Experimental study of the thermophysical properties of boric acid solutions at the parameters typical of the WWER emergency mode

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Abstract. The results of experimental studies of the thermophysical properties (density and kinematic viscosity) of boric acid solutions in the concentration range of 2.5-400 g/kg H₂O at a temperature of 289-403 K is considered in the paper. The problem of boric acid accumulation and crystallization in case of the accidents with main coolant circuit rupture and operation of passive safety systems (the hydroaccumulators systems of the first, second and third stages, as well as the passive heat removal system) is formulated. The review of the available literature data about thermal physical properties of the boric acid solutions is presented. The fact that available data are of a general nature and do not cover the entire parameters range specific for the possible accidents at NPP with WWER is established. The methods of experimental research are described. Two stages of experimental studies of boric acid solutions density are presented: measurements at atmospheric pressure and at parameters typical of NPPs with WWER emergency modes. A description of the test facility used to the density measurements of highly concentrated boric acid solutions is presented. Experimental values of the kinematic viscosity of boric acid solutions in the concentration range of 2.5-200 g/kg H₂O at a temperature of 289-363 K are obtained by capillary viscosimetry method. The approximating dependences for the density and kinematic viscosity experimental values of the boric acid aqueous solutions are obtained.

1. Introduction

The use of boron compounds in nuclear power engineering is caused by the isotopic composition of boron, its nuclear-physical and radiation characteristics. It is known that at present the Boron-10 isotope is the most demanded in nuclear power, with most of this isotope being used in the form of boric acid [1]. For NPPs with WWER and PWR reactors, one of the main applications of boric acid solutions is associated with boron control systems designed to smoothly adjust the reactor power during the campaign. In addition, boric acid solutions are used in passive safety systems to cool the reactor core in loss of coolant accidents (LOCA).

As it known, in the NPP project "AES-2006" with WWER-1200 reactor unit in the event of LOCAs, the passive safety systems operation provides at least 24 hours cooling of the reactor core by feeding a solution of boric acid with a concentration of 16 g/kg from its hydro accumulators of the first (HA-1) and the second (HA-2) stages [2], as well as the condensate flow from the steam generators.
operating in the condensation mode [3-6]. According to the WWER-TOI project safety concept, cooling of the reactor core by supplying a boric solution to it must be carried out within 72 hours. To fulfill this task, it is planned to use the hydraulic accumulators of the third stage (HA-3). Taking into account the duration of the process, the boiling of the coolant and the low content of boric acid in the vapor phase, the possibility of crystallization of boric acid on the elements of the reactor is not eliminated. The limiting concentration of boric acid in a solution, corresponding to the start of crystallization, depends on the temperature. At the temperature corresponding to the beginning of the LOCA emergency process, the limiting concentration of H$_3$BO$_3$ is approximately 450 g/kg H$_2$O. An earlier analysis [7] has shown that this value will be reached after 43 hours of the emergency process.

To calculate the processes of accumulation and crystallization of boric acid, it is important to know its thermophysical properties [8-10]. There are some data on experimental studies of the thermophysical properties of aqueous solutions of boric acid in the literature.

Experimental data on the density of aqueous solutions of boric acid covering a wide range of temperatures (298-573 K) and pressures (10-50 MPa) are presented in [11]. However, in this paper H$_3$BO$_3$ solutions with concentrations of 3.1-44.4 g/kg were considered, which is significantly lower than the possible concentration of boric acid in the WWER reactor core in case of emergency.

In [12], the values of the density and viscosity of aqueous solutions of boric acid with concentrations of 2.52; 25 and 45 g/kg at atmospheric pressure and temperatures of 339 and 373 K were obtained. Data on the dynamic viscosity of boric acid solutions in the temperature range of 298 - 423 K and pressures of 1 - 30 MPa are given in [13]. The dependence of the viscosity of aqueous solutions of boric acid on temperature at a pressure of 1 MPa for concentrations of 2 and 20 g/kg was obtained. It should be noted that studies in [12, 13] were carried out with low concentrations of boric acid in the solutions in the interval of pressures exceeding the pressure in the event of an emergency process.

