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MEASUREMENT OF THE THERMAL ACTIVITY OF DIELECTRIC LIQUIDS WITH AN ACCURACY OF $\sim 10^4$

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A method of measuring small ($\sim 10^{-4}$) relative changes in the thermal activity of liquids is developed. A theoretical substantiation of its accuracy is given based on an investigation of the factors responsible for errors in the experiment. Results of experiments on a study of the temperature dependence of the thermal activity of a solution of polystyrene in toluene are reported.

Introduction. In the practice of thermophysical measurements investigations of parameters measured with a high accuracy are of particular interest: thermal conductivity λ, thermal diffusivity a, and thermal activity [1; 2, p. 37]

$$\varepsilon = \sqrt{\rho C_p \lambda}\ . \tag{1}$$

High-accuracy measurements are needed for investigations of phase changes and the influence of electric, magnetic, temperature, and other fields on a substance.

According to the definition dating back to L. Brillouin, by accuracy is meant the ratio of the measured quantity ε to the uncertainty range of its measurement $\delta\varepsilon$ [3]. Here, a magnitude equal to the methodological error is taken as the uncertainty range $\delta\varepsilon$. As is easy to see, in this case the accuracy will be the reciprocal of the relative methodological error.

It is suggested that the two types of error (instrumental and methodological) do not differ much from each other in absolute value (in our case the instrumental error is approximately 10% of the methodoological one). The former determines the minimum value of recorded changes in the quantity investigated, while the latter indicates the certainty of its quantitative measurement.

Present-day traditional methods generally provide, in the best case, an accuracy of $\sim 10^3$ for measured parameters [4].

We consider the prospects for attaining a high accuracy of measurements within the framework of the method of short-duration measurements in the stage of an irregular thermal regime [5]. The main advantages of this method include good correspondence between the physical model of measurement and its mathematical idealization, the absence of the necessity of careful thermostating of the sample investigated, and the possibility of applying a high reference voltage to a high-resistance resistor implementing the functions of a source and a receiver of heat.

1. Schemes of the Experiment. The present method provides two ways of conducting the experiment:

1) determination of the thermal activity ε of an unknown liquid by the thermal activity ε_{ref} of a reference liquid;

2) determination of small increments of the thermal activity $\delta\varepsilon$ with quasistationary or rapid changes in any external or internal thermodynamic parameters (small changes in the concentration of solutions, temperature changes, switching a magnetic field or an electric field on or off, and so on).

As the reference and measured liquids, the same liquid is used, the thermal activity of which in the undisturbed state is known a priori and is ε_{ref}, and upon imposing disturbances it deviates by a small value $\Delta\varepsilon$ so that the changed value of the thermal activity is $\varepsilon = \varepsilon_{\text{ref}} + \delta\varepsilon$ and $\delta\varepsilon << \varepsilon_{\text{ref}}$.

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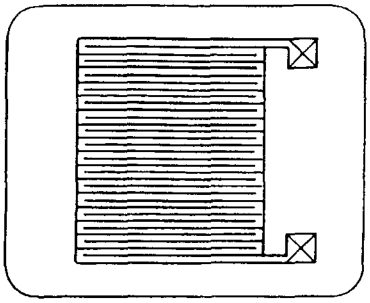

Fig. 1. Illustration of a pickup with a zigzag-type resistive element.

The first scheme of the experiment is well known [6] and the error obtained within its framework is approximately 1% of the measured quantity, which is satisfactory for ordinary technical requirements.

The second of these schemes is advantageous, first of all, for a physical experiment, and its practical value is related foremost to attaining a high sensitivity to a change in the quantity measured. From the viewpoint of the possibilities of the experiment it shows promise in distinguishing states of the investigated object that differ in thermal activity by hundredths and even thousandths of a percent, which corresponds to an accuracy $\varepsilon/\delta\varepsilon \sim 10^4-10^5$.

2. Schematic of the Experimental Setup. In organizing high-accuracy experiments it is advantageous to use a differential measurement scheme [5].

Short-duration measurements of the thermal activity in the stage of an irregular thermal regime are accomplished by means of thin-film resistance sensors (glass, quartz, polyamide, etc. can serve as the material of the substrate on which a conducting layer in the form of a foil is sprayed or glued; as the material to be deposited nickel is commonly used). To increase the sensitivity of the method it is reasonable to increase the length of the resistance paths of the sensors. This circumstance determines the geometry of their arrangement on the substrate (Fig. 1).

