Correlation of thermal resistance and excess volume for superheated aqueous solutions of glycols

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Abstract: The method of controlled pulse heating of a wire probe – resistance thermometer in thermal stabilization and constant heating power modes was used for the study of heat conduction of liquid binary solutions in stable and superheated conditions. The objects of the study were aqueous glycol solutions (ethylene glycol, diethylene glycol and triethylene glycol) with negative excess volume. The values of thermal resistance and thermal conductivity coefficient of the solutions, calculated using the primary data of pulse heating experiment were compared with the values of excess volume of the solutions. A correlation was found between the thermal conductivity of the solution and the value of its excess volume for the temperature range studied.

1. Introduction
The heat conduction of liquids [1] is, apparently, the main characteristic of heat exchange in the scale of small characteristic times and sizes and significant heat fluxes. Similar conditions are inherent during high-power local heat release in a system [2-5]. The value of the heat conduction is proportional to the density of the heat flux at a given temperature boost, accompanying the "switching on" of the heat source in the system.

In fact, the properties of solutions including thermal ones can differ substantially from the properties of their pure components. According to the hypothesis [6] based on the results of the analysis of the thermal conductivity of solutions with positive excess volume, additional thermal resistance (the reciprocal of the heat conduction) calculated with respect to the additive value for pure components arises when a second component is added to the pure liquid. The aim of this work is to elucidate the generality degree of this hypothesis with respect to solutions with a negative value of excess volume.

The studies were carried out on aqueous solutions of ethylene glycol, diethylene glycol and triethylene glycol at atmospheric pressure over the entire concentration range. Experimental temperatures rose from room temperature up to 150°C. Thus, part of the region of states, superheated with respect to the liquid-vapor equilibrium lines of the solution, is involved in the study. The measurement of thermophysical properties in this region of states is complicated by a limitation in the lifetime of the system until its spontaneous boiling-up.
2. Experimental part

Studies of heat conduction in pulse heated aqueous solutions of glycols required the use of an automated device applying the method of real-time controlling of the heating power of a wire probe – a resistance thermometer. Its operation was based on the principle of controlled thermal impact on the “probe-substance” system and the registration of the characteristic response from the heated system [7-9], see section 2.1. The concentration dependence of the thermal conductivity coefficient of a solution at thermostat temperature $T_0$ was measured by the device realizing a constant heating power mode in the probe, see section 2.2.

2.1. Controlled pulse heating: temperature plateau mode

The essence of this mode (see figure 1) is the creation of short-time isothermal conditions for the pulse heated probe in the substance and the registration of heat flux through the surface of the probe. Weight-average probe temperature rises from the initial value of $T_0$ to the selected value of $T_{st}(t_{st} > t_{hat}) \approx \text{const}$ within time $t_{hat} \approx 10^{-4}$ s and further remains constant within the time interval of $t_{st} \approx 10^{-1}$ s. The primary magnitudes measured in experiments were voltage drops across the probe and the standard resistor [9]. These magnitudes were recalculated for the probe temperature values $T_{st}(t)$, see curve 1 in figure 1 and the electric power $P(t; T_{st})$, necessary for its maintenance, see curves 2-6. Based on these results, the inverse value of the thermal resistance coefficient of the sample is calculated for the given temperature value $T_{st}$:

$$1/R_{st}(t) = P(t)/(T_{st}(t) - T_0) \cdot S_w,$$

where $S_w$ is the surface of the probe.

The change of value $1/R_{st}(t)$ is directly proportional to the change in heat conduction and reflects the difference in thermal properties of the sample when changing experimental parameters, for example, the concentration of the solution.

The uniqueness of the method lies in the fact that the measurement of the thermal resistance coefficient is possible not only in the region of stable states of a substance, where the life time of the system is arbitrarily long, but also in the region of superheated (short-lived) states at $T_{st} > T_s$ [7, 8], where $T_s$ is the liquid–vapor equilibrium temperature at the given pressure.