A number of papers are devoted to the thermophysical properties of buffered solutions of boric acid, where sodium phosphate or sodium hydroxide was used as alkalizing reagents [14, 15]. However, the parameters of the investigated coolants do not correspond to the water chemistry of Russian NPPs with WWER, addition studies were conducted at low concentrations of boric acid.

Thus, a review of literary sources has shown that the existing data on the density and viscosity of boric acid solutions are very general and do not cover the entire range of parameters (temperature, pressure, acid concentration) typical of an emergency at a WWER NPP. This led to the need for experimental studies of the density and viscosity of boric acid in the extended range of parameters.

2. The measurement technique of the density of boric acid aqueous solutions

Experimental studies of the density of aqueous solutions of boric acid can be divided into two stages: the measurement of this parameter at atmospheric pressure and at a pressure corresponding to the emergency mode of the NPP with WWER.

To prepare solutions with a given concentration, chemically pure boric acid and distilled water were used. The required amount of boric acid was weighed on the analytical scales with an accuracy of up to 0.005 g. To determine the exact concentration of the acid in the prepared solution, a standard analytical method of acid-base titration of boric acid solution with 0.1 M sodium hydroxide in the presence of glycerin was used. If the concentration necessary for the preparation exceeded the limiting value of acid solubility in water at a given temperature, the solution was heated in a water bath until the boric acid crystals dissolved completely.

Measurement of the density of solutions of boric acid with a concentration of 2.5 - 200 g/kg H$_2$O at a temperature of 298 - 363 K was carried out by a pycnometric method. The measurement of the density by a pycnometer is based on weighing the substance in it (usually in the liquid state) filling the pycnometer to the mark on the neck or to the upper edge of the capillary, which corresponds to the nominal capacity of the pycnometer. In the study, the glass pycnometers with a nominal volume of 10 ml were used. For greater accuracy, the density was determined in parallel in four pycnometers.
To study the effect of temperature on the density of the liquid, the experiment was repeated at several temperatures in the range of 298-336 K. The density of solutions of boric acid was determined by the formula:

$$\rho = \frac{m_2 - m_0}{m_1 - m_0} \cdot \rho(H_2O),$$

(1)

where $m_0$ is the mass of an empty pycnometer, $m_1$ is the mass of a pycnometer with water, $m_2$ is the mass of a pycnometer with the liquid being studied, $\rho(H_2O)$ is the density of water at a given temperature.

At the second stage of research, the density of boric acid was measured at the parameters corresponding to the emergency mode of the NPP with WWER. The pycnometric method was also used as the basis for the experiments.

The experimental facility to study the density of boric acid, with concentrations typical of the coolant of the WWER reactor facility in the event of an accident has been constructed. In Figure 1 the main and auxiliary equipment of the experimental facility and its layout are shown.

![Figure 1](image)

**Figure 1.** Principal scheme and main equipment of the test facility. 1 - mixing device, 2 – H$_3$BO$_3$ solution preparation tank, 3 - porthole, 4 – gas reducer, 5 - gas cylinder, 6 - density cells, H1-H2 - heater groups.

The structure of the facility includes: H$_3$BO$_3$ solution preparation tank and measuring cells. The main equipment of the facility is interconnected by a technological line and equipped with shut-off valves. The auxiliary equipment includes: pressure maintenance system, H$_3$BO$_3$ solution supply system and temperature maintenance system.

Instrumentation installed on the test facility allows the recording of pressure and temperature during the experiments. Pressure recording is performed using the METRAN-150 gauge (measurement error: up to ± 0.1% of the pressure range). To measure the temperature, cable K type thermocouples with a diameter of 1 mm (measurement error of 1 K) are used. The sampling frequency of measuring channels of the data acquisition system is equal to 4 Hz.

