



## Conductometric and pH metric investigations of the oxalic acid and NaAsO<sub>2</sub> reaction

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**Abstract:** The reaction between NaAsO<sub>2</sub> and oxalic acid was studied by pH-metric and conductometric measurements, applying the methods of continual variation and pH-metric and conductometric titration. It was found that oxalic acid forms a complex anion of the type [AsOC<sub>2</sub>O<sub>4</sub>]<sup>-</sup>. The relative stability constant of the complex at ionic strengths, *I*, of 0.10 ( $\log K_r = 4.70$ ), 0.20 ( $\log K_r = 4.51$ ), 0.50 ( $\log K_r = 4.24$ ) and 0 ( $\log K_r^0 = 5.05$ ) and thermodynamic parameters were calculated using the data obtained by pH-metric measurements at  $25.0 \pm 0.1$  °C ( $\Delta H = 10.5$  kJ mol<sup>-1</sup>,  $\Delta G = -29.0$  kJ mol<sup>-1</sup>,  $\Delta S = 133$  J mol<sup>-1</sup> K<sup>-1</sup>).

**Keywords:** arsenic(III); oxalic acid; complex; conductometry; pH-metry.

### INTRODUCTION

Literature data are available for Mo(VI) and W(VI) complexes, *i.e.*, complexes of a metal in the form of an oxyanion, with different monobasic acids (HAc), such as formic, acetic, propionic and ascorbic.<sup>1–3</sup> The ligand to metal ratio in these complexes, [WO<sub>3</sub>Ac<sub>2</sub>]<sup>2-</sup> and [MoO<sub>3</sub>Ac<sub>2</sub>]<sup>2-</sup>, is 2:1. With oxalic acid, Na<sub>2</sub>WO<sub>4</sub> and Na<sub>2</sub>MoO<sub>4</sub> form [WO<sub>3</sub>C<sub>2</sub>O<sub>4</sub>]<sup>2-</sup> and [MoO<sub>3</sub>C<sub>2</sub>O<sub>4</sub>]<sup>2-</sup> complexes, respectively.<sup>4</sup> Tetracycline (H<sub>3</sub>T<sub>C</sub>) forms the complexes [WO<sub>3</sub>(HT<sub>C</sub>)]<sup>2-</sup>, [WO<sub>3</sub>(H<sub>2</sub>T<sub>C</sub>)<sub>2</sub>]<sup>-</sup> and [MoO<sub>3</sub>(H<sub>2</sub>T<sub>C</sub>)<sub>2</sub>]<sup>2-</sup> in the reaction with Na<sub>2</sub>WO<sub>4</sub> and Na<sub>2</sub>MoO<sub>4</sub>.<sup>5</sup> Also, Na<sub>2</sub>HAsO<sub>4</sub> forms a complex with oxalic acid which has the formula [HAsO<sub>3</sub>C<sub>2</sub>O<sub>4</sub>]<sup>2-</sup> and a relative stability constant of  $\log K = 5.50$  at an ionic strength *I* = 0 and 25 °C.<sup>6</sup> With monobasic acids (HAc), *i.e.*, formic, acetic and propionic acid, NaAsO<sub>2</sub> forms [AsOAc<sub>2</sub>]<sup>-</sup> complexes.<sup>7</sup> With the carbonate ion, it forms the [As(OH)<sub>2</sub>CO<sub>3</sub>]<sup>-</sup> complex, starting from the As(OH)<sub>3</sub> form of the As(III) acid.<sup>8</sup>

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All the above-cited results were obtained by pH and conductometric measurements and methods, as in this work.

However, no literature data exist on the complex formed between NaAsO<sub>2</sub> and oxalic acid.

