

# Potentiometric Study of Tungsten(VI) Complex Formation with Tartrate

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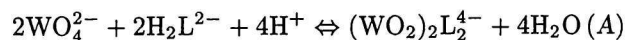
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Complexation of tungstate with tartrate has been investigated by potentiometry in the pH range 2.5–7.5 in 1 M-KNO<sub>3</sub> at 25 °C. The experimental data were evaluated with ESAB (for the calculation of protonation constants of tartrate) and OPIUM (for the calculation of formation constants of complexes) computer programs. A high number of chemical models including polynuclear complexes were considered and tested on a computer. The final model comprises five complexes that have a tungsten(VI) : tartrate ratio of 2 : 2 and 1 : 2. The following formation constants ( $\beta_{p,q,r}$ ) were calculated:  $\log \beta_{212} = 16.6 \pm 0.1$ ,  $\log \beta_{312} = 20.4 \pm 0.2$ ,  $\log \beta_{412} = 23.9 \pm 0.1$ ,  $\log \beta_{322} = 26.68 \pm 0.08$ , and  $\log \beta_{422} = 30.7 \pm 0.1$ , where  $p$ ,  $q$ ,  $r$  refer to stoichiometric coefficients in general formula  $(H)_p(WO_4)_q(C_4H_4O_6)_r^{p-2q-2r}$ . Structures of the complexes were proposed.

Although studies of complex formation between molybdenum(VI) and tartrate have been reported by many workers [1–10], little attention has been paid to the complexation of tungstate with tartrate. A review of mainly Russian research works dedicated to the study of tungsten from the analytical point of view [11], reviews that the complexes with tungstate : tartrate ratio equal to 1 : 1 have been reported by several authors, initially *Britton* and *Jackson* [1]. *Baillie* and *Brown* [4] proposed from polarimetric, conductometric, and potentiometric measurements the formation of the ML complex at pH = 8.2 and its mono- and diprotonated complexes at pH = 7 and pH = 4.2, respectively. The formation of a complex of the same stoichiometry was also demonstrated [5] with the use of tungstate as a catalyst of the reaction between iodide and hydrogen peroxide. The latest investigations concerning the tungstate complexes with  $\alpha$ -hydroxy acids (citric, malic, tartaric) were carried out by *Hlaibi et al.* using <sup>13</sup>C and <sup>183</sup>W NMR spectroscopy [12] in order to characterize the complexes formed in solution. The aim of the work was not to determine the chemical model that would clarify the presence of all the possible complexes of tungstate with tartrate (citrate, malate, etc.) in the solution, but only to determine *via* indirect photometry the conditional formation constant (which depends on the pH) of the most important complex at pH = 4.7. The authors only suggested a structure for the dimeric complex  $(4, 2)_2^{4-}$ , *i.e.*  $(WO_2)_2L_2^{4-}$ , while complex equilibrium can

be described



where  $H_2L^{2-}$  is  $C_4H_4O_6^{2-}$ .

A similar structure of a possible binuclear chelate where tartrate acts as a bridge between the two central atoms had already been proposed independently by *Bartušek* in 1980 [7].

An important piece of work was carried out by *Castaño et al.* [13]. They carried out a potentiometric study of the protonation equilibria of tartaric acid in aqueous sodium perchlorate solutions at 25 °C.

There is increasing interest on tungsten(VI) complexation with respect to bioinorganic chemistry [12, 14, 24], potential use of molybdenum and tungsten complexes in analytical chemistry, biology, clinical research, and in homogeneous and heterogeneous catalysis [24 and references therein]. However, the tungstate complexation is not sufficiently investigated. A short communication about thermodynamic study of the tungstate–tartrate system has also been published by *Cruywagen* and *Rohwer* [15]. A different chemical model including mono-, di-, and tetranuclear species has been proposed from glass electrode potentiometry data, however, no experimental details are given. The aim of this work was to find and explain the best chemical model for tungstate–tartrate equilibria taking into account also the formation of polynuclear species of tungstate. The preliminary results of this

