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 2–3% 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.

Cecil and Munch [11] recommend using the additivity rule for computing the thermal conductivity of three-component solutions.

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.

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*We will characterize the size of the molecules in terms of their molar volumes.

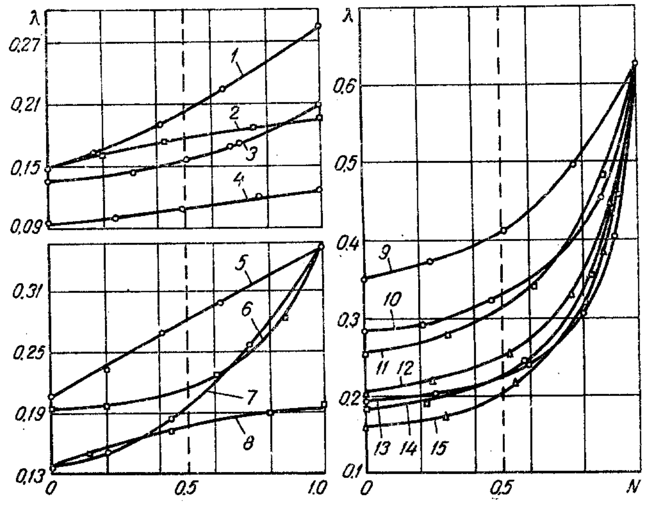

Fig. 1. Thermal conductivity of binary solutions of organic liquids as a function of concentration at 40° C (λ, W/m · deg; N, mole fractions): 1) n-butyl alcohol-glycerol; 2) n-butyl alcohol-triethylene glycol; 3) isopropyl alcohol-methyl alcohol; 4) isooctane-n-octane; 5) methyl alcohol-formamide; 6) 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.

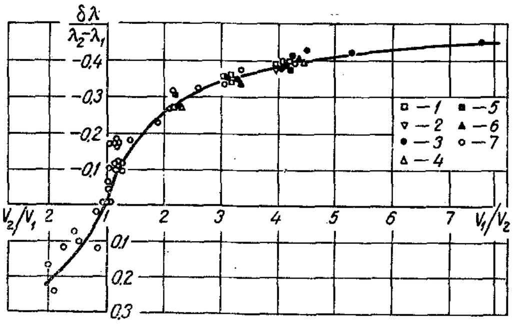

Fig. 2. Deviation of thermal conductivity of solutions from additivity as a function of the ratio of the molecular volumes of the components at N = 0.5 and various temperatures (λ, W/m • deg; N, mole fractions): 1, 2, 3, 4, 5, 6) aqueous solutions at 0, 20, 40, 60, 80, and 100° C, respectively; 7) solutions of organic liquids at 40° C.

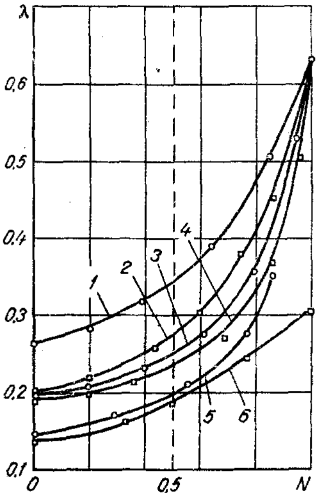

Fig. 3. Thermal conductivity of multicomponent solutions as a function of concentration at 40° C (λ, W/m • deg; N, molefractions): 1) (0.424 formamide–0.576 methyl alcohol)–water; 2) (0.165 triethylene glycol–0.835 methyl alcohol)–water; 3) (0.404 triethylene glycol–0.596 methyl alcohol)–water; 4) (0.686 triethylene glycol–0.314 methyl alcohol)–water; 5) (0.518 isopropyl alcohol–0.482 n-butyl alcohol)–water; 6) (0.4437 ethylene glycol–0.365 water–0.19113 formamide)–isopropyl alcohol.

In a pyridine-water solution, for example, associated pyridine-water complexes are formed due to the hydrogen bond between the component molecules. In this case [13] there is a considerable reduction in the rotational mobility of the molecules and an increase in relaxation time. The viscosity of the pyridine solution is roughly three times greater than that of the pure components. Similar effects are observed in a dimethyl formamide-water solution. However, there is no anomaly in the thermal conductivity of these solutions as compared with solutions in which no molecular association takes place.

Thus, despite the considerable differences in the intermolecular interactions, we were unable to establish a relationship between $\delta\lambda/(\lambda_2 - \lambda_1)$ and these interactions, which obviously indicates that this factor does not have much influence on the deviation of the thermal conductivity from additivity.

In [4,6,7,8] 13 aqueous solutions and 31 solutions of organic liquids were investigated to determine the effect of the dimensions of the component molecules on thermal conductivity. The difference in the size of the molecules was characterized by the ratio of their molecular volumes.