According to literature data,<sup>9,10</sup> different forms of As(III) acids exist in aqueous solutions, *i.e.*, H<sub>3</sub>AsO<sub>3</sub>, HAsO<sub>2</sub>, As(OH)<sub>3</sub>, AsO(OH) and H<sub>3</sub>[As(OH)<sub>6</sub>]. The acids of As(III) have not been isolated as pure acids, liquid or solid. The dissociation constant of arsenite acid in the form of HAs(OH)<sub>4</sub> or HAsO<sub>2</sub>, at 25 °C and the ionic strength  $I = 0$ , is  $pK_1 = 9.22, 9.08$  or  $9.3$ , depending on the author.<sup>10</sup> The theoretical calculated dissociation constant of HAsO<sub>2</sub> is  $pK_1 = 10.01$  at 25 °C.<sup>11</sup> According to new data,  $pK_1$  for H<sub>3</sub>AsO<sub>3</sub> is 9.22 or 9.25 at 25 °C.<sup>12</sup> In alkaline solution, the *m*-arsenite ion, AsO<sub>2</sub><sup>−</sup>, is present.<sup>9</sup>

The dissociation constants of H<sub>2</sub>C<sub>2</sub>O<sub>4</sub> are  $K_1 = 5.6 \times 10^{-2}$  and  $K_2 = 5.4 \times 10^{-5}$  at 25 °C and ionic strength  $I = 0$ .<sup>13</sup>

The aim of the present work was to investigate behavior of the NaAsO<sub>2</sub>–oxalic acid system, in which As is trivalent. The inorganic forms of arsine are more toxic than its complex organic compounds, especially the trivalent form-arsenite. Arsenic compounds are present in the environment and in biological systems. For most humans, the greatest single exposure source is through food and water. Oxalic acid and oxalates are present in many plants and vegetables. Therefore, studies of reaction of arsenic compounds with oxalic acid can help in the understanding of the biogeochemistry, toxicity and metabolism of arsenic compounds.

## EXPERIMENTAL

### Apparatus

A Jenko pH-meter 6071, calibrated with Sigma buffers of pH 7.00 and pH 4.00, was used for the pH measurements. The conductivity was measured using a Hanna Instruments conductometer. The solutions were thermostated using a Sutjeska thermostat with temperature regulation ±0.1 °C.

### Reagents and solutions

The oxalic acid (H<sub>2</sub>C<sub>2</sub>O<sub>4</sub>·2H<sub>2</sub>O, Lafoma) solutions (0.20 mol dm<sup>−3</sup>) were standardized by potentiometric titration with NaOH. The concentrations of the NaAsO<sub>2</sub> (Merck) solution (0.040 mol dm<sup>−3</sup>) were determined gravimetrically. The NaCl solutions (2.5 mol dm<sup>−3</sup>) were prepared by dissolving the required amount of dry NaCl (Merck). All reagents were of p.a. quality. The deionized water was used for preparation of the solutions.

For the determination of the composition of the complex using the Job method and by pH metric and conductometric measurements, solutions of NaAsO<sub>2</sub> and H<sub>2</sub>C<sub>2</sub>O<sub>4</sub> of initial concentration 0.020 mol dm<sup>−3</sup> were prepared.

NaCl solutions of initial concentrations 2.5, 0.50 and 0.10 mol dm<sup>−3</sup> were employed for maintaining the ionic strength of the solutions constant during the pH measurement.

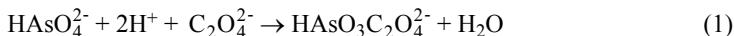
For the pH-metric and conductometric titrations, H<sub>2</sub>C<sub>2</sub>O<sub>4</sub> and NaAsO<sub>2</sub> solutions of initial concentration 0.20 and 0.020 mol dm<sup>−3</sup>, respectively, were used.

### Measurements

For the conductometric and pH-metric titrations, a series of experimental solutions in volumetric flasks were made. Each of the solutions contained an aliquot of 0.20 mol dm<sup>-3</sup> H<sub>2</sub>C<sub>2</sub>O<sub>4</sub> and 25 cm<sup>3</sup> of 0.020 mol dm<sup>-3</sup> NaAsO<sub>2</sub>. Deionized water was added to obtain a total volume of 50 cm<sup>3</sup>.