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**Table 1.** Equilibrium Constants for the Protonation of Tartrate in 1 M-KNO<sub>3</sub> at 25°C as Calculated for Different Concentrations of Tartrate

Cumulative constant	<i>c</i> /(mmol dm <sup>-3</sup> )			NIST database v. 2.0 (1995) <i>I</i> = 1.0 mol dm <sup>-3</sup>
	4.0	2.0	1.0	
log β <sub>101</sub>	3.768 ± 0.005	3.774 ± 0.006	3.776 ± 0.009	3.69 ± 0.02
log β <sub>201</sub>	6.47 ± 0.03	6.57 ± 0.03	6.58 ± 0.04	6.43 ± 0.05

study have been briefly reported elsewhere [14].

## EXPERIMENTAL

Anal. grade chemicals (all from Lachema, Brno) were used and solutions were prepared using doubly distilled water. Sodium tartrate (racemic mixture) and sodium tungstate solutions were prepared from the corresponding recrystallized salts. Precise concentrations of the stock sodium tartrate and tungstate solutions were determined gravimetrically evaporating known volume of these solutions to constant mass at elevated temperature. The nitric acid solution was standardized by titration with a commercial standard solution of sodium hydroxide checked against potassium hydrogen phthalate.

Potentiometric titrations with nitric acid in 1 M-KNO<sub>3</sub> were performed at (25.0 ± 0.1)°C using an automatic titrator, which included a PHM 84 pH-meter, ABU 80 automatic burette, TTT 81 digital titrator with a microprocessor and printer (all Radiometer, Copenhagen, Denmark). A G 202 C glass electrode and a saturated calomel electrode K 401 (both Radiometer) were used as the detection system. Nine solutions were used for the titrations, their respective initial concentrations *c*/(mmol dm<sup>-3</sup>) of tungstate and tartrate were as follows: 2, 4; 2, 2; 2, 1; 1.4, 4; 1.4, 2; 1.4, 1; 1, 4; 1, 2; 1, 1. The pH-meter was adjusted with two buffer solutions (Radiometer, Copenhagen) of pH = 4.01 ± 0.02 and pH = 7.00 ± 0.02. All solutions were kept at a constant ionic strength of 1 M with respect to nitrate ions by addition of potassium nitrate (three times recrystallized). A stream of purified nitrogen gas was bubbled slowly through the titration solution. Equilibrium was established quickly, thus on average 43 experimental points were obtained within 20 min. Experimental data and details about paper electrophoretic measurements of the system mentioned above are described elsewhere [7].

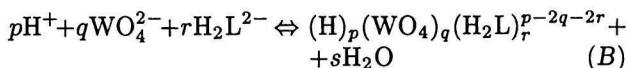
Evaluation of the titration data for the protonation constant estimation was done using the ESAB [16] program. The best chemical model was searched for by the OPIUM [17] program running on a POWER CHALLENGE XL under a UNIX operating system. The parameters (stability constants, mobilities, etc.) for a certain chemical model were calculated by the same program fitting through ex-

perimentally (potentiometric, electrophoretic) derived data.

## RESULTS AND DISCUSSION

The protonation constants of tartrate in 1 M-KNO<sub>3</sub> were calculated by the ESAB program [16] from the data obtained in separate potentiometric titrations of tartrate at *c*/(mmol dm<sup>-3</sup>) equal to 4, 2, and 1 of total concentration of the ligand. The results are given in Table 1 and it can be seen that they correspond with those published for 1 M-NaClO<sub>4</sub>, log β<sub>101</sub> = 3.70 ± 0.02 and log β<sub>201</sub> = 6.41 ± 0.01 [13], and for 1.0 M-NaCl, log β<sub>101</sub> = 3.69 ± 0.03 and log β<sub>201</sub> = 6.38 ± 0.03 [10]. The differences for both values of the protonation constants of tartrate for different ionic medium can be explained by the formation of weak sodium-tartrate complexes [16].

