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SHORT COMMUNICATIONS

Influence of Pressure in the 0.1–100 MPa Interval on the First Dissociation Constant of Arsenous Acid in Water Solutions at 298.15 K

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Abstract—The influence of pressure on the dissociation of arsenous acid H_3AsO_3 was studied at 298.15 K by the potentiometric method. In the pressure interval from 0.1 to 100 MPa the values of $\log K_1^\circ = -9.32 + 0.00246P$. The change in the molar volume of the reaction of the dissociation of H_3AsO_3 from the first step ($\Delta V_1^\circ = -15.4 \pm 1$ cm^3/mol) and the partial molar volume of its dissociation product, $H_2AsO_3^-$ ($V^\circ = 32.1 \pm 1$ cm^3/mol) were determined.

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INTRODUCTION

Arsenic is widespread in both the Earth's crust and biosphere. It is involved in many geo- and biochemical processes. Reliable thermodynamic characteristics of arsenous acid, one of the basic forms of arsenic in solutions, are needed to quantitatively describe the chemistry of water solutions of arsenic over a wide range of physical and chemical parameters. The absence of data on the influence of pressure on the dissociation of arsenous acid (H_3AsO_3) is one of the gaps in our information on the subject. Our study was aimed at eliminating this shortcoming.

The dissociation of arsenous acids occurs according to the reaction

$$H_3AsO_3^0(\mathrm{sol}) = H_2AsO_3^- + H^+, \qquad (1)$$

$$K_1^\circ = \frac{[H_2AsO_3^-][H^+]}{[H_3AsO_3^0]} \frac{\gamma_{H_2AsO_3^-}}{\gamma_{H_3AsO_3^0}\gamma_{H^+}}, \qquad (2)$$

where γ are the activity coefficients.

Our study was concerned with measuring pH of H_3AsO_3 + NaOH solutions of known concentration (mol/kg H_2O) at different pressures (up to 100 MPa) and subsequently calculating the thermodynamic constants of Eq. (1).

EXPERIMENTAL

The initial solution of arsenous acids (~0.1 mol As/kg H_2O) was prepared by dissolution of a weighed amount of As_2O_3 (reactant) at 358.15 K for five weeks in distilled water degassed by boiling. Three working solutions with contents of ~0.015, 0.02, and 0.03 mol As/kg H_2O were prepared by adding an exact quantity of the initial solution of H_3AsO_3 and a titrated NaOH solution to the degassed water. The concentration of the NaOH solution was specified by titration with standard HCl solution, the normality of which was in turn established by using tris(hydroxymethyl)aminomethane (Merck, Germany) in the presence of methyl red indicator. The final concentration of NaOH in the working solutions was 0.010 mol/kg H_2O. The exact content of arsenic in the solutions was established by titration (iodometry). The preparation of all solutions was, along with the titration, performed in an inert argon atmosphere so as to completely exclude the possibility of contact with air and thus prevent oxidation of As(III) to As(V) and pollution with carbon dioxide.

Potentiometric measurements were performed at 298.15 K and pressures from 0.1 to 100 MPa in a cell made of VT-8 titanium alloy, the design of which is described in detail in [1]. The temperature was kept constant within the limits of ±0.2 K. The pressure was set up by means of a manual hydraulic press and measured with a tensometric D100 gauge and a OBMGb 1-160 manometer calibrated on a load-piston MT-2500 manometer. The error in the pressure measurement in the range 20 to 100 MPa was ±1 MPa. The electromotive force (EMF), pressure and temperature were recorded by means of a multichannel measuring device with a resolution of 0.1 mV, connected to a computer. The pH values were measured in an isothermal cell with a liquid junction consisting of a measuring glass electrode and a silver chloride reference electrode of original design [1] (such electrodes can work for long periods of time independent of pressure):

$$\underset{\text{Measuring electrode}}{\underleftrightarrow{\text{Ag, AgCl}|0.1m\ \text{HCl}|\text{pH membrane}}}|\text{solution under study}||3m\ \underset{\text{Reference electrode}}{\underleftrightarrow{\text{KCl}|\text{AgCl, Ag}}}$$

It should be noted that the glass electrodes were unloaded with respect to pressure, i.e., the pressure inside and outside the H^+-sensitive membrane was the same. Two measuring glass electrodes and two reference electrodes were used simultaneously.

The electrode system was calibrated at 298.15 K and pressures of 0.1, 20, 50, 70, and 100 MPa on two buffer solutions: an acetic–acetate solution ($0.25m$ CH_3COOH + $0.25m$ CH_3COONa) with $pH_{0.1\ MPa}$ 4.69, and a borate solution with $pH_{0.1\ MPa}$ 9.18 before each experiment. The pH values at the elevated pressures for the acetate and borate buffers were taken from [1] and [2], respectively, and are given in Table 1. Calibration showed that the standard electrode potential of the cell and the slope of the straight line in the E–pH coordinates was –58.69 mV/units pH and was independent of the pressure over the studied range.