The compositions of the complex formed from oxalic acid and NaAsO<sub>2</sub> was determined by the Job method<sup>15</sup> using the pH-metric and conductometric measurements described in previous papers.<sup>4,6,7</sup>

The base of these methods is the reaction of complex formation in which H of the ligand is a direct component of the reaction, as in the case of the oxalate complex with Na<sub>2</sub>HASO<sub>4</sub>, *i.e.*, with HAsO<sub>4</sub><sup>2-</sup>:



which was cited in previously papers.<sup>1,2,4-7</sup> In this reaction, the change of the H<sup>+</sup> concentration, *i.e.*, pH, is a measure of the amount of formed complex. Also, a change of the solution conductivity is caused by a concentration change of the very mobile H<sup>+</sup>, as well as of other ions, *i.e.*, the conductivity change is also a measure of the amount of complex formed.<sup>4,6,7</sup> Since in the reaction solution all the present H<sup>+</sup> exert an influence on the pH and on the conductivity, together with all the other ions present, the change of pH and of conductivity during Reaction (1) can be calculated using measurements of pH and conductivity of the following three solution systems:

- a)  $x \text{ cm}^3$  of the initial H<sub>2</sub>C<sub>2</sub>O<sub>4</sub> solution and  $(50 - x) \text{ cm}^3$  of the initial NaAsO<sub>2</sub> solution,
- b)  $x \text{ cm}^3$  of the initial H<sub>2</sub>C<sub>2</sub>O<sub>4</sub> solution and  $(50 - x) \text{ cm}^3$  of water and
- c)  $(50 - x) \text{ cm}^3$  of the initial NaAsO<sub>2</sub> solution and  $x \text{ cm}^3$  of water.

In the series of solutions a, b and c,  $x$  was varied from 5 to 45 cm<sup>3</sup>. In order to calculate the relative stability constant of the complex, the experiments were performed at different ionic strengths. Measuring the pH values of the solutions for ionic strengths of 0.10, 0.20 and 0.50 mol dm<sup>-3</sup>, Job curves were constructed. The initial solutions of NaAsO<sub>2</sub> and H<sub>2</sub>C<sub>2</sub>O<sub>4</sub> were  $4.0 \times 10^{-2}$  mol dm<sup>-3</sup> and that of NaCl 0.50, 1.0 and 2.5 mol dm<sup>-3</sup>, for the preparation of solutions with ionic strengths 0.10, 0.20 and 0.50 mol dm<sup>-3</sup>, respectively. Three series of solution systems were made:

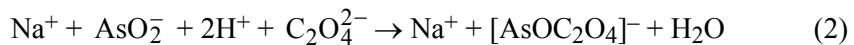
- d)  $x \text{ cm}^3$  H<sub>2</sub>C<sub>2</sub>O<sub>4</sub>, 10 cm<sup>3</sup> NaCl and  $(25 - x) \text{ cm}^3$  NaAsO<sub>2</sub>,
- e)  $x \text{ cm}^3$  H<sub>2</sub>C<sub>2</sub>O<sub>4</sub>, 10 cm<sup>3</sup> NaCl and  $(25 - x) \text{ cm}^3$  water and
- f)  $(x + 15) \text{ cm}^3$  water, 10 cm<sup>3</sup> NaCl and  $(25 - x) \text{ cm}^3$  NaAsO<sub>2</sub>.

In these solutions,  $x$  was varied from 2.5 to 22.5 cm<sup>3</sup> and deionized water was added to a final volume of 50 cm<sup>3</sup>.

The pH and conductivity were measured after thermostating the solutions for 24 h at 25 °C. Also the pH values were measured for solutions with  $I = 0.10$  mol dm<sup>-3</sup>, at 20 and 30 °C, to determine the thermodynamic parameters of complex formation.