The tests were carried out in six series with different temperatures (343 - 403 K), in the pressure range of 0.1-0.4 MPa, typical of the WWER reactor facility in case of LOCA. The experiments were performed according to the following procedure.

At the beginning of the experiment, all the valves are closed. Then, valve V1 (Figure 1) opens and 60% of the required volume of distilled water comes through it into the solution preparation tank. After that the heating of the tank up to 328 K occurs. When the required temperature is reached, a predetermined mass of boric acid powder and the remaining part of the distilled water are supplied.
into the tank volume, after which the valve V1 is closed. The required mass of H$_3$BO$_3$ was measured with the CAPTOM BP2100 electronic scales with an error of 0.1 g. Next, the valve V2 opens. Through the gas reducer, the gas volume is filled with nitrogen in order to establish the necessary pressure to prevent the solution from boiling.

Then, the solution of boric acid starts warming up to the temperature set in the test program using a group of heaters H1. Temperature control is carried out according to the thermocouple readings. After reaching the required temperature in the solution preparation tank, a mixing device is turned on, which ensures complete dissolution of the boric acid. Control for the state of the solution is carried out visually, through the portholes on the body of the tank. The set temperature is maintained with an accuracy of ± 1 K throughout the entire experiment.

Simultaneously with the heating of the solution preparation tank, the density measuring cells are heated. With the help of electrical heaters of group H2, the cells are heated to a temperature exceeding the tank temperature by 3 K. Temperature control is carried out according to the thermocouple readings. The set temperatures are maintained with an accuracy of ± 1 K throughout the entire experiment using a relay controller.

Before start of tests, the measuring cells are dried in a drying oven to constant weight. The volume of cells is determined by the weight of the water that fills them according to the method described above. After preparing the boric acid solution in the tank and its thermo stating, the liquid is fed into the measuring cells with the open lower ball valves. After the constant temperature of the solution in the cells was established, the ball valve was closed. The filled cells were dried to constant weight. Weighing of the measuring cells was carried out on electronic scales with an accuracy of 0.01 g. For greater accuracy, the density was determined in parallel in six measuring cells. The density of solutions of boric acid was determined from formula (1).

3. The measurement technique of the kinematic viscosity of aqueous solutions of boric acid
To measure the kinematic viscosity of aqueous solutions of boric acid, the method of capillary viscometry was used. This method relies on Poiseuille law on a viscous fluid, which describes the laws of fluid motion in a capillary. To measure the viscosity of clear liquids, which include aqueous solutions of boric acid, the Ubbelohde type viscometers were used. For more correct results, two viscometers of this type were used. Before starting work, both viscometers were calibrated with distilled water to clarify their constants. Calibration consists in determining the time of flow through the viscometer of the reference liquid. Before the measurements, the viscometers were washed with acetone and dried.

The method of capillary viscometry is based on the measurement of the time of the flow of the liquid under study through a capillary. A viscometer with a known volume of boric acid solution was placed in a water thermostat with a predetermined temperature. The time of thermostating was 30 minutes. Then, the liquid level in the capillary was raised above the upper mark on the viscometer. After this, the level rise stops, and the level of liquid in the capillary begins to drop. The time it takes for the meniscus of the solution level to pass the distance between the upper and lower mark of the viscometer was measured by a stopwatch with an accuracy of 0.1 s.

The kinematic viscosity of aqueous solutions of boric acid was calculated from formula (2). The flow time of the test solutions is determined as the mean value obtained in not less than five measurements. The obtained data were considered acceptable, provided that the results of two consecutive measurements differ by not more than 1%.

\[
\nu = \left( \frac{g}{9.807} \right) \cdot \tau \cdot K,
\]

where \(\nu\) is the kinematic viscosity of the liquid, sq. mm/s; \(\tau\) is liquid flow time, s; \(K\) is the constant of the viscometer, sq. mm/sq. s; \(g\) is acceleration of gravity at the measurement site, m/sq. s.
4. Results of experimental measurements

As was mentioned above, experiments on H$_3$BO$_3$ solutions density measurement were carried out in two stages. At the first stage, the density of aqueous solutions of boric acid with concentration of 2.5-200 g/kg H$_2$O in a temperature range of 298-363 K was measured. At the second stage of research, the boric acid concentration in the solution was changed in the range of 50-450 g/kg H$_2$O at a temperature of 323-403 K. In Figure 2 graphs combining two stages of experimental studies are presented.