The reaction of tungstate and tartrate can be summarized by the following equation



The individual species are described in terms of the stoichiometric coefficients which define their composition, *i.e.* (*p*, *q*, *r*)<sup>*p-2q-2r*</sup>, while mixed formation constants concerning equilibria (*B*) denoted by β<sub>*pqr*</sub> include both, activities and concentrations.

Primary titration data {*V*, pH} pairs were normalized into the form of a *Z*(pH) function representing the number of protons bound per one metal ion

$$Z = \frac{(c_{\text{H}^+} - a_{\text{H}^+} + K_w/a_{\text{H}^+})}{c_M} \quad (1)$$

where *c*<sub>H<sup>+</sup></sub> is the total concentration of protons, *a*<sub>H<sup>+</sup></sub> is an activity of free protons measured by a glass electrode, *K*<sub>w</sub> is the ionic product of water, and *c*<sub>M</sub> is the total analytical concentration of the metal ion. The normalized titration curves of solutions with different ratio of tungstate and tartrate are presented in Fig. 1.

The titration data were evaluated with the OPIUM computer program [17]. This program can automatically generate different chemical models and examine them one after the other. This approach is similar to that one proposed by Sillén in his species selector STYRE [18]. A large number of models can be tested to find complex species of the chemical model

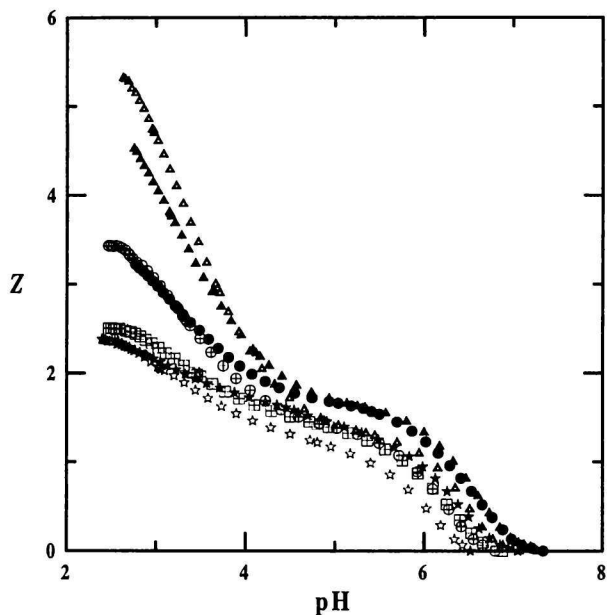


Fig. 1. Experimental data normalized into the form of  $Z$ — $pH$  function. Symbols represent different concentrations  $c/(\text{mmol dm}^{-3})$  of tungstate and tartrate as follows:  $\boxplus$  (1.4; 2),  $\oplus$  (1; 2),  $\bullet$  (2; 4),  $\star$  (2; 2),  $\star$  (1; 1),  $\Delta$  (1; 4),  $\blacktriangle$  (1.4; 4).

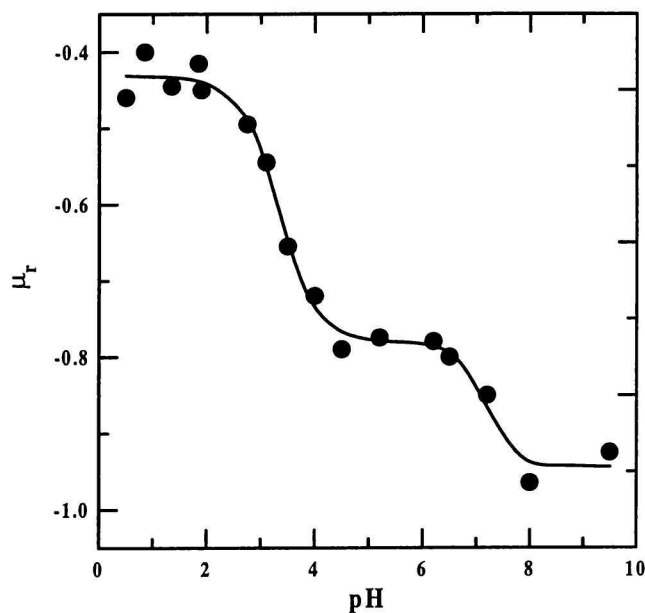


Fig. 2. The experimental data [7] obtained from paper electrophoresis fitted by theoretical curve based on the best chemical model (cf. Table 2b).