### RESULTS AND DISCUSSION

The results given in Table I show that the solutions of the mixtures of NaAsO<sub>2</sub> and H<sub>2</sub>C<sub>2</sub>O<sub>4</sub> (a) have higher pH values than the corresponding H<sub>2</sub>C<sub>2</sub>O<sub>4</sub> solutions (b), analogous to reactions with other complexing agents, as well as oxalate, as explained in previous papers<sup>4,6,7</sup> and Reaction (1). The decrease in the H<sup>+</sup> concentration can be ascribed to the following reaction:



A reaction occurs between  $\text{C}_2\text{O}_4^{2-}$ ,  $\text{AsO}_2^-$  and  $\text{H}^+$ . This reaction can develop as a third-order reaction, but it is more probable that it develops as two second-order reactions.

TABLE I. pH and conductivity ( $\chi$ ) values of the solution mixtures:  $\text{NaAsO}_2$  and  $\text{H}_2\text{C}_2\text{O}_4$  (a),  $\text{H}_2\text{C}_2\text{O}_4$  and  $\text{H}_2\text{O}$  (b) and  $\text{NaAsO}_2$  and  $\text{H}_2\text{O}$  (c). Concentrations of the stock solutions:  $c(\text{H}_2\text{C}_2\text{O}_4) = c([\text{NaAsO}_2]) = 2 \times 10^{-2} \text{ mol dm}^{-3}$ . Total volume:  $50 \text{ cm}^3$ ;  $t = 25.0 \pm 0.1^\circ\text{C}$

$V / \text{cm}^3*$	Solution					
	a		b		c	
	pH	$\chi / \text{mS cm}^{-1}$	pH	$\chi / \text{mS cm}^{-1}$	pH	$\chi / \text{mS cm}^{-1}$
5	9.51	1.31	2.80	0.69	10.35	1.29
10	9.01	1.27	2.59	1.30	10.26	1.14
15	8.12	1.20	2.38	1.95	10.20	0.97
20	4.12	1.07	2.29	2.51	10.17	0.80
25	3.15	1.05	2.20	3.09	10.10	0.71
30	2.71	1.74	2.14	3.61	10.02	0.58
35	2.49	2.58	2.09	4.11	9.91	0.40
40	2.37	3.45	2.04	4.62	9.86	0.30
45	2.29	3.97	1.99	5.28	9.69	0.15

\*Volume of the oxalic acid solution for mixtures a and b, and volume of deionized water for mixture c

The decrease in the  $\text{H}^+$  concentration is proportional, according to Eq. (2), to the quantity of the formed complex and was calculated using the equation:

$$\Delta c(\text{H}^+) = c_a(\text{H}^+) - (c_b(\text{H}^+) + c_c(\text{H}^+)) \quad (3)$$

where  $c_a(\text{H}^+)$ ,  $c_b(\text{H}^+)$  and  $c_c(\text{H}^+)$  are the  $\text{H}^+$  concentrations in solutions a, b and c, respectively.

The change in conductivity,  $\Delta\chi$ , due to the formed  $\text{H}_2\text{O}$  was calculated according to the equation:

$$\Delta\chi = \chi_a - (\chi_b + \chi_c) \quad (4)$$

where  $\chi_a$ ,  $\chi_b$  and  $\chi_c$  are the conductivity of solutions a, b and c, respectively.

The dependencies of  $\Delta c(\text{H}^+)$  and  $\Delta\chi$  on the mole fraction of  $\text{H}_2\text{C}_2\text{O}_4$  ( $x$ ) are shown in Figs. 1 and 2, respectively. The Job curves have a maximum at  $x = 0.5$ , which indicates the formation of a complex in which the  $\text{C}_2\text{O}_4^{2-}:\text{AsO}_2^-$  ratio is 1:1. This result is in agreement with Eq. (2). The results obtained for complexes with monobasic acids (HAc) and  $\text{NaAsO}_2$  in the literature,<sup>7</sup> indicate the formation of complexes in which molar ratio  $\text{NaAsO}_2:\text{HAc}$  is 1:2. In the case that only the neutralization reaction occurs:



the molar ratio for monobasic acids,  $\text{NaAsO}_2:\text{HAc}$ , must be 1:1 and for dibasic acid, such as oxalic,  $\text{NaAsO}_2:\text{H}_2\text{C}_2\text{O}_4$ , 1:0.5.