In the course of measurement the sensor is brought in contact with the substance investigated and is heated by a rectangular current pulse. In one version of a measuring cell the sensor is mounted on two isolated current leads in a test tube filled with the liquid investigated. In another version the sensor is located on the bottom of a small flat cuvette in which a thin layer of the investigated liquid is poured.

The pulse duration is determined by the parameters of the sensor and the properties of the medium. To decrease the influence of convection, it is better to choose rather short pulses. On the other hand, they must provide such sensor heating as to create as large a useful signal as possible (here, for a linear approximation of the dependence of the sensor resistance on the temperature increment to be valid, heating must not exceed $1-5^0$). Simultaneously, the change in the temperature of the resistive element under the action of the heating pulse is measured, which gives information about the thermal activity of the substance investigated.

A schematic of the setup is depicted in Fig. 2. A generator sends rectangular pulses of length about 10^{-4} sec and voltage about 2 V to a high-voltage transistor, which opens at this moment and connects a 300-V power source to the measuring bridge circuit. Two flat pickups (a measuring element and a compensation pickup) are connected to two arms of the bridge circuit. A difference signal from the bridge scheme arrives at the differential inlet of an oscillograph operating in a waiting regime. At this moment the signal is displayed on a screen. By adjusting resistors R_1 and R_3 an operator succeeds in compensating the difference signal, and the resistance values set are used in calculations (R_2 and R_4 remain unchanged).

In the approximation of a linear dependence of the sensor resistance on the temperature the thermal activity in measurement based on the compensation-type circuit is calculated by the relation [6]

$$\varepsilon = (\varepsilon_{\rm ref} + \varepsilon_{\rm s}) \left(\frac{R_{10}}{R_1}\right)^3 \left(\frac{R_{\rm m}}{R_{0\rm m}}\right) - \varepsilon_{\rm s} , \qquad (2)$$

where the resistances R_{10} and $R_{0\rm m} = R_{10} - R_{30}$ are determined in compensation of the bridge circuit, the measuring pickup of which is brought in contact with the reference liquid (with the thermal activity $\varepsilon_{\rm ref}$ being known a priori),

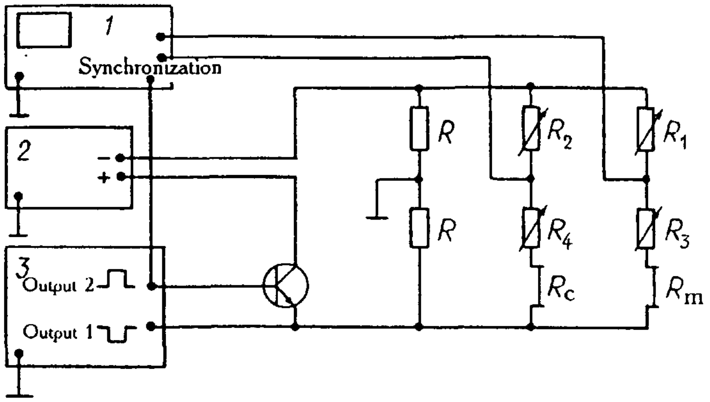

Fig. 2. Schematic of the experimental setup: 1) oscillograph with a differential input; 2) power source (300 V); 3) generator of synchronized low-voltage pulses of two different polarities (ouput 1 and output 2). The resistances R of the two resistors of the voltage divider exceed those of the bridge resistors by approximately an order of magnitude.

while the resistances R_1 and $R_m = R_1 - R_3$ are determined when the bridge circuit, the pickup of which interacts with the liquid whose thermal activity ε is unknown, has reached compensation. By ε_s in formula (2) is understood the thermal activity of the substrate.

In a first approximation in small changes in the quantities entering formula (2) the latter can be represented as

$$\frac{\delta\varepsilon}{\varepsilon_{\text{ref}} + \varepsilon_s} = \frac{\delta R_m}{R_m} - 3\frac{\delta R_1}{R_1} = \frac{\delta R_1 - \delta R_3}{R_1 - R_3} - 3\frac{\delta R_1}{R_1}, \tag{3}$$

where δR_1 and δR_3 are the changes in the resistance of the variable resistors R_1 and R_3 that must be achieved in order to provide compensation of the bridge scheme upon changing the thermal activity of the liquid investigated by a small value $\delta\varepsilon$. Within the framework of the experiment this implies that if, for instance, on applying any external field to the liquid investigated the compensation of the bridge scheme has been disturbed slightly (here, to attain compensation it is necessary to change the resistance of the variable resistors), then the relative change in the thermal activity is determined by formula (3).

