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THERMAL CONDUCTIVITY OF AQUEOUS SOLUTIONS OF NaCl

V. D. Yusufova, R. I. Pepinov, V. A. Nikolaev,
and G. M. Guseinov

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We present the results of an experimental study of the thermal conductivity of aqueous solutions of sodium chloride at concentrations of 5, 10, 15, 20, and 25% NaCl over the temperature range 20-330°C.

At the present time, the problem of seawater and saline-water use in industry is aquiring real importance. Up to this time, however, reliable experimental data on the thermophysical properties of saline water over a broad range of temperatures and salt concentrations is lacking. As is well known, seawater has a rather complex salt and gas composition. The main part of the ionic component is chlorine and sodium (about 78% of all salts),which characterize the hydrochemical nature of seawater by their presence and lend great importance to the study of the thermophysical properties of aqueous solutions of sodium chloride as a basic component of seawater. Studies of aqueous solutions of electrolytes may prove to be fruitful for studies of the structure of liquids and of the nature of the thermal motion of their particles.

The structure of the solvent, i.e., water, plays a decisive role in the determination of the properties of electrolyte solutions. At the present time, the theory of Samoilov [3] has received the greatest recognition of all the numerous models of the structure of liquid water. According to [18], the thermal conductivity of water, to a first approximation, is defined as the sum of the thermal conductivity of a quasicrystalline framework and the thermal conductivity of a system of molecules located inside voids within the framework which move through the system of voids. The main contribution to the total thermal conductivity is made by the thermal conductivity of the framework, which decreases as the temperature increases, as it does in ice. The anomalous rise in the thermal conductivity of water in the range 0-130°C is explained by the positive contribution from the thermal conductivity of the system of molecules in the voids. Where movement of molecules within voids is made difficult by small passages between voids in the structure of ice [3], the passages increase in size in the liquid phase as the temperature rises and the thermal motion of the molecules in the voids increases. Further rise in temperature produces a reduction of short-range order through which the thermal conductivity of the molecular system within the voids is reduced and becomes small in comparison with the thermal conductivity of the framework [18].

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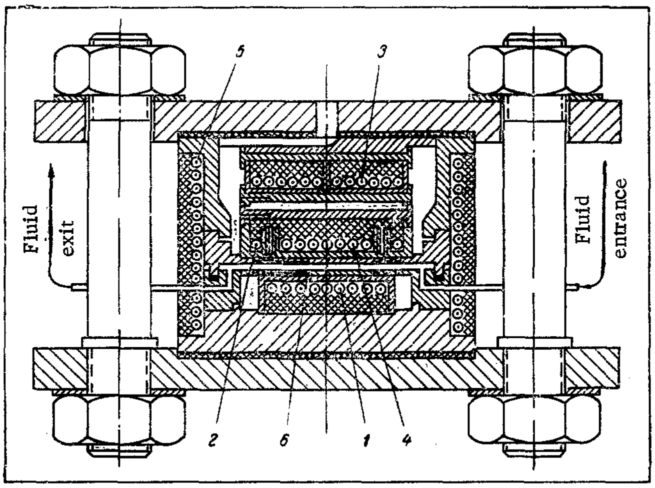

Fig. 1. Diagram of measuring unit of device. 1) Lower heater; 2) lateral guard heater; 3) upper guard heater; 4) main heater; 5) outer heater; 6) thermocouples.

Addition of an electrolyte such as the ions Na^+ and Cl^- has an effect on the structure of water which changes the value of the thermal conductivity [19].

In the transfer of thermal motion in electrolyte solutions, the most favorable condition for translational motion, which consists of sequential replacement of water molecules in a tetrahedral shell, should be the extreme closeness of ion size to the size of the "replaceable" water molecule – 1.4 Å. Ions of a size less than that of a water molecule which possess intense electrostatic fields stiffen the water structure and thereby hinder translational motion of both ions and water molecules. On the other hand, ions of a size greater than that of a water molecule reaching a nodal point of the quasicrystalline structure significantly distort, disrupt, and weaken the structure, which creates more favorable conditions for translational thermal motion of ions and molecules and thereby increases the thermal conductivity of the solution. According to the values for radii of individual ions in aqueous solutions given in [4], the dimensions of Na^+ and Cl^- ions are close to the dimension of a water molecule (1.4 Å) and are, respectively, 1.26 and 1.53 Å.

The work of a number of investigators [5-11] who considered the effect of individual ions on solvent structure showed that in aqueous solutions of sodium chloride, the main effect on solvent structure was produced by Na^+ cations which promote stiffening of the solvent structure and hinder translational thermal motion of both the ions themselves and of the water molecules and thereby reduce the thermal conductivity of the solution. At the same time, the chlorine ions do not have a significantly disturbing effect on solvent structure [5].