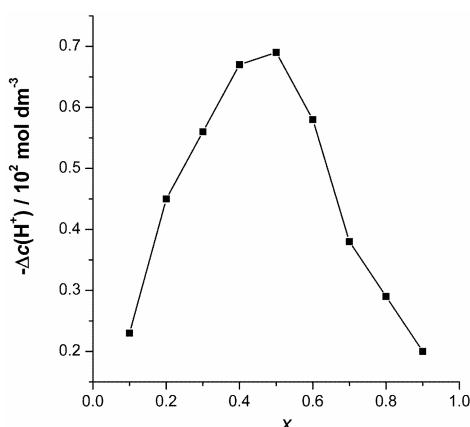


Fig. 1. Job curve obtained by pH-metric measurements.

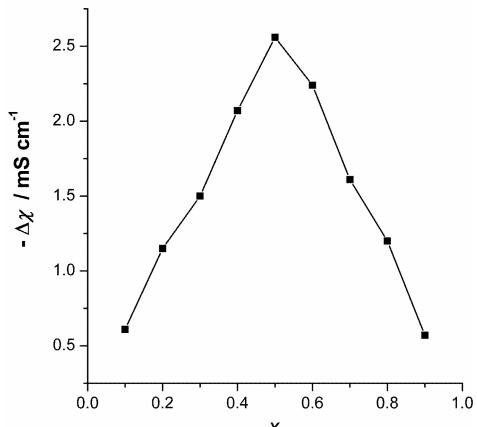
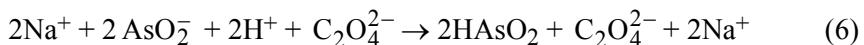


Fig. 2. Job curve obtained by conductometric measurements.

The results of the conductometric titration (Fig. 3) are in agreement with those obtained using the Job curve. An expressed equivalence point at the molar ratio C<sub>2</sub>O<sub>4</sub><sup>2-</sup>:NaAsO<sub>2</sub> of 1:1 was obtained, indicating the formation of the AsO-C<sub>2</sub>O<sub>4</sub><sup>-</sup> complex.

Second, not expressive, equivalent point which can be observed on the conductometric titration curve (Fig. 3) corresponds to the NaAsO<sub>2</sub>:H<sub>2</sub>C<sub>2</sub>O<sub>4</sub> = 2:1 molar ratio. The 2:1 molar ratio corresponds to an existence an acid-base reaction:



i.e., the neutralization reaction; it is dominant in excess NaAsO<sub>2</sub> but negligible in excess H<sub>2</sub>C<sub>2</sub>O<sub>4</sub>, due to complex formation.