3. Main Components of the Methodological Error [7]. The violation of the condition of one-dimensionality of the problem and the influence of the two-dimensionality of the temperature field can be evaluated by the following relation:

$$\frac{\Delta\varepsilon}{\varepsilon} = \frac{|\sqrt{\text{Fo}_m} - \sqrt{\text{Fo}_c}|}{\sqrt{\pi}}, \tag{4}$$

where $\text{Fo} = a_s t/L^2$ is the Fourier number; a_s is the thermal diffusivity of the sensor substrate.

As is seen from formula (4), this error can be minimized by choosing measuring and compensation pickups with characteristics as close as possible.

The violation of the linearity of the heat-conduction equation adopted in the linearized problem and the influence of its nonlinearity can be determined by the formula

$$\frac{\Delta\varepsilon}{\varepsilon} = \left| T_{0m}\left(\frac{\alpha_m}{6} - \beta_m\left(\frac{\pi}{4} - \frac{1}{3}\right)\right) - T_{0c}\left(\frac{\alpha_c}{6} - \beta_c\left(\frac{\pi}{4} - \frac{1}{3}\right)\right)\right|, \tag{5}$$

where T_0 is the initial temperature of the pickups; α and β are the coefficients of the linear dependence of the thermal conductivity and heat capacity of the liquids on the temperature according to the relations

$$\lambda = \lambda_0 (1 + \alpha \Delta T), \tag{6}$$

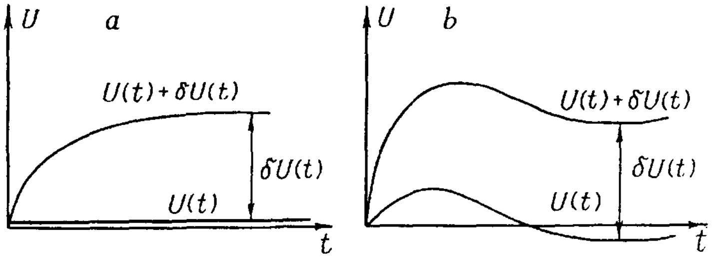

Fig. 3. Shapes of the useful signal on the oscillograph screen: a) ideal case; b) real case.

$$C_p = C_{p0}(1 + \beta\Delta T). \tag{7}$$

The influence of the intrinsic heat capacity of the sensor under the assumption of closeness of the initial temperatures of the measuring and compensation pickups can be evaluated by the expression

$$\frac{\Delta\varepsilon}{\varepsilon} = \frac{\sqrt{\pi}}{6}\left|\frac{3\mu_{\mathrm{m}}^2 - 1}{\mu_{\mathrm{m}}\sqrt{\mathrm{Fo}_{\mathrm{m}}}} - \frac{3\mu_{\mathrm{c}}^2 - 1}{\mu_{\mathrm{c}}\sqrt{\mathrm{Fo}_{\mathrm{c}}}}\right|. \tag{8}$$

Here $\mu = \varepsilon_{\mathrm{res}}/\varepsilon_{\mathrm{s}}$ is the ratio of the thermal activities of the metal resistive element of the pickup and the substrate.

As follows from formula (8), the influence of the intrinsic heat capacity of the pickup can be neglected if

$$\mathrm{Fo} \gg \mu^2. \tag{9}$$

Here, the methodological error is determined by the formula

$$\frac{\varepsilon}{\delta\varepsilon} = \frac{\varepsilon}{\Sigma\Delta\varepsilon}, \tag{10}$$

where the summation in the denominator is done over the contributions of the factors enumerated above and here is about 10^4.

4. Features of a Visual Account of Methodological Errors. In using present-day measuring devices the instrumental error can be decreased to the threshold of thermal noise in pickups and electronic circuits. Therefore, hereinafter the instrumental error will be assumed to be not higher than the methodological one. The form of the curve describing the useful signal on the oscillograph screen will be identified sufficiently clearly to determine visually the methodological deviations of the actual signal from the ideal one. These deviations are regular and systematic and are repeated in each pulse provided the thermophysical parameters of the medium remain unchanged, since methodological errors are described uniquely by the parameters of the system.

Figure 3a depicts ideal time scanning of the useful signal in a position close to full compensation of the bridge circuit ($U(t)$ is a line parallel to the time axis) and in a position where a small change occurred in the thermophysical properties of the liquid investigated that has resulted in an increment $\delta U(t)$ in the signal. The signal increment is proportional to the change in pickup heating δT due to the change in the conditions of heat exchange with the medium investigated (here, the voltage in the pulse applied to the bridge circuit is, naturally, assumed to be the same).

