the carboxyl groups connect the dimeric units in a single framework, is formed only after the complete removal of water.

It may be noted that it is difficult, on the basis of the proposed[11] crystal structure of the trihydrate, to explain fully the dehydration of $Cu(C_6H_5COO)_2.3H_2O$, accompanied by the formation of dimers, since the benzoate ions in the structure are packed fairly closely, parallel to the *b* axis of the cell. Copper benzoate $Cu_2(C_6H_5COO)_4$ (irrespective of its origin) absorbs atmospheric moisture and is converted into the trihydrate. This process, which involves the conversion of the dimeric fragments into chains of Cu atoms, is also difficult to explain on the basis of the published crystal structure[11].

After even brief contact with air at room temperature, the EPR spectrum of $Cu_2(C_6H_5COO)_4$ begins to show a line characteristic of isolated copper atoms; this can be attributed to the formation of the trihydrate. The X-ray diffraction patterns of the compounds from which the ligands L had been removed and which had been kept for a longer time in air at room temperature showed lines due to the trihydrate, in addition to the lines due to the compound $Cu_2(C_6H_5COO)_4$.

Thus our experiments show that there is only one form of copper benzoate $Cu_2(C_6H_5COO)_4$, with characteristic magnetic properties (EPR spectrum, magnetic susceptibility, and X-ray diffraction patterns). The reported[1-4] differences in the magnetic properties of copper benzoate are due to the fact that the magnetic susceptibility measurements were made with specimens which had absorbed some moisture. This is also apparently true of a study[13] of the EPR spectra of copper benzoate obtained by removing acetone from the corresponding adduct. The EPR spectrum described[13] was observed by us for the same material after it had been in contact with air.

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Institute of Chemistry,
Academy of Sciences of the
Moldavian SSR

Kazan' Physicotechnical
Institute, Academy of
Sciences of the USSR

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Acid Dissociation Constants of Tellurous Acid

E.Sh.Ganelina and V.A.Borgoyakov

The constants for the dissociation of tellurous acid have been determined by potentiometric titration and solubility measurement: $K_1 = (0.7 \pm 0.2) \times 10^{-6}$, $K_2 = (0.4 \pm 0.2) \times 10^{-8}$.

A handbook[1] quotes the first and second dissociation constants of tellurous acid obtained by Blanc[2]: $K_1 = 2.7 \times 10^{-3}$ and $K_2 = 1.8 \times 10^{-8}$. These values were determined by measuring the pH of 0.0075 M sodium tellurite solution. Issa and Awad[3] determined the constants of the acid and basic dissociation of tellurous acid from solubility measurements. The calculation was made by the method given by Rossotti and Rossotti[4]. $K_{\text{acid}} = 2.51 \times 10^{-6}$ and $K_{\text{basic}} = 3.1 \times 10^{-11}$.

Sekinc[5] studied the dissociation of sulphurous, selenous, and tellurous acids by the method of extraction between two liquid phases (benzene, chloroform, TBP, and isobutyl methyl ketone) in perchloric acid; pK values for tellurous acid of 3.16 and 2.46, and in 3 M $NaClO_4$ medium, 4.17 and 3.07 were obtained.

This paper reports an attempt to determine the dissociation constants of tellurous acid by potentiometric titration and solubility methods. Sodium tellurite was made by dissolving the calculated quantity of tellurium dioxide in 5 *N* NaOH. Crystals of $Na_2TeO_3.5H_2O$ were salted out from the filtrate with alcohol. "Chemically pure" grade NaCl was recrystallised twice. Sodium tellurite solutions of various concentrations were titrated with HCl or H_2SO_4 solutions in a supporting electrolyte of 1.5 M NaCl on an LPU-01 potentiometer with a calomel and flow silver chloride electrodes. Fig. 1 shows the nature of the titration curve obtained for 2×10^{-2} M Na_2TeO_3. The experimental results were used to calculate the Bjerrum function[6] $\bar{n}$ (Fig. 2):

$$\bar{n} = \frac{H - h}{[\mathrm{Te}]},$$

where *H* is the total analytical concentration of hydrogen ions introduced into the solution, *h* the equilibrium concentration of free hydrogen ions, and [Te] the sodium tellurite concentration, calculated for each point of the titration. According to the Bjerrum method,

$$K_1 = \left(\frac{1}{[\mathrm{H}^+]}\right)_{\bar{n} = n - \frac{1}{2}}$$

where $n = 2$ for the removal of a hydrogen ion from H_2TeO_3, that is, $pK_1 = (pH)_{\overline{n}=1.5}$ and $K_2 = \left(\frac{1}{[H^+]}\right)_{\overline{n}=n-\frac{1}{2}}$, where $n = 1$ for the loss of a hydrogen ion from the ion $HTeO_3^-$, that is, $pK_2 = (pH)_{\overline{n}=0.5}$. The values found for pK_1 and pK_2 at $\overline{n} = 1.5$ and $\overline{n} = 0.5$ gave $K_1 = 0.8 \times 10^{-6}$ and $K_2 = 0.5 \times 10^{-8}$. Potentiometric titrations were also made with 1.67×10^{-3}, 3.18×10^{-3}, and 1.305 M sodium tellurite solutions. The curves are similar to that in Fig. 1. The mean values obtained for the dissociation constants of tellurous acid were $K_1 = (0.9 \pm 0.1) \times 10^{-6}$ and $K_2 = (0.5 \pm 0.1) \times 10^{-8}$.

