THERMAL CONDUCTIVITY OF SOLUTIONS

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The results of an experimental and theoretical study of the thermal conductivity of binary, ternary, and multicomponent solutions are presented. A probable mechanism of heat conduction in solutions is proposed and calculation formulas are obtained.

The thermal conductivity of binary solutions is the subject of papers [1-8]. The maximum error of the conductivity measurements did not exceed 2-5% in [1-3, 5] and 1% in [4, 6-8].

Several equations have been proposed for calculating the thermal conductivity of binary solutions. These include the equations of Filippov and Novoselova [1], Bondi [10], and Barrat and Nettleton [9]. We have proposed two equations—one for solutions of organic liquids [7] and another [8] for aqueous solutions of organic liquids in the temperature interval 0-100° C.


An analysis of these equations shows that for many solutions they give serious errors, are purely empirical in character, and do not reflect the physical essence of the phenomena of heat transport in solutions.

The present research was intended to supplement the existing experimental material with new data on the thermal conductivity of solutions. A proposed mechanism of heat conduction in solutions of nonelectrolytes is also discussed.

Binary solutions. The thermal conductivities of 15 solutions were measured at 40° C on the apparatus described in [12]. The solutions were prepared directly before the experiment from chemically pure reagents. The conductivity measuring error did not exceed 1%.

Figure 1 presents the experimental data on the conductivity of the investigated solutions as a function of the mole concentration. For all the aqueous solutions investigated and most of the solutions of organic liquids the conductivity tends to be less than predicted by the additive law (negative deviation). However, it is clear from Fig. 1 that a positive deviation is also possible, e.g., for isopropyl alcohol-triethylene glycol and n-butyl alcohol-triethylene glycol, while, within the limits of experimental accuracy, the system methyl alcohol-formamide has a thermal conductivity that obeys the additivity rule. It is a common characteristic of all the solutions that in all cases the thermal conductivity of the solution lies between the values for the pure components.

To a large extent, the structure and properties of liquid solutions are determined by two factors—the intermolecular forces and the size of the component molecules.

We will consider the effect of each of these factors on heat transport in solutions. This effect will be estimated with respect to the deviation of the \( \lambda = f(N) \) relation from the additive law.

This deviation may conveniently be characterized by the dimensionless quantity \( \delta \lambda / (\lambda_2 - \lambda_1) \), where \( \delta \lambda \) is the difference between the experimental conductivity and that calculated from the additivity rule. Obviously, the magnitude and sign of this deviation must be determined by the physical properties as well as the concentration of the components.

First, we will consider the effect of the intermolecular forces on the thermal conductivity of solutions.

Among the investigated solutions, e.g., organic liquids in water, it is possible to select solutions in which the size of the molecules* of the organic components are approximately the same, though the intermolecular forces are different. For example, the systems n-propyl alcohol-water and glycerol-water. Here, the interaction between the molecules of the pure components is basically determined by the hydrogen bond, but the intensity of this interaction is much greater between the glycerol molecules, which have three OH groups, than between the molecules of n-propyl alcohol.

But the deviation of the conductivity from additivity in these solutions is almost the same. The same may be said about the systems ethylene glycol-water and ethyl alcohol-water, 1,2-propylene glycol-water, and isopropyl alcohol-water. A similar pattern is observed in solutions of organic liquids. For example, in the systems toluene-methyl alcohol and n-hexyl alcohol-methyl alcohol the sizes of the toluene and n-hexyl alcohol molecules are almost the same, but the intermolecular forces are much more intense between the alcohol molecules. The interaction between the different molecules in the toluene-methyl alcohol system is determined by the relatively weak dispersion forces, while in n-hexyl alcohol-methyl alcohol systems the interaction between molecules of the same and different kinds is similar in nature—basically the hydrogen bond superimposed on the van der Waals forces. But for these solutions the deviation from additivity is the same.

In order to clarify the effect of molecular association on the thermal conductivity of solutions, we selected systems in which the component molecules form complexes without there being any significant compensating effects.

*We will characterize the size of the molecules in terms of their molar volumes.
Fig. 1. Thermal conductivity of binary solutions of organic liquids as a function of concentration at 40°C (λ, W/m·deg; N, mole fractions):
1) n-butyl alcohol-glycerol; 2) n-butyl alcohol-triethylene glycol;
3) isopropyl alcohol-methyl alcohol; 4) isooctane-n-octane; 5) methyl alcohol-formamide; 6) triethylene glycol-formamide; 7) isopropyl alcohol-formamide; 8) isopropyl alcohol-triethylene glycol; 9) formamide-water; 10) glycerol-water; 11) ethylene glycol-water;
12) diethylene glycol-water; 13) triethylene glycol-water; 14) dimethylformamide-water; 15) pyridine-water.