An analysis of these solutions showed that as the difference in the molecular volumes of the components increases, so does the deviation of the solution conductivity from additivity.

In Fig. 2 the relation between $\delta\lambda/(\lambda_2 - \lambda_1)$ and the molecular volume ratio is shown for 44 solutions in equimolar concentrations. Along the axis of abscissas unity has been taken as the coordinate origin with values of V_1/V_2 plotted on the right and values of V_2/V_1 on the left (when $V_1 < V_2$). The graph indicates a good correlation between the deviation from additivity and the ratio of molecular volumes. As the difference between molecular volumes increases, the deviation from additivity increases, first rapidly (up to about $V_1/V_2 = 2.2$), and then more slowly, tending in the limit to a constant value.

For aqueous solutions we always have $\lambda_2 > \lambda_1$ and $V_2 < V_1$. However, for solutions of organic liquids when $\lambda_2 > \lambda_1$ it is possible to have $V_2 < V_1$, $V_2 > V_1$, or $V_2 = V_1$.

In the first case the conductivity has a negative deviation from additivity, in the second a positive deviation. Systems with a positive deviation include isopropyl alcohol-triethylene glycol (Fig. 1), furfural-acetone [7], isooctane-n-tetradecane, n-octane-n-heptadecane, and n-heptane-n-hexadecane [6].

When $V_2 = V_1$, the $\lambda = f(N)$ relation is additive. Methyl alcohol-formamide, dichloroethane-furfural [7], etc., are examples of such solutions.

Thus, heat transport in binary solutions is importantly affected by the geometric factor, i.e., the ratio of the sizes of the component molecules.

In [14] it was shown that heat transport in liquids depends chiefly on collisions between molecules vibrating in their equilibrium positions, only a small part of the heat being transmitted by self-diffusion. In this case it may be assumed that the thermal conductivity of a liquid λ_a at given temperature is proportional to the collision frequency

$$\lambda_a = a\nu. \tag{1}$$

In the solution each molecule is in the company of molecules of the same type and molecules of the other component. Hence two types of collisions are possible, i.e., between molecules of the same and different kinds, and the probability of collisions of the first type is reduced. Then the thermal conductivity of a component of the solution λ_{ap} changes and can be found from the formula

$$\lambda_{ap} = a\nu W. \tag{2}$$

If the solution is binary, its thermal conductivity will be composed of the thermal conductivities of the components, i.e.,

$$\lambda = a_1\nu_1 W_1 + a_2\nu_2 W_2 = \lambda_1 W_1 + \lambda_2 W_2. \tag{3}$$

If $V_1 = V_2$, then, assuming a completely random distribution, the probability of molecules of the same kind colliding will depend only on the concentration and is numerically equal to

$$W_2 = N_2 \text{ and } W_1 = 1 - W_2 = 1 - N_2 = N_1, \tag{4}$$

then

$$\lambda = \lambda_1 N_1 + \lambda_2 N_2. \tag{5}$$

When $V_1 > V_2$, the probability of the smaller molecules colliding with each other will be

$$W_2 = \frac{1}{1 + \left(2\frac{V_1}{V_2} - 1\right)\frac{N_1}{N_2}}, \tag{6}$$

while for the molecules of the other component

$$W_1 = 1 - W_2 = \frac{\left(2\frac{V_1}{V_2} - 1\right)\frac{N_1}{N_2}}{1 + \left(2\frac{V_1}{V_2} - 1\right)\frac{N_1}{N_2}}. \tag{7}$$

Then when $V_1 > V_2$

$$\lambda = \frac{\lambda_2 N_2}{N_2 + \left(2\frac{V_1}{V_2} - 1\right)N_1} + \frac{\lambda_1\left(2\frac{V_1}{V_2} - 1\right)N_1}{N_2 + \left(2\frac{V_1}{V_2} - 1\right)N_1}. \tag{8}$$

When $V_1 < V_2$

$$\lambda = \frac{\lambda_2\left(2\frac{V_2}{V_1} - 1\right)N_2}{N_1 + \left(2\frac{V_2}{V_1} - 1\right)N_2} + \frac{\lambda_1 N_1}{N_1 + \left(2\frac{V_2}{V_1} - 1\right)N_2}. \tag{9}$$

From an analysis of Eqs. (8) and (9) it is clear that the former gives a negative deviation from additivity and the latter a positive deviation, a greater ratio of molecular volumes corresponding to a greater deviation from additivity.

However, for all solutions of organic liquids, in view of the small values of λ and $(\lambda_2 - \lambda_1)$, the accuracy of the experimental data should be higher than 1%.