![Figure 1](image-url)  
**Figure 1.** General scheme of the temperature plateau mode: (a) line 1 – temporal dependence of probe temperature $T_{st}(t) = 150^\circ$C; 2, 3, 4, 5, 6 – power values $P(t; T_{st})$, necessary for the thermal stabilization of the probe in aqueous TEG solution samples with water content (wt.%); at the given $T_{st}(t)$ value: 100, 67, 47, 28 and 0, correspondingly; (b) lines 7, 8 – values of power (7) and reciprocal of thermal resistance (8) at $t = 5$ ms depending on water content (wt.%). The dashed lines represent the additive values for corresponding functions.
Let us consider the results presented in figure 1. Power $P(t)$ necessary to maintain the designed temperature value $T_{st}(t)$ of the probe in the substance appears to be sensitive to changes in heat conduction. The higher the heat conduction, the higher the value of $P(t)$. By measuring the values of $P(t)$ in pure components, the additive power values can be calculated for the corresponding solution concentrations, see figure 1a, dashed lines 3-5. A comparison of the power values calculated from the additive law to the measured values of $P(t)$, see solid curves 3-5 at figure 1a, indicates a decrease in the heat conduction of the solution with respect to the additive value. In figure 1b the experimental concentration dependences $P(t)$ (curve 7) and $1/R_{c}(t)$ (curve 8) at timing $t = 5$ ms are shown by symbols; the dashed lines show corresponding additive values.

2.2. Controlled pulse heating: stable power mode

The thermal conductivity coefficient is measured using the controlled probe pulse heating method in constant power mode [9]. The most important condition for the implementation of this method is to maintain the constant heat flux from the probe to the medium. Such a condition is a key requirement of the conventional model [10]. The fulfillment of this requirement is equivalent to maintaining the constant electric power during the pulse with a sufficiently high accuracy. The task of maintaining a constant power is complicated due to the change in the initial resistance of the probe during the measuring process. The solution of this problem (by introducing a high-speed feedback into the scheme) distinguishes our approach [10] from the widespread THW-method [11].

The following experimental parameters were applied in the course of measurement: the length of heating pulse was 2 s, temperature rise was not higher than 5 K and the accuracy of maintenance of power value stability was not less than 99.95%. The probe was a platinum wire 20 μm in diameter and 10 cm in length.

The values of the current in the probe circuit and the voltage drop on the probe were recorded in the course of experiment, see figure 2. The power value was calculated using these data. The length of the probe was refined in test experiments on substances with known thermal conductivity. The slope of $T(t)/\ln t$ curve was determined from the characteristic linear part of this dependency, see figure 3. Thermal conductivity coefficient was calculated using the classical method [11]:

$$\lambda = q/4\pi \tan \alpha,$$

where $\lambda$ is the thermal conductivity coefficient, $q$ is the linear density of heat flux, and $\alpha$ is the inclination angle of the linear part of the temperature rise to the axis of the time logarithm.

**Figure 2.** Primary data of the thermal conductivity experiment: the current in the probe circuit (curve 1) and the probe voltage drop (curve 2).
Figure 3. Temperature rise against logarithmic time at selected power level (solid line) and its approximation (dotted line) for water at atmospheric pressure. The graph is represented in semi-log coordinates in accordance with the computational model.

2.3. Measurement details

Experiments on the solution samples were carried out at atmospheric pressure at three temperature values of $T_{st}$: 363 K, 393 K, 423 K. The main data array was obtained in the region of superheated states. In the case of an aqueous solution of ethylene glycol, this region is located above line 1 in figure 4. When measuring heat conduction, the variation range of $T_{st}$ value was limited from above by the condition $T_{st} < T_{st}^*$, where $T_{st}^*$ denotes the spontaneous boiling-up temperature at the given heating mode [7,12], see curve 3 in figure 4.

Figure 4. The phase diagram of aqueous EG solution: 1 – liquid-vapor equilibrium line; 2 – vapor-liquid equilibrium line; 3 – attainable superheat line for thermal stabilization mode. The symbols on the isotherms indicate water content (wt.%) of the solution.
The measurements were carried out on a platinum probe with a diameter of 20 μm and an initial resistance $R_0 = 2.84 \, \Omega$ at $T_0 = 25^\circ C$. The properties of the samples were measured by means of an automated apparatus [13] including: a probe temperature stabilization circuit, a high-speed analogue-to-digital converter and a unique software to record the primary values to the file and calculate the corresponding values of $T(t)$ and $P(t)$. From 3 to 5 measurements were taken for each concentration and then the data were averaged and smoothed out. A few fragments of the array of experimental data are presented in figures 5–8. Additive function values are constructed for the available solutions concentrations from the measured values for pure components and compared with the corresponding experimental values.