which would be in best agreement with the experimental data. The criteria for a selection of the models are based on goodness of fit functions such as the residual function (the residual square  $U$ -function, the observed  $\chi^2$ , Curtosis and Skewness coefficients, the standard deviation, etc.) and the values of the tested parameters (formation constants) and their standard deviations, respectively. A criterion based on information theory [19] was also introduced into the program (e.g. Akaike Information Criterion, AIC [19]), which helps to discriminate between various chemical models with different number of species. The numerical value of the criterion has a minimum for the “best” chemical model and it represents an attempt to quantify Ockham’s knife theorem [20].

### Search for the Model (Potentiometric Data)

Bartušek *et al.* [7] described the formation of  $(4, 1, 2)^{4-}$  and  $(2, 1, 2)^{2-}$  species in solution with an excess of tartrate by means of paper electrophoresis and Hlaibi *et al.* [12] proved the existence of  $(4, 2, 2)^{4-}$  species. The chemical model including these species was the starting point in the search (Table 2a, Model 3). Model 1, described by Žák *et al.* [14] gives worse fit in comparison to Model 3 or with respect to the model without  $(4, 2, 2)^{4-}$  species (Model 2). In Model 4, we have used the ESI (Estimation of Stoichiometric Indices) approach [21] based on the fact that stability constants and corresponding stoichiometric indices are

varied simultaneously as real numbers. As it is possible to see, the stoichiometric indices  $p$  came out integer values, therefore a new species  $(3, 2, 2)^{5-}$  was also included (Model 5a). The AIC has a minimum which means that the introduction of the new species leads to a better explanation of the experimental data. Including polymeric species of tungstate hydrolysis [22], the fit does not change dramatically (Model 5b). In case when we added  $(3, 1, 2)^{3-}$  species (Models 6 and 7) we had some difficulties in the evaluation of stability constant of the species coming out from the fact that the protonation constant of  $(2, 1, 2)^{4-}$  species is the same as the protonation constant of  $(3, 1, 2)^{3-}$  species. This problem can be eliminated by the treatment of joined experimental data obtained by different experimental techniques.

In the light of the previous studies on complex formation of tungsten(VI) and molybdenum(VI) with  $\alpha$ -hydroxy carboxylic acids, it is evident that large number of species of different composition can be formed. Therefore, we applied also a “trial and error” method with the aim to determine the correct chemical model. We proposed a scenario consisting of a basic set of  $(2, 1, 2)^{4-}$ ,  $(4, 1, 2)^{2-}$ , and  $(4, 2, 2)^{4-}$  species, as well as the set of 3–5 different  $(p, q, r)^{p-2q-2r}$  species ( $1 \leq p \leq 8$ ,  $1 \leq q \leq 4$ ,  $1 \leq r \leq 4$ ), taking into account that tetranuclear species can be formed as well, as demonstrated recently by Cruywagen and Rohwer for the case of molybdate–tartrate [10] and tungstate–tartrate systems [15]. The scenario contained over 35 000 possibilities that were generated automatically and tested. All models were calculated and examined

**Table 2.** Results of Model Testing with the Computer Program OPIUM [17]. Log  $\beta_{pqr}$  are Formation Constants for  $(\text{H})_p(\text{WO}_4)_q(\text{C}_4\text{H}_4\text{O}_6)_r^{p-2q-2r}$  Species

