Experimental study of the surface tension of highly concentrated boric acid solutions applicable to VVER emergency cooling

A S Sakhipgareev, A S Shlepkin and A V Morozov

State Scientific Centre of the Russian Federation – Leypunsky Institute for Physics and Power Engineering, Joint-Stock Company

E-mail: sas@ippe.ru

Abstract. The results of the experimental studies of the surface tension of aqueous solutions of boric acid in a range of concentrations of 2.5-150 g kg\(^{-1}\)H\(_2\)O are presented in the paper. As a result of a literature review, it was found that the present information about surface tension of boric acid solutions is contradictory and does not cover the entire range of parameters characteristic of a possible emergency at nuclear power plants (NPPs) with the VVER reactor. The technique of the experimental research is described. The results of the measurements of the surface tension of aqueous solutions of boric acid are presented. The existence of the temperature dependence is confirmed. The effect of concentration on the surface tension of aqueous solutions of boric acid in the studied range of parameters is shown.

1. Introduction

At present, the research of the processes of boric acid mass transfer in the core of modern NPPs with the VVER reactor is of particular relevance. It is due to the safety requirements for new-generation nuclear power plants. In case of a loss-of-coolant accident (LOCA), it is planned to cool the reactor by the long-term (up to 72 hours) operation of passive safety systems, such as the passive core flooding system and the passive heat removal system from the steam generator (SG) [1-2].

Crystallization of boric acid in the core is possible considering the following reasons: the duration of emergency cooling, supplying of condensate from the SG operating in the condensation mode [3], boiling of the coolant and a low content of boric acid in the steam phase. It is known that the solubility limit of H\(_3\)BO\(_3\), at which its precipitation begins, depends on temperature [4]. In the case of LOCA, the pressure in the primary circuit will be in the range of 0.2-0.5 MPa [5], while the maximum concentration of boric acid in the core will exceed several hundred grams per kilogram of solution [6].

It is necessary to know the thermophysical properties (such as density, viscosity, and surface tension) of the boric acid that affect the processes of its accumulation and crystallization in the core to carry out computational modeling of processes in an emergency at NPPs with VVER. To date, experimental data on the density and kinematic viscosity of boric acid solutions in a wide range of parameters have been obtained at IPPE JSC [7-8]. Surface tension \(\sigma\) also has a significant effect on the boiling heat-transfer rate. The decrease in the surface tension contributes to the formation of a larger number of steam bubbles, since less energy is consumed for their appearance. According to the authors of [9], the presence of boric acid in the coolant improves heat transfer when it is boiling in the core as compared to pure water.
Surface tension is a consequence of the existence of internal pressure, in other words, the force drawing molecules into the liquid and directed perpendicular to the surface [10]. The more polar the substance, the higher the internal pressure, because it is caused by the action of molecular forces. Internal pressure draws the molecules located on the surface of the liquid inward and thereby tends to reduce the surface to a minimum under the given conditions.

There are two types of methods for determining surface tension: static and dynamic [11]. Dynamic methods, such as oscillating a jet flowing out of an irregularly shaped hole, make it possible to measure the surface tension of a newly formed surface immediately after its formation. Static methods allow measuring the surface tension at the interface, which came into equilibrium. The following methods for determining the surface tension are most widely used:

- a method for measuring the mass or depth of object immersion in a test liquid (plate method);
- a method for measuring the geometric dimensions of the free surface (a lying, hanging or rotating drop, a sitting or hanging bubble);
- a stalagmometric method (method of counting drops);
- a method of measuring the force of object separation from the interface (separation of the cylinder - Paddy method, separation of the ring - Du Nouy method);
- a capillary method of raising the liquid;
- a method for measuring the maximum pressure in a gas bubble or a drop of liquid (Rehbinder method).

Literature provides limited information on the surface tension of aqueous solutions of boric acid and its dependence on the concentration of boric acid, temperature, and pressure. For example, in a study presented in [12], the surface tension of boric acid solutions was measured by the capillary method of raising the liquid. The inner diameter of the capillary was 1 mm. The measurements were carried out at atmospheric pressure and in the temperature range of 20-30°C. According to the author of [12], the obtained experimental data are best described by the Szyszkowski equation:

\[ \sigma = \sigma_0 - R \cdot T \cdot \Psi \cdot \ln(1 + \frac{C_M}{b}) \]  

where \( \sigma_0 \) is the surface tension of water, \( \text{mN} \cdot \text{m}^{-1} \); \( T \) is the temperature, \( \text{K} \); \( R \) is the universal gas constant, \( \text{J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1} \); \( C_M \) is the molar concentration of boric acid, \( \text{mol} \cdot \text{L}^{-1} \); \( \Psi \) and \( b \) are empirical constants determined by the best fit with the experimental data.