The equations obtained also give a good description of the temperature dependence of the thermal conductivity of the solutions. Thus, for aqueous solutions of organic liquids we calculated values of the thermal conductivity on the interval from 0 to 100° C. The mean deviation of the calculated values was 2% for the data of [4] and 1.6% for our data.

For solutions of organic liquids the mean deviation of the experimental values from those calculated from Eqs. (8) and (9) was 1.2%.

Thus, using simple physical notions of the heat transport mechanism in solutions, we have obtained relations that reflect the experimentally established facts quantitatively as well as qualitatively.

Multicomponent solutions. The above approach can be applied to multicomponent solutions also.

The probability of collisions between molecules of the k-th component of a solution containing n components is then

$$W_k = \left(2\frac{V_k}{V_m} - 1\right)\frac{N_k}{N_m} \times$$
$$\times \left[1 + \left(2\frac{V_1}{V_m} - 1\right)\frac{N_1}{N_m} + \left(2\frac{V_2}{V_m} - 1\right)\frac{N_2}{N_m} + \dots \right.$$
$$\left. \dots + \left(2\frac{V_n}{V_m} - 1\right)\frac{N_n}{N_m}\right]^{-1} =$$
$$= \frac{A_{mk}\dfrac{N_k}{N_m}}{1 + \sum\limits_{\substack{i=1\\ i\neq m}}^{n} A_{mi}\dfrac{N_i}{N_m}}. \qquad (10)$$

The thermal conductivity of the n-component solution

$$\lambda = \frac{\lambda_1\left(2\dfrac{V_1}{V_m} - 1\right)\dfrac{N_1}{N_m}}{1 + \sum\limits_{\substack{i=1\\ i\neq m}}^{n}\left(2\dfrac{V_i}{V_m} - 1\right)\dfrac{N_i}{N_m}} +$$
$$+ \frac{\lambda_2\left(2\dfrac{V_2}{V_m} - 1\right)\dfrac{N_2}{N_m}}{1 + \sum\limits_{\substack{i=1\\ i\neq m}}^{n}\left(2\dfrac{V_i}{V_m} - 1\right)\dfrac{N_i}{N_m}} + \dots$$
$$\dots + \frac{\lambda_n\left(2\dfrac{V_n}{V_m} - 1\right)\dfrac{N_n}{N_m}}{1 + \sum\limits_{\substack{i=1\\ i\neq m}}^{n}\left(2\dfrac{V_i}{V_m} - 1\right)\dfrac{N_i}{N_m}}. \qquad (11)$$

It is clear from (10) that if the molecular volumes of all the components are equal, the collision probability for any component is equal to its concentration. Then, in accordance with (11), the concentration dependence of the solution conductivity will be additive. With increase in the difference of molecular volumes and the thermal conductivity of the pure components the deviation of the solution conductivity from additivity increases and may reach large values.

In order to test the equation obtained we conducted experiments on 16 three-component, 2 four-component, and 2 five-component solutions.

Data on the thermal conductivity of some of these solutions are presented in Fig. 3 as a function of mole concentration. Values of the conductivity of the pure component are plotted along one of the vertical axes, and along the other axis values of the conductivity of the two- or three-component solution of given constant composition, whose mean molecular mass was determined from the formula

$$M_{\text{mean}} = \frac{1}{\sum\limits_{i=1}^{n}\dfrac{p_i}{M_i}}. \qquad (12)$$

Mole fractions of the components are plotted along the horizontal axis.

This graph makes it possible to trace the concentration dependence of the thermal conductivity of multicomponent solutions by analogy with binary systems.

For some systems we prepared binary solutions of different concentrations. Therefore several curves on the graph may correspond to the same three-component solution.

The experimental values were compared with those calculated from (11). The mean deviation for 20 solutions was 1.1%, while the maximum deviation did not exceed 5.2%.

Using our data, we tested the equation recommended by Cecil and Munch for computing the thermal conductivity of three-component systems. The deviation from the experimental values may reach 30% or more for aqueous solutions.

In conclusion we note that in deriving Eqs. (8) and (11) we assumed a completely random distribution of the molecules. Further research should aim at a fuller and more comprehensive allowance for the intermolecular forces and the structure of the solution.

NOTATION

λ is the thermal conductivity of the solution; λ_1, λ_2, and λ_n denote the thermal conductivities of components; N_1, N_2, and N_n are the mole fractions of components; V_1, V_2, and V_n are the molecular volumes of components; p_i is the mass fraction of components; M_i is the molecular mass of components; $\delta\lambda$ is the difference between the experimental value of the thermal conductivity of the solution and the value computed from the additivity rule; a is the proportionality factor; ν is the molecular collision frequency; W is the probability of collision of molecules of the same type; $A_{mi} = (2V_i/V_m - 1)$ is a dimensionless quantity weakly dependent on temperature; m is the subscript denoting component with least molar volume.

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