These conclusions are confirmed by our experimental results. Over the entire temperature range investigated, the value of the thermal conductivity for aqueous solutions of NaCl was below the thermal conductivity of pure water (Fig. 2).

The experimental study of the thermal conductivity of aqueous solutions of sodium chloride was carried out with an experimental device constructed for this purpose by means of the relative flat-layer method [1]. The construction of the measuring unit of the device is shown in Fig. 1. Temperature measurements were made with three Chromel–Alumel thermocouples which were installed in specially milled slots in the upper and lower plates of the measuring unit. The thermocouple connections made it possible to measure both the absolute temperature of the "cold" and "hot" plates and also just the temperature difference between them. The rigorous directionality of the heat flux from the main heater was ensured by two guard heaters and was monitored with 10-junction Chromel–Alumel differential thermocouples. The temperature gradient between the main and guard heaters was kept within the range 0.00-0.03°C during the measurements.

An 800-W Nichrome heater was located on the outer surface of the measuring-unit system. The heater and the entire measuring-unit system were carefully insulated

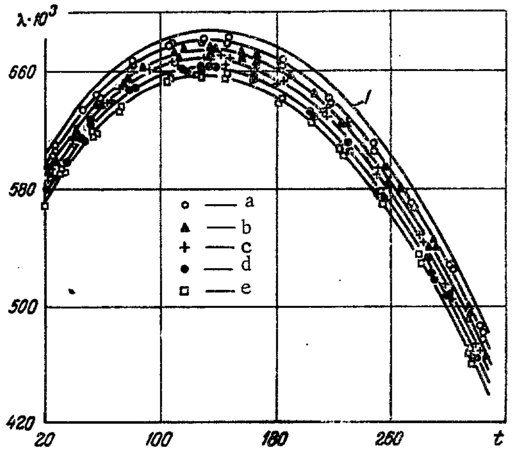

Fig. 2. Temperature dependence of thermal conductivity [W/(m · deg)] of aqueous solutions of sodium chloride: 1) data for pure water [17]; a) 5% NaCl; b) 10% NaCl; c) 15% NaCl; d) 20% NaCl; e) 25% NaCl. t, °C.

for maximum reduction of thermal losses to the surroundings. The overall temperature of the entire measuring unit was brought to a definite level by means of the outer heater, and a temperature gradient in the layer of test fluid was created by the main heater, which made it possible to make measurements for gradients in the range 0.5-1.5°C. The "zero" readings of the differential thermocouples were recorded before the beginning of each measurement. The thickness of the flat layer was determined by calibration of the device with distilled water over the entire temperature range studied and was found to be 0.83 mm. The thermal conductivity of benzene was measured up to 160°C in order to check the operation of the device. Benzene is an organic material for which the thermal conductivity has been thoroughly studied in this temperature range. The maximum discrepancy between our experimental data and the handbook data [2] for benzene did not exceed 2% over the entire temperature range. The studies were made with allowance for possible production of convection in the flat layer of fluid, which, as is well known, is determined by the product of the Grashof and Prandtl numbers, i.e., by the Rayleigh number. The maximum value of the Rayleigh number amounted to 1200 at high temperatures, and good reproducibility of the experimental data for pure water before and after experiments with aqueous solutions of NaCl made it possible to assert that there was practically no convection over the entire range of temperatures studied; furthermore, there was no deposition of salts on the internal surfaces of the plates of the measuring unit of the device. Using this device, studies were made in the temperature range 20-330°C for aqueous solutions of sodium chloride with the following weight concentrations: 5, 10, 15, 20, and 25% NaCl. The thermal conductivity of aqueous solutions of electrolytes and its dependence on concentration have been studied most inadequately up to the present time. There are many contradictions in the existing experimental data for the thermal conductivity of aqueous solutions of electrolytes. This may be explained in part by insufficient accuracy of the method used for experimental study of thermal conductivity. Since the effect of dissolved materials on thermal conductivity is small in absolute magnitude, it is not revealed by measurements that are insufficiently accurate.