RESULTS AND DISCUSSION

Table 2 shows the results of pH measurements in H_3AsO_3 solutions at pressures of 0.1 to 100 MPa. To increase the accuracy of our calculations when determining the pressure dependence of balance constant Eq. (1), we used not the pH values themselves but their changes (ΔpH) upon a pressure increase, as compared to the pH values at 0.1 MPa ($pH_{0.1}$). We should note that in such an approach, the importance of the diffusion potential is eliminated due to a slight change in the solution composition and the mobility of ions with an increase in pressure. The $pH_{0.1}$ values were calculated on the basis of the value $\log K_1^\circ = -9.32$ [3]. The $pH_{0.1}$ values we measured differ from the calculated values by less than 0.01, except for one solution (0.03 units pH). The error in determining $\Delta pH = pH_P - pH_{0.1}$ is within the limits of 0.003–0.007. Using the OptimA computer program [4], we then minimized the difference between the experimental and calculated $\Delta_f G_P^\circ$ values of the $H_2AsO_3^-$ ion at three pressure values (50, 70, and 100 MPa). The properties of all other particles in the As–Na–O–H system under study, except for $H_2AsO_3^-$, were taken from the Slop98 base of thermodynamic data [5]. The error in determining $\Delta_f G_P^\circ(H_2AsO_3^-)$ at a confidence level of 95% is ±0.065 kJ/mol at the accepted error of determining pH (0.01 units). The values $\log K_1^\circ = -(\Delta_f G_P^\circ(H_2AsO_3^-) - \Delta_f G_P^\circ(H_3AsO_3(sol)))/2.303RT$ are given in Table 2. The error $\log K_1^\circ$ at elevated pressure is determined mainly by the error in the accepted $\log K_1^\circ$ value at a pressure of 1 bar.

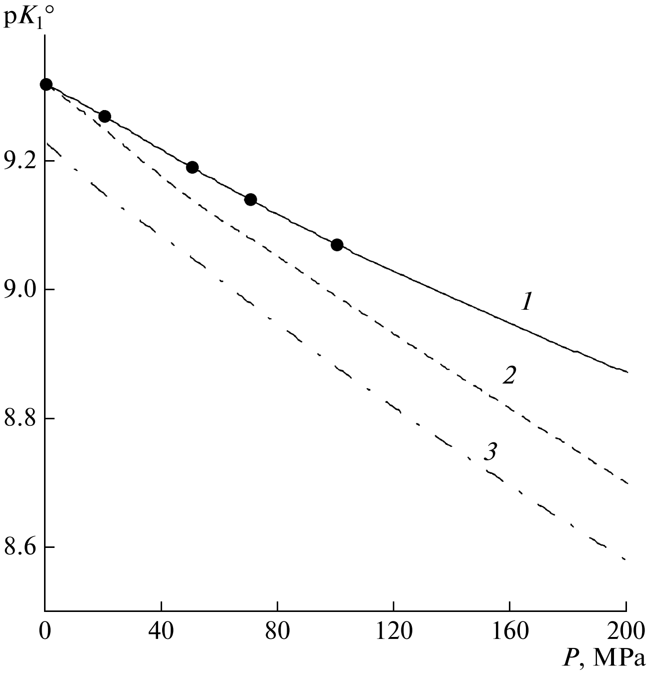
Table 1. pH values of buffer solutions $0.025m$HAc + $0.025m$ NaAc (A)a $0.01m Na_2B_4O_7$ (B) used to calibrate the potentiometric cell (298.15 K)

P, MPa	A [1]	B [2]
0.1	4.69	9.18
50	4.59	8.91
70	4.56	8.81
100	4.51	8.65

Table 2. Results from pH measurements of solutions $0.010m$ NaOH $- xm$ As $(OH)_3$ at 298.15 K and pressures of 0.1 to 100 MPa, along with the values of $\log K_1^\circ$

P, MPa	ΔE, mV	$-\Delta pH^{exp}$	pH	$-\log K_1^\circ$
		$x = 0.031$		
0.1			8.950	9.32
50	7.2 ± 0.2	0.123 ± 0.003	8.827	9.19
70	10.0 ± 0.2	0.170 ± 0.003	8.780	9.15
100	14.0 ± 0.3	0.238 ± 0.005	8.712	9.08
		$x = 0.021$		
0.1			9.243	9.32
50	7.4 ± 0.3	0.126 ± 0.005	9.117	9.19
70	10.1 ± 0.3	0.172 ± 0.005	9.071	9.15
100	14.5 ± 0.4	0.247 ± 0.007	8.996	9.07
		$x = 0.016$		
0.1			9.526	9.32
50	7.5 ± 0.2	0.128 ± 0.003	9.398	9.19
70	10.3 ± 0.3	0.175 ± 0.005	9.351	9.14
100	14.6 ± 0.3	0.249 ± 0.005	9.277	9.07

Note: $\Delta E = E_P - E_{0.1}$, change in EMF, observed upon a 0.1 MPa to P increase in pressure; change in ΔpH^{exp} as calculated from experimental values of ΔE; the calculated values for $pH = pH_{0.1}^{calc} + \Delta pH^{exp}$ are given; $\log K_1^\circ$ values at P = 0.1 MPa, as calculated according to [3].



Pressure dependences of pK_1° of the dissociation reactions of arsenous acid on the first step from pressure at 298.15 K. Dots show our experimental data; lines (*1*) the extrapolation of our experimental data according to the HKF model [6], (*2*) our calculations according to [3], and (*3*) our calculations according to [5].

Arsenous acid dissociates more strongly upon an increase in pressure:

$$\log K_1^\circ = -9.32 + 0.00246P \quad (P = 0.1\text{–}100 \text{ MPa}), \quad (3)$$

corresponding to the reduction of the molar volume of Eq. (1) with pressure; $\Delta V_1^\circ = -15.4 \pm 1$ cm^3/mol. The figure shows the values $pK_1^\circ = -\log K_1^\circ$ at pressures up to 200 MPa, determined from our experimental data. The analogous dependences calculated according to refs. [3] and [5] are shown for comparison. The molar volume $V^\circ(H_2AsO_3^-) = 32.1 \pm 1$ cm^3/mol was calculated on the basis of the obtained ΔV_1° value and V° (H_3AsO_3(sol)) = 47.5 ± 1 cm^3/mol [7].

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