It was found that in the studied concentration range of boric acid \((10^{-6}-10^{-4} \text{ mol} \cdot \text{L}^{-1})\), a weak dependence on the concentration is observed, and the experimental values vary within 65-73 mNm\(^{-1}\).

In [13], the authors used the plate method to study the static surface tension and the maximum bubble pressure method to determine the dynamic surface tension. The second method allows observing the growth of the surface of the bubbles, thus determining the dynamic surface tension. The concentration of boric acid ranged from 0 to 14.5 gkg\(^{-1}\) of solution. All measurements were carried out at atmospheric pressure. According to the authors of [13], the dynamic surface tension with additives is lower than that of the pure water, and the static surface tension is lower than the dynamic. When measuring the static surface tension, it was found that there is no explicit dependence on the concentration of boric acid, at the same time, strong temperature dependence is observed.

Similarly to [12], at a temperature of 20°C, the surface tension for concentration of boric acid from 0 to 14.5 gkg\(^{-1}\) of solution is in the range of 59-73 mNm\(^{-1}\). The study of dynamic surface tension also did not reveal a dependence on the concentration of boric acid. For a temperature of 25°C it amounted to 71-72 mNm\(^{-1}\); for 40°C, it is 70 mNm\(^{-1}\); for 53°C, it is 65-67 mNm\(^{-1}\); for 66°C, it is 65 mNm\(^{-1}\); and for 79°C, it is 63 mNm\(^{-1}\).

In [14], the results of studies of the surface tension of aqueous solutions of boric acid (with concentrations of 14.2, 137.1, and 256.8 gkg\(^{-1}\) of solution) and solutions of boric acid with buffer additives that maintain pH in the coolant (NaOH, Na\(_2\)PO\(_4\), Na\(_2\)B\(_2\)O\(_4\)) at a temperature of 65.6 and 100°C are presented. The measurements were carried out using a digital tensiometer DST 60 equipped...
with a measuring cell with a thermostatically controlled chamber connected to a thermostat with ethylene glycol. The authors of [14] claim that the surface tension values for all studied solutions were lower than that of pure water at the same temperature, regardless of the presence or absence of buffer additives. An increase in the concentration of boric acid led to an increase of the surface tension in the case of solutions without buffer additives.

The analysis of literature [7, 9-12] showed that the results presented, to some extent, contradict each other in terms of changes in surface tension from the concentration of boric acid and cover a limited range of parameters. For this reason, it becomes necessary to carry out additional experimental measurements of the surface tension coefficient $\sigma$ of aqueous solutions of the boric acid at the $\text{H}_3\text{BO}_3$ concentrations characteristic of possible emergencies at new generation NPPs with VVER equipped with passive safety systems.

2. Experimental equipment and techniques
Experimental studies of the surface tension of aqueous solutions boric acid in a concentration range of 2.5-150 gkg$^{-1}\text{H}_2\text{O}$ were carried out at IPPE JSC. The experiments were performed using the digital tensiometer DST 30 in combination with a thermostatically controlled chamber with double walls and circulation thermostat LABTEX LT-TWC/7 (figure 1).

![Figure 1. Experimental facility for measuring the surface tension. 1 – digital tensiometer DST 30, 2 – thermostatically controlled chamber with double walls, 3, 4 – circulation circuit of heating fluid, 5 – side doors, 6 – mechanical table, 7 – Du Nouy ring, 8 – boric acid solution, 9 – heating fluid, 10 – circulation thermostat, 11 – water chamber.](image)

The digital tensiometer DST 30 used in studies allows measurements of the surface tension coefficient by two methods: using the Du Nouy ring and Wilhelmy plate. Preliminary measurements using these methods did not show any significant differences. The difference in readings was within the margin of the equipment error (± 1%). Thus, it was decided to conduct further research using the Du Nouy ring.

The ring method is based on measuring the maximum force to detach a ring with a known geometry (wetting length) made of a well wettable material (wetting angle of 0°) [15]. When lifting the ring, the liquid tends to drain from it, which leads to gradual thinning of the liquid film and tearing off the ring.