Some experimental data for the thermal conductivity of aqueous solutions of sodium chloride up to 160°C are given in [12], and in [13] for low temperatures (20-30°C). As is clear from Fig. 3, our experimental data are in good agreement with the data of [12, 13]. The maximum discrepancy does not exceed 0.6% over the entire range of measurement. At the same time, there are significant differences from the results given in [14, 15] (see Fig. 3). The maximum reduction in the coefficient of thermal conductivity for a concentration of 25% NaCl relative to the thermal conductivity of pure water ranges from 5% at 20°C to 9% at 330°C. In addition, the agreement of our experimental data with theoretical data obtained from the Riedel method [16] was checked. In studying solutions of salts, Riedel started from the assumption that the radicals and metals, i.e., anions and cations, formed in an aqueous solution of a salt change the thermal conductivity of water independently

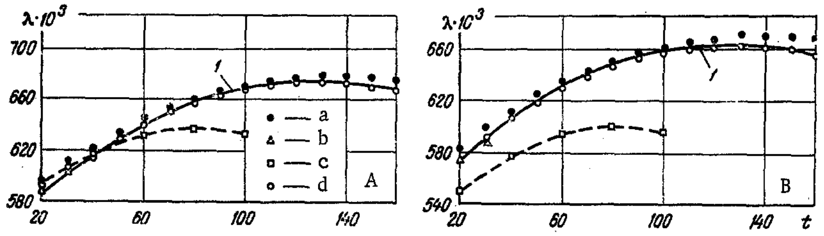

Fig. 3. Thermal conductivity [W/(m · deg)] of aqueous solutions of 10% (A) and 20% (B) sodium chloride according to various authors: 1) [12]; a) from Riedel formula; b) [13]; c) [14]; d) experimental data. t, °C.

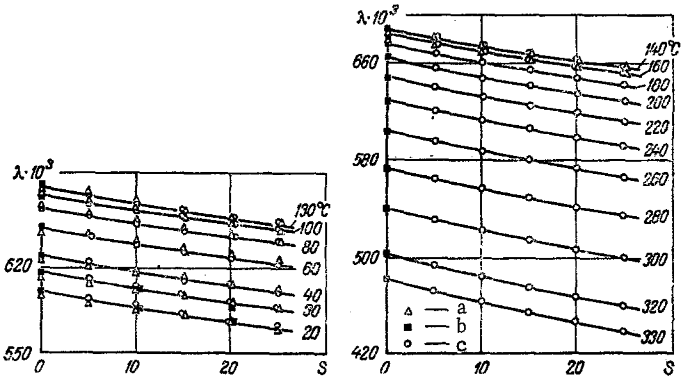

Fig. 4. Dependence of thermal conductivity of aqueous solutions on weight concentration S of sodium chloride: a) [12]; b) [13]; c) experimental data. λ, W/(m · deg).

of one another and that the change in the coefficient of thermal conductivity of the solution is determined by an algebraic sum which includes the effects of anions and cations, i.e.,

$$\lambda_s = \lambda_w + \sum_i a_i C_i .$$

The Riedel formula gives good agreement with experiment at low temperatures, namely, up to the maximum thermal conductivity of a solution, which occurs at 130-140°C. Thus the maximum deviation of our experimental data from data obtained with the Riedel formula is 1.2% for the isotherms 20-140°C and 25% NaCl concentration. As temperature increases, the deviation between our experimental data and that calculated from the Riedel formula increases and amounts to 6% at 330°C and the maximum concentration studied. From our point of view, the discrepancy between experimental data and theoretical values (from the Riedel formula) is explained in the following manner. The Riedel formula was derived for calculation of the thermal conductivity of solutions of salts and acids at 20°C. Furthermore, it was emphasized that the formula might not correspond to actual conditions at high concentrations. Because of the reduction in short-range order in the structure of the solution and the increase in thermal motion of molecules created by the rise in temperature, additional frictional mechanisms may arise which are not considered in the Riedel formula and which, in the final analysis, reduce the thermal conductivity of the solution in comparison with the theoretical value.

The experimental data obtained were analyzed with a Nairi-2 computer and an expression was obtained which describes the dependence of the thermal conductivity of the solutions on concentration and temperature in the following form:

$$\lambda_s = \lambda_w[1 - (2.3434\cdot10^{-3} - 7.924\cdot10^{-6} t + 3.924\cdot10^{-8} t^2) S + (1.06\cdot10^{-5} - 2\cdot10^{-8} t + 1.2\cdot10^{-10} t^2) S^2].$$

The relative root-mean-square error of the thermal-conductivity measurements did not exceed 2%. Figure 4 shows the dependence on concentration of the thermal conductivity of aqueous solutions of NaCl.

NOTATION

A, size of ions; λ_s, solution thermal conductivity, W/(m · deg); λ_w, thermal conductivity of water [17]; C_i, electrolyte concentration in moles per liter of solution; a_i, coefficient characteristic of each ion determined experimentally; t, temperature, °C; S, concentration of dissolved material in solution, wt. %.

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