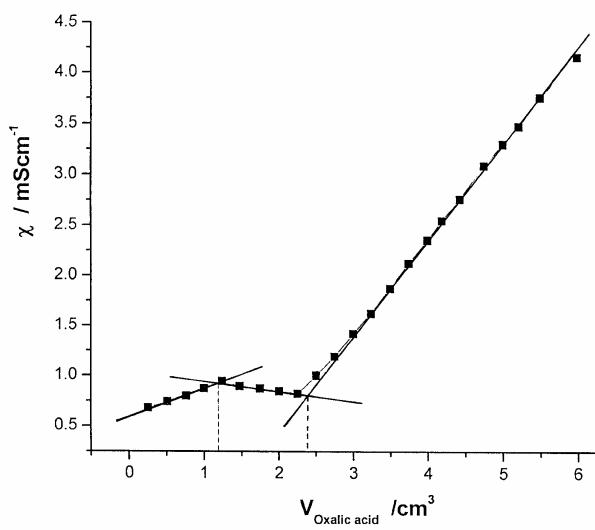


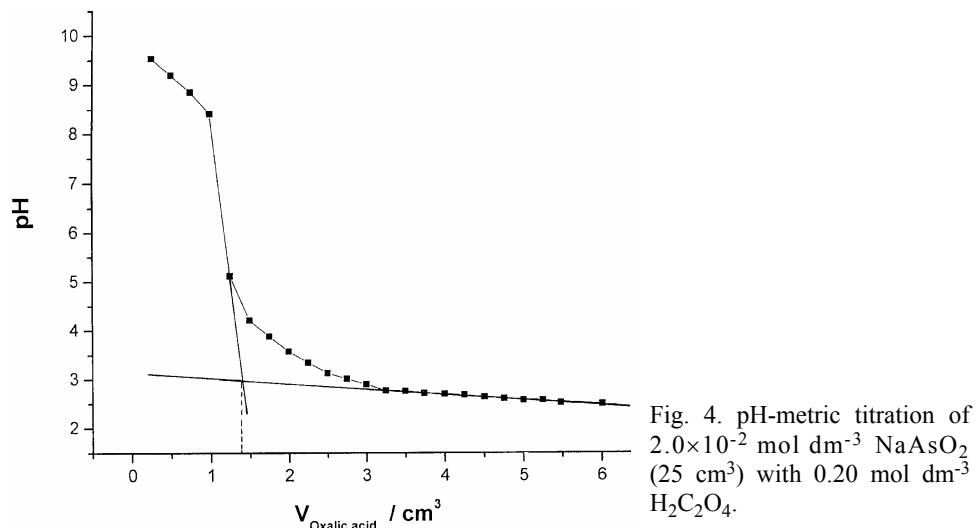
Fig. 3. Conductometric titration of  $2.0 \times 10^{-2} \text{ mol dm}^{-3}$  NaAsO<sub>2</sub> ( $25 \text{ cm}^3$ ) with  $2.0 \times 10^{-1} \text{ mol dm}^{-3}$  H<sub>2</sub>C<sub>2</sub>O<sub>4</sub>.

The conductometric titration curve which shows a slight increase in the conductivity of the solution up to the first equivalence point ( $V_{\text{oxalic acid}} = 1.25 \text{ cm}^3$ ), corresponding to the formation of the weakly dissociated arsenite acid, indicates the occurrence of this reaction. Since the  $\text{NaAsO}_2$  salt was used, it is more likely that Reaction (6) occurs with  $\text{HAsO}_2$ .

The decrease in conductivity until the second equivalence point is a consequence of the formation of the  $[\text{AsOC}_2\text{O}_4]^-$  complex, because the number of ions before and after the addition of oxalic acid remains practically the same, while the mobility of  $[\text{AsOC}_2\text{O}_4]^-$  is smaller than that of  $\text{AsO}_2^-$ . After the second equivalence point, the conductivity of the solution increases because of the surplus  $\text{H}_2\text{C}_2\text{O}_4$ . If only the acid–base reaction had occurred, the conductivity of the solution would have started to increase immediately after the first equivalence point. The reaction of complex formation (Eq. (2)) is independent of the form of the arsenite acid.<sup>9,10</sup>

On the basis of the above discussion, it can be concluded that arsenite acid is formed when there is more  $\text{NaAsO}_2$  than  $\text{H}_2\text{C}_2\text{O}_4$ , whereas a complex formation reaction occurs with increasing acid/arsenite ratio.

A pH-metric titration curve of a solution of  $\text{NaAsO}_2$  with a solution of  $\text{H}_2\text{C}_2\text{O}_4$  is shown in Fig. 4. The equivalence point on the curve occurs when the ratio  $\text{NaAsO}_2:\text{H}_2\text{C}_2\text{O}_4$  is 2:1, which indicates the formation of arsenite acid. This means that, in addition to the complex formation reaction, a neutralization reaction also occurs. This reaction was also evidenced by the results of the conductometric titration.



The absence of a second equivalence point, corresponding to complex formation, indicate that the second dissociation constant of  $\text{H}_2\text{C}_2\text{O}_4$ ,  $k_2$ , and the equilibrium constant,  $K_e$ , of the complex reaction have similar values, resulting

in a relatively long slope of the titration curve after the well-formed first equivalence point (Fig. 4).