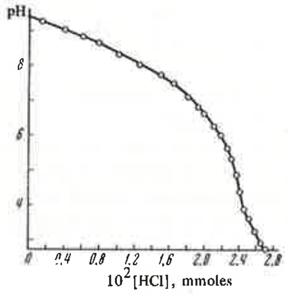

Figure 1. Curve for the potentiometric titration of sodium tellurite with hydrochloric acid. $V_{Na_2TeO_3} = 5$ ml, $[Na_2TeO_3] = 2.0 \times 10^{-2}$ M, $I = 1.5$ M, $[HCl] = 0.09$ M.

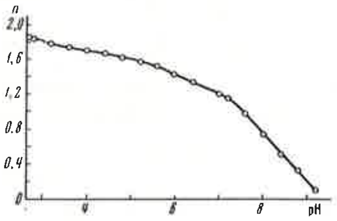

Figure 2. Variation of $\overline{n}$ with pH. $V_{Na_2TeO_3} = 5$ ml, $[Na_2TeO_3] = 2.0 \times 10^{-2}$ M. $[HCl] = 0.09$ M.

We also repeated Issa and Awad's experiments on the solubility of TeO_2 in buffer solutions with pH 2.06–9.16. Tellurium dioxide was treated with the buffer solution in a solubility vessel and kept in a thermostat at 25°C with vigorous stirring. Equilibrium was reached after 4–5 h. The pH was measured on an LPU-01 potentiometer. The tellurium concentration was determined by back titration[7]. The acidity constant, calculated in Issa and Awad's experiments[3] on solubility, varied markedly with the pH of the solution. Thus at pH 4.93, $pK = 3.73$; at pH 7.93, $pK = 5.84$.[3] This is because the equation for calculating pK from solubilities is not applicable for all pH ranges. Fig. 3 gives the results of the experiment as a graph of S against pH, where S is the concentration of tellurium (M). pK_1 was determined by the equation:

$$\lg\left(\frac{A}{[HA]} - 1\right) = -(\lg[H^+] + \lg K_1)\,, \tag{1}$$

where A is the concentration of tellurite ion $HTeO_3^-$, which exists from the isoelectric point (pH 3.9) to pH 7.65. We found the isoelectric point to almost coincide with the value given by Issa and Awad[3]. [HA] is the H_2TeO_3 concentration at the isoelectric point, which we denote S_0'; we find the value 1.2×10^{-4} M.

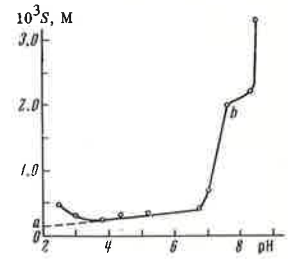

Figure 3. Variation of the tellurium concentration with pH in the dissolution of TeO_2 in buffer solutions. Point a corresponds to S_0', b to S_0''.

In the calculation of K_2, S_0'' equals the concentration of $HTeO_3^-$. The solubility of tellurous acid at pH 7.65 was $S_0'' = 2.0 \times 10^{-3}$ M. A is the tellurite ion concentration at pH ≃ 8. The ranges of existence of the species H_2TeO_3, $HTeO_3^-$, and TeO_3^{2-} that we found[8] agree with published information[9]. Using Bugaevskii's method[10], we determined the pH range at which K_1 and K_2 must be calculated. The equation

$$X_i = pH - \lg \varkappa_i \tag{2}$$

Calculation of the number of titratable hydrogen ions of tellurous acid. $K_1 = 0.9 \times 10^{-6}$, $\varkappa_1 = 1.1 \times 10^{6}$, $K_2 = 0.5 \times 10^{-8}$, $\varkappa_2 = 2 \times 10^{8}$.

pH	X_1	X_2	$y(X_1)$	$y(X_2)$	$\sum_{i=1}^{2} y(X_i)$
5.50	−0.54	−2.80	0.2238	0.0016	0.2254
6.00	−0.04	−2,30	0.4770	0.0050	0.4820
6.50	0.46	−1.80	0.7425	0.0156	0.7581
7.00	0.96	−1.30	0.9012	0.0477	0.9489
7.50	1.46	−0.80	0.9665	0.1368	1.1033
8.00	1.96	−0.30	0.9892	0.3339	1.3231
8.50	2.46	0.20	0.9965	0.6131	1.6096
9.00	2,96	0.70	0.9989	0.8337	1.8326
9.50	3.46	1.20	0.9996	0.9406	1.9402

which he derived[10] was used to calculate the values of X_i, where $\varkappa_i$ are the stability constants, equal to $\varkappa_1 = 1/K_1$ and $\varkappa_2 = 1/K_2$. To calculate $\varkappa_1$ and $\varkappa_2$ (see the Table), we used the acidity constants measured by potentiometric titration.