The interfacial tension force is calculated on the base of the difference between the maximum force applied to the ring tearing off and the force of the liquid hydrostatic column under the ring. Data for the force of the hydrostatic column of liquid can be taken from special tables or calculated based on
the difference in phase densities, geometric data of the ring, and the height of the rise of a thin layer of liquid. The angle of wetting between the liquid and the standard ring is zero for most well-known liquids (except for mercury).

The method of Du Nouy ring is suitable for measuring surface/interfacial tension in the range from 2 to 100 mN m\(^{-1}\).

The experiments to determine the surface tension were carried out by the following procedure. First, solutions of boric acid of various concentrations were prepared. For this purpose, a portion of 200 g of deionized water (the conductivity is 5 mS cm\(^{-1}\)), and the required amount of boric acid is mixed on an MSH-300 mixing device with a hot plate. The water is weighed on the electronic balance (maximum measuring mass is 2100 ± 0.1 g). The grade chemically pure boric acid is weighed on A&D GR-200 analytical balances (maximum measuring weight is 210 ± 0.0003 g). Next, the resulting \(\text{H}_3\text{BO}_3\) solution with a given concentration is poured into a plastic laboratory jar with a screw cap and placed in a Julabo TW8 water bath for further thermostating. The temperature is maintained 1-2°C higher than required, since, in the future, it takes time to pour the solution into the thermostatically controlled chamber of the tensiometer during which the liquid is inevitably cooling.

During the preparation of a solution with a concentration above 50 g kg\(^{-1}\) \(\text{H}_2\text{O}\), the solution's weighted components are poured directly into a plastic jar and heated in a water bath until the \(\text{H}_3\text{BO}_3\) crystals are completely dissolved.

In parallel with the preparation of solutions, the tensiometer is prepared for work according to the manual.

Further, the test fluid sample is poured into the thermostatically controlled chamber to approximately half its volume. The ring is lowered at least 5 mm below the liquid's surface to provide the most distinct tear off the ring from the surface of the liquid. Next, the ring is slowly taken out from liquid. The maximum force applied to the ring, and the value of the surface tension coefficient are recorded. These actions are repeated five times for each concentration of the solution.

3. Results of experimental research

The results of measuring the surface tension of aqueous solutions of boric acid in a concentration range of 2.5-150 g kg\(^{-1}\) \(\text{H}_2\text{O}\) and a temperature of 26-86°C is present. To the convenience of preparing the solution the concentration dimension g kg\(^{-1}\) \(\text{H}_2\text{O}\) was adopted. The main characteristics of the studied solutions are presented in Table 1.

| Temperature, °C | Concentration of boric acid, g kg\(^{-1}\) \(\text{H}_2\text{O}\) |
|----------------|----------------------------------|
| 26             | 0; 2.5; 25; 50                   |
| 40             | 0; 2.5; 25; 50; 75               |
| 70             | 0; 2.5; 25; 50; 75; 100; 150     |
| 86             | 0; 2.5; 25; 50; 75; 100; 150     |

The results of surface tension measurements are presented in figures 2 and 3.

Figure 2 shows that there is an explicit temperature dependence of the surface tension coefficient. This result correlates well with existing literature data [7-10].

In figure 3, it is observed that an increase in the concentration of boric acid in the solution leads to an increase in the surface tension coefficient. This result coincides with the results of studies for boric acid without buffer solutions given in [14]. Simultaneously, as it is noted in [14], the addition of buffer additives characteristic of the water chemistry of PWR leads to a decrease in surface tension with increasing the concentration of \(\text{H}_3\text{BO}_3\). The additional studies are advisable for a more detailed clarification of the effect of the buffer additives corresponding to the water chemistry of VVER reactors.
Figure 2. The values of surface tension of aqueous solutions of boric acid at different temperatures.

Figure 3. Effect of the concentration of boric acid on the values of surface tension.

Conclusions

The study of the static surface tension of the aqueous solutions of boric acid was performed at IPPE JSC. The experiments were carried out using the method of Du Nouy ring with $H_3BO_3$ concentrations in the range of 2.5 to 150 gkg$^{-1}$ $H_2O$. The data obtained allow us to expand the range of known parameters of boric acid solutions.

The measurement results confirmed the presence of temperature dependence and showed the effect of concentration on the surface tension of aqueous solutions of boric acid in the studied range of parameters.

The obtained experimental data on the surface tension of aqueous solutions of boric acid are of great practical importance. They can be used for the computational simulation of emergency conditions at new generation NNPs with VVER reactors equipped with passive safety systems.

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