## a) Potentiometric Data

Model	$(p, q, r)^{p-2q-2r}$ $\log \beta_{pqr} \pm \sigma(\log \beta_{pqr})$			$U$	$\frac{R}{\%}$	MEP	AIC		
1	$(2, 1, 2)^{4-}$ $17.25 \pm 0.08$	$(4, 2, 2)^{4-}$ $30.1 \pm 0.2$	$(5, 2, 2)^{3-}$ $33.3 \pm 0.3$	40.28	8.07	0.1340	-614.4		
2	$(2, 1, 2)^{4-}$ $17.35 \pm 0.08$	$(3, 1, 2)^{3-}$ $21.1 \pm 0.2$	$(4, 1, 2)^{2-}$ $24.9 \pm 0.1$	44.78	8.52	0.151	-582.0		
3	$(2, 1, 2)^{4-}$ $17.29 \pm 0.07$	$(4, 1, 2)^{2-}$ $24.1 \pm 0.1$	$(4, 2, 2)^{4-}$ $30.1 \pm 0.1$	25.18	6.38	0.0843	-758.2		
4	$(p, 1, 2)^{p-6}$ $19.8 \pm 0.6$ $p = 2.8 \pm 0.2$	$(4, 1, 2)^{2-}$ $23.9 \pm 0.1$	$(p, 2, 2)^{p-6}$ $28.0 \pm 0.1$ $p = 3.24 \pm 0.02$	14.36	4.82	0.0480	-926.0		
5a	$(2, 1, 2)^{4-}$ $16.5 \pm 0.1$	$(4, 1, 2)^{2-}$ $24.03 \pm 0.09$	$(4, 2, 2)^{4-}$ $30.9 \pm 0.1$	$(3, 2, 2)^{5-}$ $26.69 \pm 0.07$	12.42	4.48	0.0424	-972.5	
5b	$(2, 1, 2)^{4-}$ $16.3 \pm 0.2$	$(4, 1, 2)^{2-}$ $23.94 \pm 0.08$	$(4, 2, 2)^{4-}$ $30.92 \pm 0.08$	$(3, 2, 2)^{5-}$ $26.57 \pm 0.08$	12.02	4.42	0.0412	-982.5	
6	$(2, 1, 2)^{4-}$ $15 \pm 3$	$(4, 1, 2)^{2-}$ $23.8 \pm 0.1$	$(4, 2, 2)^{4-}$ $30.9 \pm 0.1$	$(3, 2, 2)^{5-}$ $26.78 \pm 0.07$	$(3, 1, 2)^{3-}$ $20.7 \pm 0.1$	11.58	4.33	0.0399	-992.0
7	$(2, 1, 2)^{4-}$ $16.5$ (fixed)	$(4, 1, 2)^{2-}$ $24.03$ (fixed)	$(4, 2, 2)^{4-}$ $30.9$ (fixed)	$(3, 2, 2)^{5-}$ $26.69$ (fixed)	$(3, 1, 2)^{3-}$ $20.3 \pm 0.2$	12.03	4.41	0.0395	-988.1

Model 5b corrected for tungstate hydrolysis at  $I = 1$  M-NaCl [23]. $U$  is residual square sum function,  $R$  is Hamilton R factor, MEP is a mean error prediction, AIC is Akaike Information Criterion, the parameters of fit are defined in [19].