![Figure 2](image1.png)

**Figure 2.** Summary graph of the density of aqueous solutions of boric acid with concentration of 2.5-400 g/kg H$_2$O at a temperature of 298-403 K.

![Figure 3](image2.png)

**Figure 3.** Kinematic viscosity of aqueous solutions of boric acid with concentration of 2.5-200 g/kg H$_2$O at a temperature of 298-363 K.

As can be seen from the graph shown in Figure 2, the density values obtained in two stages are in good correlation. The total error of measurements carried out at atmospheric pressure does not exceed 0.7%. For measurements conducted at parameters typical of the emergency modes of NPPs with WWER, the total error is not more than 7%.

The experimental data obtained are described with high accuracy by the dependence:

$$\rho_{sol} = A + B \cdot C_{H_3BO_3}. \quad (3)$$

Coefficients have the form: $A = 1141 - 0.48 \cdot T_{sol}$; $B = 39217 \cdot T_{sol}^{-0.843}$,

where $T_{sol}$ is temperature of the solution, K; $C_{H_3BO_3}$ is concentration of boric acid in solution, kg/kg H$_2$O.

The approximating dependence (3) obtained gives a good description of the experimental data. The maximum mismatch of calculated and experimental data does not exceed 2%.

The results of an experimental study of the kinematic viscosity of aqueous solutions of boric acid with a concentration of 2.5-200 g/kg H$_2$O at a temperature of 298-336 K are presented in Figure 3.

The total error in measuring the viscosity of aqueous solutions of boric acid, carried out by the method of capillary viscometry, does not exceed 2%.

The obtained experimental data can be generalized in the form of the following dependence:

$$\nu_{sol}(T_{sol}, C_{H_3BO_3}) = \nu_{H_2O}(T_{sol}) + A \left( C_{H_3BO_3} \right)^B. \quad (4)$$

The coefficients have the following form:

$$\nu_{H_2O}(T_{sol}) = \frac{1.78 \cdot 10^{-6}}{1 + 3.37 \cdot 10^{-2} \cdot (T_{sol} - 273.15) + 2.21 \cdot 10^{-4} \cdot (T_{sol} - 273.15)^2};$$

$$A = 1.86 \cdot 10^{-7} + 1.08 \cdot 10^{-5} \cdot e^{-0.119(T_{sol} - 273.15)};$$

$$B = 1.224 - 2.83 \cdot 10^{-2} \cdot (T_{sol} - 273.15) + 2.19 \cdot 10^{-4} \cdot (T_{sol} - 273.15)^2;$$
where $\nu_{H_2O}(T_{\text{sol}})$ is the viscosity of distilled water at the appropriate solution temperature; $T_{\text{sol}}$ is temperature of the solution, K; $C_{H_3BO_3}$ is concentration of boric acid in solution, kg/kg H$_2$O.

The approximating dependence obtained satisfactorily describes the experimental data. The maximum discrepancy between the calculated and experimental data does not exceed 5.5%.

5. Conclusion
As a result of the experimental studies, experimental data on the thermophysical properties (density and kinematic viscosity) of highly concentrated boric acid solutions were obtained for the first time at the parameters typical of the emergency modes of NPPs with WWER. The results obtained make it possible to expand significantly the range of known thermophysical parameters of boric acid solutions. The obtained experimental data on the density and kinematic viscosity of aqueous solutions of boric acid are of great practical importance for NPPs with a new generation of WWER reactors equipped with passive safety systems, since they can be used to verify calculation codes used to simulate emergency processes in a reactor facility.

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