THERMAL CONDUCTIVITY OF LIQUID MIXTURES

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This paper adopts a phenomenological approach and presents a new model of a mixture of nonreacting liquids as a mixture of two interpenetrating continuous media. An analytical relationship for calculating the effective thermal conductivity of a mixture of liquids is given and the results are compared with experimental data.

We will consider the process of heat transfer through liquid mixtures of two classes—solutions and emulsions. Solutions are mixtures of two or several substances which are mixed molecularly. Emulsions are disperse systems consisting of two or more immiscible liquids, which are distributed in the form of drops in one of the liquids.

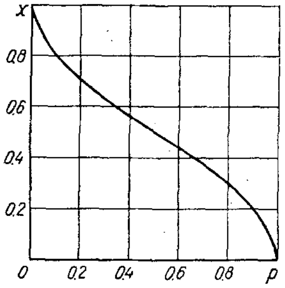

Fig. 1. Graph of function x = x(p).

Transfer processes in liquid mixtures are usually regarded from the viewpoint of molecular kinetic theory, which can reveal the structure of the effective thermal conductivity of the mixture. There is a fairly complete review of such investigations in [1, 2]. Heat-transfer processes have not yet been sufficiently well investigated even in homogeneous liquids and, hence, the theoretical formulas for the calculation of their thermal conductivities are inadequate. The problem becomes even more complicated in the case of analysis of transfer through liquid mixtures. The absence of a sufficiently reliable analytical method of calculating the thermal conductivity of liquid mixtures necessitates the derivation and extensive use of empirical relationships. The best known empirical formula is that of Filippov and Novoselova [3], which gives good agreement (to within 1–5%) with the experimental data of various authors:

$$\lambda = \lambda_1 (1 - n_2) + \lambda_2 n_2 - 0.72 (\lambda_2 - \lambda_1) n_1 (1 - n_2). \qquad (1)$$

There is another possible approach to the analysis of heat transfer through binary liquid mixtures. This approach is based on their representation in the form of a mechanical mixture of two nonreacting interpenetrating continuous media.

We regard each liquid component as a continuous medium with a thermal conductivity equal to that of the liquid at the given temperature. Such a mixture of two liquids will have a different structure according to the physical properties of the components. If the mixture forms an emulsion its structure will consist of separate inclusions of one component surrounded by the binding substance of the second component. The effective thermal conductivity λ of mixtures of such structure can be calculated from Odelevskii's formula for matrix systems of solid mixtures [4]

$$\lambda = \lambda_1 \left(1 - \frac{p}{1/(1-\nu) - (1-p)/3} \right), \quad \nu = \frac{\lambda_2}{\lambda_1}. \qquad (2)$$

The subscripts of the components in (2) cannot be interchanged, since this leads to incorrect results owing to the geometrical nonequivalence of the components [4].

If the mixture of liquids forms a solution, then the previous model does not describe its structure, since the molecules of the solution are not localized at any particular point in space and can move freely throughout the volume of the mixture. Hence, the two components at any instant form two spatial continuous interpenetrating lattices. Heat transfer through a mixture of such structure was investigated in [5], where the author presented the following relationship for the determination of the effective thermal conductivity of the mixture:

$$\lambda = \lambda_1 \{ x^2 + \nu (1-x)^2 + 2\nu x (1-x) / [\nu x + (1-x)] \}, \qquad (3)$$

where x is a lattice parameter connected with the volume concentration by the relationship

$$p = 2x^3 - 3x^2 + 1, \qquad (4)$$

which is shown in graphical form in Fig. 1.

The suitability of the proposed model of liquid binary solutions and formulas (3) for the determination of their effective thermal conductivity was determined by a comparison of the theoretical and experimental values of the effective thermal conductivity of about thirty different mixtures of normal and associated liquids. Figures 2 and 3 compare the experimental data (points) from [1, 3, 6, 7] with the values calculated from formula (3) (curves). The solvent and solute formed the following combinations of investigated liquids: normal + normal, normal + associated, and associated + associated. The experimental results for the first two kinds of mixture (Fig. 2) show a systematic deviation and lie above the theoretical values. The maximum deviation—for the methylformate + carbon tetrachloride mixture—was 14%. The mean deviation for the different mixtures varied from 2 to 7%.