## b) Electrophoretic Data

Model	$(p, q, r)^{p-2q-2r}$ $\log \beta_{pqr} \pm \sigma(\log \beta_{pqr})$ $\mu_r \pm \sigma(\mu_r)$			$U$	$\frac{R}{\%}$	MEP	AIC
1	$(2, 1, 2)^{4-}$ $16.0 \pm 0.4$ $-0.77_0 \pm 0.01_3$	$(4, 1, 2)^{2-}$ $22.6 \pm 0.4$ $-0.44_1 \pm 0.01_1$	$(0, 1, 0)^{2-}$ $-0.94_6 \pm 0.02$	$7.64 \times 10^{-3}$	3.21	$1.59 \times 10^{-3}$	-112.4
2	$(2, 1, 2)^{4-}$ $16.1 \pm 0.4$ $-0.77_9 \pm 0.02_1$	$(3, 1, 2)^{3-}$ $21 \pm 2$ $-0.80_6 \pm 0.04_4$	$(4, 1, 2)^{2-}$ $21 \pm 2$ $-0.42_9 \pm 0.01_1$	$(0, 1, 0)^{2-}$ $-0.94_7 \pm 0.01_8$			
3	$(2, 1, 2)^{4-}$ $16.0$ (fixed) $-0.78_2 \pm 0.01_2$ $-0.774^*$	$(3, 1, 2)^{3-}$ $19.4 \pm 0.2$ $-0.59_7 \pm 0.04_1$ $-0.580^*$	$(4, 1, 2)^{2-}$ $22.6$ (fixed) $-0.43_1 \pm 0.01_1$ $-0.386^*$	$4.90 \times 10^{-3}$	2.57	$6.39 \times 10^{-3}$	-119.4

\* Calculated according to eqn (2).

c) Combined (Electrophoretic + Potentiometric) Data,  $\mu_r$  (Tungstate(VI))  $-0.946$ 

Model	$(p, q, r)^{p-2q-2r}$ $\log \beta_{pqr} \pm \sigma(\log \beta_{pqr})$ $\mu_r \pm \sigma(\mu_r)$					$U$	$\frac{R}{\%}$	MEP	AIC
1	$(2, 1, 2)^{4-}$ $16.6 \pm 0.1$ $-0.774^*$	$(3, 1, 2)^{3-}$ $20.4 \pm 0.2$ $-0.580^*$	$(4, 1, 2)^{2-}$ $23.9 \pm 0.1$ $-0.386^*$	$(3, 2, 2)^{5-}$ $26.68 \pm 0.08$ $-0.659^*$	$(4, 2, 2)^{4-}$ $30.7 \pm 0.1$ $-0.550^*$	13.50	4.67	$4.38 \times 10^{-2}$	-1011.1
2	$(2, 1, 2)^{4-}$ $16.7 \pm 0.3$ $-0.774^*$	$(3, 1, 2)^{3-}$ $20.5 \pm 0.1$ $-0.580^*$	$(4, 1, 2)^{2-}$ $23.8 \pm 0.1$ $-0.386^*$	$(3, 2, 2)^{5-}$ $26.66 \pm 0.08$ $-0.659^*$	$(4, 2, 2)^{4-}$ $30.8 \pm 0.1$ $-0.550^*$	11.57	4.33	$3.78 \times 10^{-2}$	-1061.0

\* Calculated according to eqn (2). Model 2 corrected for tungstate hydrolysis (the hydrolytic constants at  $I = 1$  M-NaCl [23] were used).

according to different statistical criteria. Model 5 (Table 2) is identical to that one obtained by the "trial and error" method.

### Search for the Model Using Electrophoretic Data [7]

Keeping in mind the results from the previous paragraph, we tried to explain experimental electrophoretic data taken from literature [7] in solution with an excess of tartrate. In the data [7b], the stability constants of species  $(2, 1, 2)^{4-}$  and  $(4, 1, 2)^{2-}$

(Table 2b, Model 1) were estimated using the graphical method, therefore the species  $(3, 1, 2)^{3-}$  was also included (Table 2b, Models 2 and 3). Afterwards,  $\log \beta$  values of the species  $(2, 1, 2)^{4-}$  and  $(4, 1, 2)^{2-}$  were fixed and the stability constant of  $(3, 1, 2)^{3-}$  species was calculated. Relative electrophoretic mobilities ( $\mu_r$ ) of the complex species of relative molecular mass  $M_r$  having charge  $Z$  were found to correlate well with the empirical *Jokl's* linearized equation [7]

