	57.37 ± 0.57	$\leqslant 0.01$
$TeO(OH)_5Na$	0.1855 ± 0.0019	40.53 ± 1.99	$\leqslant 0.01$
$HClO_4$	0.4611 ± 0.0002	45.46 ± 0.23	$\leqslant 0.10$
$HClO_4$	—	45.42[a]	0.15–2.50
$NaClO_4$	—	44.795	1.00

[a] Ref. [6]

The partial molar volume of an electrolyte in an ionic medium can be estimated by the ionic strength principle, *Young*'s rule and the specific interaction model [5]. Whichever approach is used, φ_{solute} is found to depend linearly on m_{solute} (i.e. for $m_{solute} \ll I$). This fact is related to our

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* φ_{solute}, ρ, M_{solute}, m_{solute} are the apparent molar volume, density, molar mass and molality of the substance studied; m_i, M_i are the molalities and molar masses of the constituents of the solvent including H_2O and ρ_0 is the density of the solvent.

experimental result that plots of $(\rho - \rho_0)/\rho_0$ versus m_{solute} fall on straight lines.

The value obtained for $\bar{V}^{\infty}_{\mathrm{Te(OH)_6}}$ amounts to ca. 80% of the molar volume of solid $Te(OH)_6$. In the perovskite type structure of telluric acid the $Te(OH)_6$ octahedrons fill only 66.7% of the volume available [7]. This simple crystallographic argument predicts correctly that the volume of $Te(OH)_{6(aq)}$ is considerably smaller than $Te(OH)_{6(cubic)}$.

The volume change for the dissociation of $Te(OH)_6$ is within the range expected for simple deprotonation reactions.

Experimental

The hydrolysis of orthotelluric acid has been investigated by potentiometric titrations using a glass electrode and an Ag/AgCl reference system. The application of the more accurate hydrogen electrode was impossible due to the reduction of Te(VI) to metallic tellurium in alkaline media. Details of the procedure applied are given by *Sagmüller* [8].

Density measurements were performed on a *Paar* digital density meter model DMA 60/602. The temperature in the cell of the density meter was set to 25 °C and controlled within 0.01 °C by a digital precisions thermometer *Paar* DT 100–20. The density meter was calibrated against water and dry air. Multiple measurements within an experimental run agreed on the average to 1 ppm. For density experiments $NaClO_4$ was dried for 24 h at 220 °C, powdered, stored for another 12 h at the same temperature and used without further purification; stock solutions were prepared by weight. $HClO_4$ solutions were analyzed using NaOH standards. For sodium hydroxide stock solutions, 100 g NaOH were dissolved in 100 cm^3 of water, filtered through a sintered glassfilter (type G4) and stored in polyethylene bottles. This solutions were diluted by weight and titrated with $HClO_4$. Telluric acid has been dried in a vacuum desiccator before use. All reagents used were of Merck analytical grade or similar quality.

Sodium tellurate, $TeO(OH)_5Na$, solutions were prepared by mixing equimolar amounts of $Te(OH)_6$ and NaOH. The density of $Te(OH)_{6(aq)}$ was measured in solutions containing 0.01 mol kg^{-1} $HClO_4$ in addition to 1.0 mol kg^{-1} $NaClO_4$ and the value for ρ_0 was the density of the $HClO_4/NaClO_4$ mixture.

Data sets m_{Te}, $\bar{n}$, pH and $(\rho - \rho_0)/\rho_0$, m_{solute} are available on request.

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