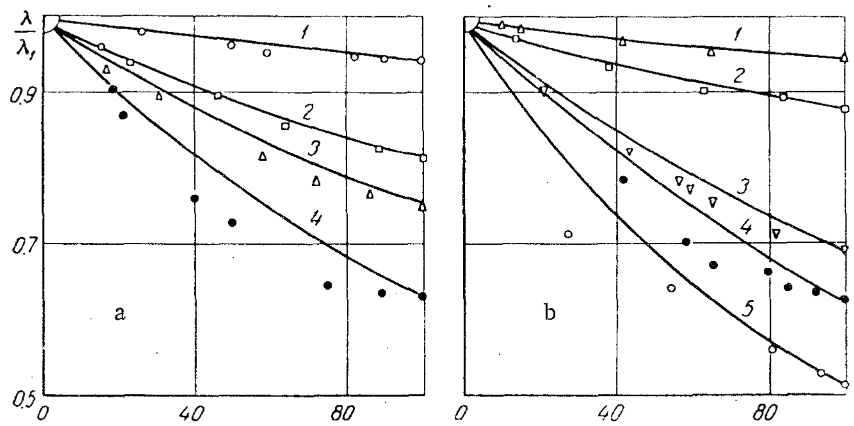

Fig. 2. Effective thermal conductivity of: a) a binary mixture of normal liquids (1—chloroform + carbon tetrachloride, ν = = 0.94; 2—ethylformate + toluene, 0.812; 3—methylformate + + benzene, 0.748; 4—methylformate + chloroform, 0.633); b) a binary mixture of associated and normal liquids (1—methanol + methylformate, ν = 0.95; 2—acetone + benzene, 0.88; 3—isobutanol + methylformate, 0.68; 4—methanol + chlorobenzene, 0.62; 5—methanol + carbon tetrachloride, 0.51). Volume concentration p (x axis) in %.

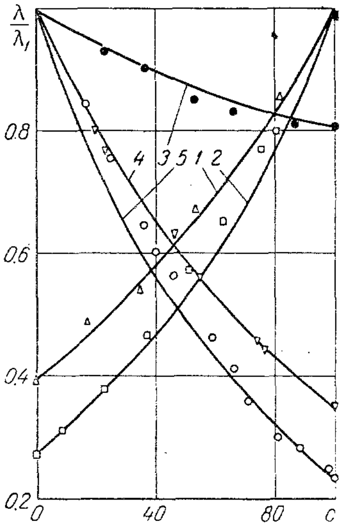

Fig. 3. Effective thermal conductivity of binary mixture of associated liquids: 1) acetone + water; 2) ethanol + water; 3) acetone + + isobutanol; 4) water + + methanol; 5) water + isopropanol. On x axis p in %.

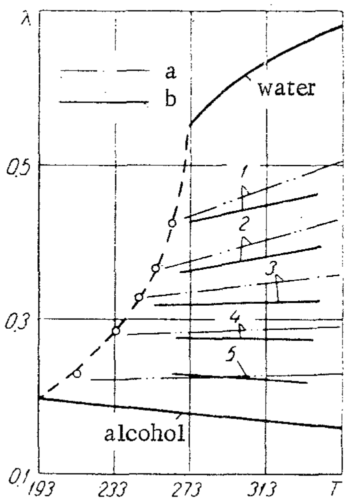

Fig. 4. Effective thermal conductivity λ (W/m · deg) of a solution of ethanol in water as a function of the temperature T (°K) and the volume concentration p (%): 1) 25; 2) 38; 3) 50; 4) 65; 5) 80; a) experimental data; b) data calculated from (3).

Slightly higher experimental values than the theoretical values were characteristic of mixtures of two associated liquids (Fig. 3). The maximum deviation from the experimental data was −7% (for the ethanol + water mixture) and the mean deviation was 0 to −3%. In addition to the binary mixtures shown in Figs. 2 and 3 we compared the theoretical and experimental values of the effective thermal conductivity for mixtures in which the components formed the following combinations: carbon tetrachloride + benzene, nitrobenzene, or ethylformate, benzene + toluene (the two components are normal liquids); isobutanol + carbon tetrachloride, chloroform + ethanol, methylformate + acetone (one of the components is a normal liquid and the other is an associated liquid); water + n-propanol, acetone + + isobutanol, water + glycerol; water + ethylene glycol, water + propylene glycol (the two components are associated liquids). Figure 4 shows the experimental data taken from [1] and the theoretical curves plotted from formula (3).

From the results of this investigation we can conclude that in the analysis of transfer processes in liquid mixtures their structure must be taken into consideration. A comparison of the theoretical and experimental data for the effective thermal conductivity of liquid mixtures shows that the proposed model of a liquid mixture as a system of interpenetrating continuous media satisfactorily predicts heat transfer in such systems. This confirms the great influence of the structure on transfer processes.

NOTATION

λ is the effective thermal conductivity of liquid mixture; λ_1, λ_2 are the thermal conductivity of components; n_1, n_2 are the weight concentration of components; p is the volume concentration of second component forming inclusions; x is the geometric parameter of structure.

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