$$\frac{\mu_r}{Z} = \frac{a}{\sqrt{M_r}} + b \quad (2)$$

where  $a$  and  $b$  are empirical parameters. The authors

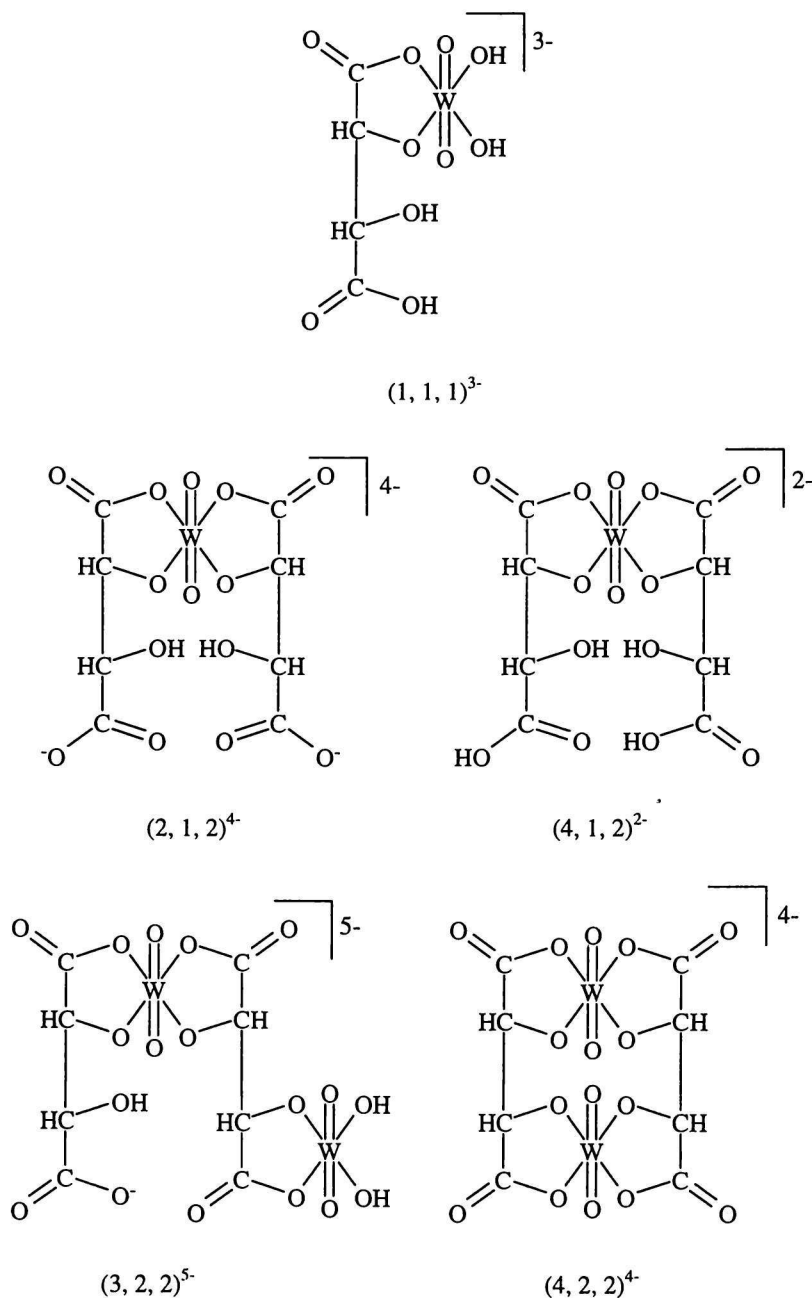
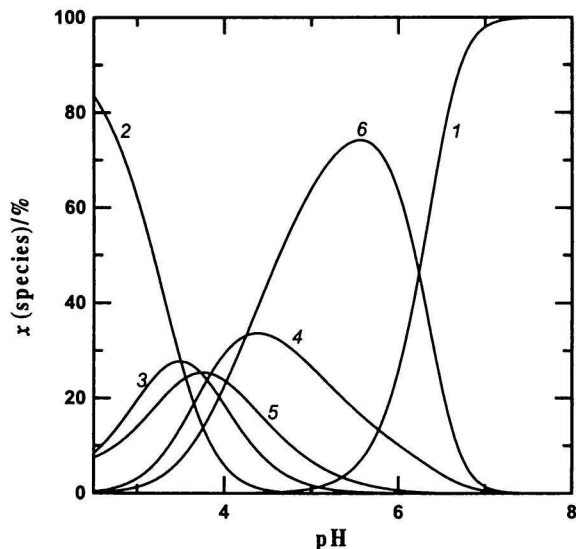