Using the calculation method from previous papers<sup>7,14,16-18</sup> and the data obtained by pH measurements in solutions with a molar ratio H<sub>2</sub>C<sub>2</sub>O<sub>4</sub>:NaAsO<sub>2</sub> ≥ 1 (pH ≤ 2.9), the relative stability constant of the complex was calculated using Eqs. (7)–(12) for different values of the ionic strength, regulated by the corresponding addition of a NaCl solution.

The equilibrium constant of the Reaction (2) is:

$$K_e = \frac{c(\text{AsOC}_2\text{O}_4^-)c(\text{H}_2\text{O})}{c(\text{AsO}_2^-)c(\text{C}_2\text{O}_4^{2-})c(\text{H}^+)^2} = K_r \frac{c(\text{H}_2\text{O})}{c(\text{H}^+)^2} \quad (7)$$

where  $K_r$  is the relative stability constant of the 1:1 complex ([AsOC<sub>2</sub>O<sub>4</sub>]<sup>-</sup>).

The relative stability constant was calculated according to the equations for the total metal, ligand and H<sup>+</sup> concentrations and for the dissociation constants of the ligand:

$$c_0(\text{H}_2\text{C}_2\text{O}_4) = c(\text{H}_2\text{C}_2\text{O}_4) + c(\text{HC}_2\text{O}_4^-) + c(\text{C}_2\text{O}_4^{2-}) + c(\text{AsOC}_2\text{O}_4^-) \quad (8)$$

$$c(\text{H}^+) = c(\text{HC}_2\text{O}_4^-) + 2c(\text{C}_2\text{O}_4^{2-}) \quad (9)$$

$$c_0(\text{AsO}_2^-) = c(\text{AsO}_2^-) + c(\text{AsOC}_2\text{O}_4^-) \quad (10)$$

$$k_1 = \frac{c(\text{HC}_2\text{O}_4^-)c(\text{H}^+)}{c(\text{H}_2\text{C}_2\text{O}_4)} \quad (11)$$

$$k_2 = \frac{c(\text{C}_2\text{O}_4^{2-})c(\text{H}^+)}{c(\text{HC}_2\text{O}_4^-)} \quad (12)$$

The total stoichiometric concentrations are marked by the subscript “0”.

The dissociation of HAsO<sub>2</sub> was neglected since the reaction of complex formation occurs between the arsenite oxygen and the oxalate ion, according to Eq. (2).

The equilibrium constant,  $K_e$ , according Eq. (7), depends of the H<sup>+</sup> concentration and can be calculated for the corresponding pH value.

The H<sup>+</sup> activity factor was calculated using the equation:

$$-\log f_{z_\pm} = 0.509z^2 \left( \frac{\sqrt{I}}{1+\sqrt{I}} - 0.2I \right) \quad (13)$$

for the employed ionic strength,  $I$ .

The H<sup>+</sup> concentration was calculated from the pH and the H<sup>+</sup> activity factor and used for the calculation of the concentration of the corresponding ions and of the complex relative stability constant for three ionic strengths. On the basis of the average values of  $K_r$ , acquired from 5 repeated measurements at the given ionic strength of the solutions, on the temperature 25±0.1 °C, the relative stability

constant of the complex at  $I = 0$ ,  $K_{r,0}$ , was graphically determined using the equation:

$$\log K_r = \log K_{r,0} - S\sqrt{I_c} \quad (15)$$

The obtained results are given in Table II ( $\log K_{r,0} = 5.05$ ).

TABLE II. The average values of relative stability constants of the  $[\text{AsOC}_2\text{O}_4]^-$  complex for different values of the ionic strength,  $I$ ;  $t = 25 \pm 0.1^\circ\text{C}$ ;  $\text{pH} \leq 2.9$ ;  $SD$ : standard deviation

$I$	$(\bar{K}_r \pm SD) \times 10^4$	$\log \bar{K}_r$
0.10	$4.99 \pm 0.08$	4.70
0.20	$3.22 \pm 0.07$	4.51
0.50	$1.74 \pm 0.04$	4.24

In order to determine the thermodynamic parameters of the complex, measurements of the pH of the solutions in which the  $\text{NaAsO}_2:\text{H}_2\text{C}_2\text{O}_4$  ratio was 1:1 were made to make complex formation dominant. The thermodynamic parameters of the complex were calculated from the values of relative stability constants at 293, 298, and 303 K as the average value of three measurements. At constant ionic strength of 0.10 these values are  $\Delta H = 10.5 \text{ kJ mol}^{-1}$ ,  $\Delta S = 133 \text{ J mol}^{-1} \text{ K}^{-1}$  and  $\Delta G = -29.0 \text{ kJ mol}^{-1}$  (298 K).