Fig. 4 shows the variation of $y(X_1)$, $y(X_2)$, and $\sum_{i=1}^{2} y(X_i)$ with pH. From Fig. 4, clearly the processes for the titration of the first and second hydrogen ions are superimposed within the pH range 7.3–8.6. Only the first hydrogen ion is titrated at pH 3.5–7.3, only the second at pH 8.6–10.5. Calculation by Eqn. (1) for the above pH limits gave the following results:

pH	6,50	6.67	7.07	7,30	7.65	
pK_1	6.03	6.26	6.29	6.26	6.49	$(pK_1)_{av.} = 6.27 \pm 0.02$
pH	8.40	8.55	8.70	8.80	9.16	
pK_2	9.30	8.74	8.45	8.42	8.44	$(pK_2)_{av.} = 8.43 \pm 0.02$

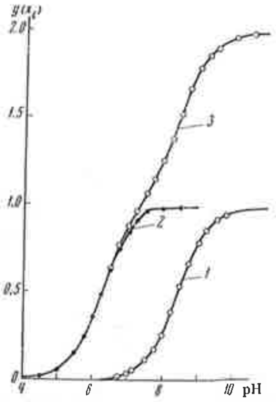

Figure 4. Variation of $y(X_1)$, $y(X_2)$, and $\sum_{i=1}^{2} y(X_i)$ with the pH of the solution.

The increased value of pK_1 at pH 7.65 is explained by the superposition at this pH of the titration of the second hydrogen.

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Gertsen Leningrad
Pedagogic Institute

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Acid Dissociation Constants of Orthotelluric Acid

V.P.Biryukov and E.Sh.Ganelina

The acid dissociation constants of orthotelluric acid have been determined by potentiometric titration and electrical conductivity methods: $K_1 = (3.4 \pm 0.3) \times 10^{-8}$, $K_2 = (4.6 \pm 0.2) \times 10^{-10}$. The titration ranges of the hydrogen ions of the acid have been calculated.

To characterise orthotellurates thermodynamically the acid dissociation constants of orthotelluric acid must be known; however, the published data are contradictory (Table 1).

Jandert and Kienbaum[4] calculated the first acidity constant from the degree of dissociation. The values of the dissociation constant varied with the concentration of the solution, owing to polymerisation of the acid. Herbert and coworkers[5] calculated the values of K_1 and K_2 from the curve for the titration of H_6TeO_6 by KOH solution by the equation:

$$[H^+]^2 = \frac{K_1 \cdot K_{H_2O}}{[H_5TeO_6^-]} + K_1 \cdot K_2 \ .$$

Table 1. Constants of telluric acid.

K_1	K_2	t, °C	Reference	K_1	K_2	t, °C	Reference
$2.29 \cdot 10^{-8}$	$6.46 \cdot 10^{-8}$	18	[1]	$pK_1 = 7.70$	$pK_2 = 10.95$	25	[5]
$1.6 \cdot 10^{-9}$	—	20					
$6.8 \cdot 10^{-7}$	$4.1 \cdot 10^{-11}$	25		$6.8 \cdot 10^{-7}$	$4.1 \cdot 10^{-10}$		[6]
				$1.6 \cdot 10^{-9}$	—		
$2.29 \cdot 10^{-8}$	$6.46 \cdot 10^{-12}$		[2]				
$2 \cdot 10^{-8}$	$5 \cdot 10^{-11}$		[3]	$2 \cdot 10^{-8}$	$9 \cdot 10^{-12}$		[7]
$2.51 \cdot 10^{-8}$	—				$K_3 = 3 \cdot 10^{-15}$		
$2.75 \cdot 10^{-7}$	—	25	[4]	$pK_a = 7.64$			[8]

They considered that

$$K_1 \cdot K_2 > \frac{K_1 \cdot K_{H_2O}}{[H_5TeO_6^-]}$$

and neglected the first term of the equation in their calculations. According to these investigators[4,5], solutions of telluric acid do not contain polymeric forms when $[H_5TeO_6^-] \leq 10^{-3}$ M. Evidently at such tellurate ion concentrations the first term of the equation becomes commensurate with the second. From Table 1, clearly the values of K_1 fluctuate from 10^{-7} to 10^{-9} and K_2 from 10^{-10} to 10^{-12}.

The present paper deals with the determination of the acidity constants of telluric acid by potentiometric titration of sodium tellurate with hydrochloric acid and of telluric acid with sodium hydroxide.

Reagents and Method

Telluric acid was made by the oxidation of elemental tellurium with hydrogen peroxide and was recrystallised