Fig. 3. Proposed structure of tungsten—tartrate complexes (the charge of the species is given in the right upper corner).



**Fig. 4.** The distribution diagram of species present in the solution ( $c_M = 1 \text{ mmol dm}^{-3}$ ,  $c_L = 4 \text{ mmol dm}^{-3}$ ). 1.  $\text{WO}_4^{2-}$ ; 2.  $(4, 1, 2)^{2-}$ ; 3.  $(3, 1, 2)^{3-}$ ; 4.  $(2, 1, 2)^{4-}$ ; 5.  $(4, 2, 2)^{4-}$ ; 6.  $(3, 2, 2)^{5-}$ .

found the following values of empirical parameters (cf. eqn (2)):  $a = 7.57$  and  $b = -0.14$  (with correlation coefficient 0.917 [7b]). Calculated relative electrophoretic mobilities are in a good agreement with those calculated according to eqn (2) (cf. Table 2b). The fit of the best model is drawn as the solid line through experimental points (cf. Fig. 2).

### Search for the Model Using Joined Potentiometric and Electrophoretic Data

In comparison to electrophoresis, the presence of some other species was found by means of glass electrode potentiometry. We consider that the use of electrophoretic data only is insufficient. Therefore, another attempt to improve the chemical model determination was done, joining electrophoretic and potentiometric data together. Evaluation of quite different data is possible with the OPIUM program. This is the advantage of the OPIUM program, as it is possible to evaluate at the same time joined data from very different experimental techniques. A weight equal to one was given to each experimental potentiometric as well as electrophoretic data point. Relative mobilities of each complex species were calculated according to Jokl's equation and the values were fixed during the calculation. The presence of species as demonstrated by potentiometry was confirmed (Models 1 and 2) and the stability constants were calculated (Table 2c). Taking into account the fact that the solutions were titrated to the final pH of 2.7, the complex  $(p, 1, 1)^{p-4}$  is present in solution at only low concentrations because the dimeric  $(p, 2, 2)^{p-8}$  species are formed from the monomer  $(p, 1, 1)^{p-4}$ . Therefore it is difficult to

calculate its stability constant. It was observed that lowering of the tungstate-tartrate concentration level caused the increase of the  $(p, 1, 1)^{p-4}$  species concentration. The formation of dimer can be further supported by the estimation of the stability constant for the dimer  $(4, 2, 2)^{4-}$  from the stability constants of monomer  $(p, 1, 1)^{p-4}$  ( $p = 1, 2$ ) obtained by Yatsimirskii [5] from kinetic measurements. The estimate  $\log \beta_{4,2,2}$  equal to 30.7 was obtained. Comparing this value found with that one obtained here ( $30.7 \pm 0.1$ ), we can see that the values are in the very good agreement.

The formation of two different protonated species,  $(p, 1, 2)^{p-6}$  ( $p = 2, 3, 4$ ) and  $(p, 2, 2)^{p-8}$  ( $p = 3, 4$ ), was proved. The proposed structural formulas of complex species discussed above are shown in Fig. 3. For the species  $(2, 1, 2)^{4-}$ , two protonation constants 3.8 and 3.3 were calculated. Comparing with the first protonation constant of tartrate, 3.8, we can conclude that one carboxylic group of tartrate is not bound as was shown independently by paper electrophoresis. Distribution diagram for tungstate-tartrate system calculated using equilibria constants found in this work is given in Fig. 4.

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