3. Results and discussion

Our data on the thermal conductivity of pure components were compared with NIST reference data. The results of the experiments for intermediate solution concentrations were formally compared with linear approximation see figure 9. It can be seen from the experimental data that the value of thermal conductivity deviation from the additive value has a peak at a water concentration of ~ 40%, see figure 9. Let us turn to the heat conduction. Based on the data obtained, it has been revealed that the heat conduction of aqueous solutions of glycols in the studied temperature variation region has negative deviation from that of additive value. Similar behavior is demonstrated by these solutions with respect to the dependence of the excess volume on the concentration, see figures 10 and 11. Let us take into account that only a small volume of the studied sample is heated during the experiment. The bulk of the material has a thermostat temperature. Thus, it is reasonable to compare the change in the heat conduction of a pulse heated solution with the change in its excess volume at initial temperature $T_0$.

It was found that the deviation maxima positions on the experimental thermal resistance curves depending on the solution concentration fairly correlate with those for the excess volume curves. In addition, a characteristic sequence was revealed in the location of the curves with respect to the molecular weight of the second component. The curve of the sought dependency has the least scale of change in the aqueous ethylene glycol solution and the curve for the aqueous triethylene glycol solution has the largest scale. It can be assumed that for water-polyethylene glycol solutions an

![Figure 5](image1.png)  
**Figure 5.** Probe heating power necessary for its thermal stabilization in pure components and in 50% solutions at $T_{st} = 90^\circ C$ (solid lines) and the corresponding additive function values (dashed lines). Indicated numbers are identified in the caption for figure 6.

![Figure 6](image2.png)  
**Figure 6.** Similar data for $T_{st} = 150^\circ C$. The value of water content (wt. %) serves as a parameter: 1 – 100; 2 – additive 47.470 for EG; 3 – experimental 47.470 for EG; 4 – additive 47.602 for DEG; 5 – additive 47.108 for TEG; 6 – experimental 47.602 for DEG; 7 – experimental 47.108 for TEG; 8 – EG; 9 – DEG; 10 – TEG; 11 – isopropanol.
increase in the additional thermal resistance will be observed with simultaneous increase in the excess volume (in absolute values).

Finally, the data obtained on the thermal resistance of aqueous solutions of glycols qualitatively coincide with the reference data on the thermal conductivity of these solutions [14]. In future studies, it is necessary to expand the range of experimental parameters to higher superheating degrees. The attainable superheat boundary for these solutions will be determined by the method of pulse monotonic heating, previously used to study highly superheated states of polymer solutions [15].

Figure 7. Probe heating power necessary for its thermal stabilization in aqueous TEG solution at $T_{st} = 150^\circ$C: line 0 – the probe temperature in time; the value of water content (wt. %) serves as a parameter: 1 – 100; 2 – additive 67.121; 3 – experimental 67.121; 4 – additive 47.108; 5 – experimental 47.108; 6 – additive 27.691; 7 – experimental 27.691; 8 – 0.

Figure 8. Probe heating power necessary for its thermal stabilization in the studied solutions at $T_{st} = 150^\circ$C and $t = 5$ ms (solid lines): 1 – EG; 2 – DEG; 3 – TEG; the corresponding additive values are shown by dashed lines.

Figure 9. The values of thermal conductivity coefficient for aqueous TEG solution on water content (vol. %): 1 – dashed line shows additive values of thermal conductivity; 2 – experimental values are shown by symbols averaged with solid line.
The coefficients of thermal resistance and thermal conductivity of aqueous solutions of glycols have been measured in the regions of stable states and superheated states as well. It is shown that solutions of this type (solutions with a negative excess volume) are characterized by a negative deviation of the heat conduction from the additive characteristics.

4. Conclusion

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