The obtained results are given in Table III and Fig. 5.

TABLE III. The average values of thermodynamic parameters for the complex reaction obtained from three measurements;  $c(\text{H}_2\text{C}_2\text{O}_4) = c(\text{NaAsO}_2) = 4.0 \times 10^{-2} \text{ mol dm}^{-3}$ ,  $I = 0.10$

$T / \text{K}$	$\Delta G / \text{kJ mol}^{-1}$	$\Delta H / \text{kJ mol}^{-1}$	$\Delta S / \text{J mol}^{-1} \text{ K}^{-1}$
293	-28.2	10.5	132
298	-29.0	10.5	133
303	-29.8	10.5	133

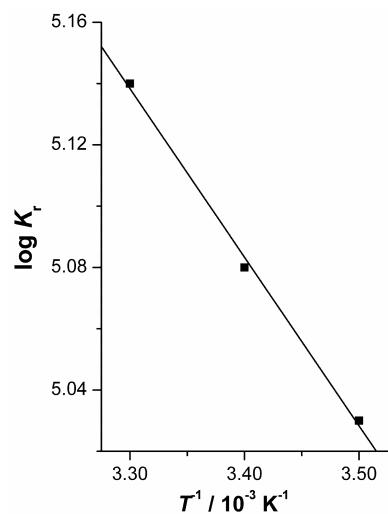


Fig. 5. Temperature dependence of the logarithm of the relative stability constant.

The obtained values for  $\log K_r$  can be compared to the corresponding values for oxalate complexes of W(VI) ( $\log K_r$  7.52 and 6.45 at pH 4.55 and 5.55, respectively),<sup>4</sup> Mo(VI) ( $\log K_r$  7.29 and 5.60 at pH 4.55 and pH 5.48, respectively)<sup>4</sup> and As(V) ( $\log K_r$  4.85 and 4.56 at pH 3.07 and 2.97, respectively).<sup>6</sup> Since there is no significant difference in the  $\log K_r$  values, it may be concluded that the interaction of the oxygen from the oxy anions and the H<sup>+</sup> ion from the acid has a greater influence on the reaction than the type of metal in the oxy anion.

## ИЗВОД

КОНДУКТОМЕТРИЈСКА И РН-МЕТРИЈСКА ИСПИТИВАЊА  
РЕАКЦИЈЕ ОКСАЛНЕ КИСЕЛИНЕ И NaAsO<sub>2</sub>

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Реакција NaAsO<sub>2</sub> са оксалном киселином испитана је мерењем pH и проводљивости, методом континуалне варијације и pH-метријским и кондуктометријским титрацијама. Најено је да оксална киселина гради комплекс [AsOC<sub>2</sub>O<sub>4</sub>]<sup>-</sup>. На основу pH-метријских мерења израчуната је релативна константа стабилности комплекса на 25±0,1 °C при јонским јачинама од 0,10 ( $\log K_r = 4,70$ ), 0,20 ( $\log K_r = 4,51$ ), 0,50 ( $\log K_r = 4,24$ ) и 0 ( $\log K_{r,0} = 5,05$ ), као и термодинамички параметри реакције комплексирања на 25±0,1 °C ( $\Delta H = 10,5 \text{ kJ mol}^{-1}$ ,  $\Delta G = -29,0 \text{ kJ mol}^{-1}$ ,  $\Delta S = 133 \text{ J mol}^{-1} \text{ K}^{-1}$ ).

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