In the case of a plane pickup and the ideal model the time dependence of the signal increment is as follows:

$$\delta U \sim \delta T \sim \sqrt{t} \quad \text{or} \quad \delta U = F\sqrt{t}, \tag{11}$$

where the dimensional function F determines the dependence of the signal increment on all other parameters (with the exception of time).

Introducing the increments of the resistance of the variable resistors R_1 and R_3 in the arms of the bridge scheme in the form δR_1 and δR_3, respectively, the magnitude of the signal can be returned to the initial one before the indicated change in the thermophysical properties of the medium, and then these increments can be used to calculate the change in the thermal activity $\delta\varepsilon$.

Thus, by the value of δU one can judge the change $\delta\varepsilon$ in the quantity investigated.

In the ideal case the time dependence of the signal increment has the form of (11). In reality, however, deviations from the ideal model that are manifested as the presence of a more complicated dependence on time are observed (Fig. 3b), so that instead of (11) we have

$$\delta U = F(\sqrt{t} + f(t)), \tag{12}$$

where $f(t)$ is the deviation of the actual dependence from the ideal one. It is important to bear in mind that $f(t)$ is not a random function but is a function completely determined by the parameters of the system. From the viewpoint of solving the corresponding heat-conduction problem, the quantity $f(t)$ consists of all remaining terms of the series presenting the time dependence of the signal that take into account various disturbing factors (the deviation from one-dimensionality of the problem, etc.).

Thus, the function $f(t)$ is related to the methodological error $\Pi_{\mathrm{m.e}}$, i.e.,

$$\max |f(t)| \sim F\,\Pi_{\mathrm{m.e}}. \tag{13}$$

The possibility of measuring the increment $\delta\varepsilon$ in a real case, as in the ideal one, is based on the possibility of returning the signal changed by δU (the upper curve in Fig. 3b) to its initial form (the lower curve in Fig. 3b) by introducing resistance increments of the variable resistors in the arms of the bridge circuit δR_1 and δR_3. By changing the resistances of these resistors, one can control the amplitude of the signal, with the shape of the latter remaining unchanged, which allows the signal to be returned to its initial form, i.e.,

$$\delta U = \delta U(R_1, R_3, \varepsilon) = F(R_1, R_3, \varepsilon)(\sqrt{t} + f(t)), \tag{14}$$

where $F(R_1, R_3, \varepsilon)$ is the signal amplitude and $\sqrt{t} + f(t)$ is its time dependence. The initial value is $\delta U \sim 0$.

If ε is changed by $\delta\varepsilon$, the signal increment is

$$\delta U = \frac{\partial \delta U(R_1, R_3, \varepsilon)}{\partial \varepsilon}\,\delta\varepsilon\,(\sqrt{t} + f(t)). \tag{15}$$

In designing a measuring cell and calculating the regime of its heating, we tried to approach, as much as possible, the ideal model in which the time dependence of the signal is $\sqrt{t}$. Therefore in the real model a situation is provided in which the specific contribution of a dependence of the type $\sqrt{t}$ prevails over the disturbing factors $f(t)$ so that the main contribution to δU is made precisely by the dependence $\sqrt{t}$.

By changing the resistances R_1 and R_3 slightly, one can return the signal to its initial (zeroth) form if these changes δR_1 and δR_3 satisfy the relation

$$\frac{\partial \delta U(R_1, R_3, \varepsilon)}{\partial \varepsilon}\,\delta\varepsilon = \frac{\partial \delta U(R_1, R_3, \varepsilon)}{\partial R_1}\,\delta R_1 + \frac{\partial \delta U(R_1, R_3, \varepsilon)}{\partial R_3}\,\delta R_3. \tag{16}$$

Instrumental errors create additional disturbances that are manifested as noise and interference causing broadening of the curve and imposing on it extraneous periodic and nonperiodic oscillations.

Experience has shown that for reliable measurement of $\delta\varepsilon$ its instrumental errors must be smaller than the methodoloogical ones by at least an order of magnitude. In this case reliable recognition of the curve shape and, consequently, the possibility of returning the signal to its initial magnitude are provided after a small change in the thermal activity of the medium.

5. Instrumental Error. In order to record thermal activity at the level of accuracy that is possible within the framework of the given implementation of the mathematical model, it is necessary to provide the corresponding level of sensitivity of the measuring devices.

The useful-signal voltage on the measuring pickup in the bridge circuit (see Fig. 2) near the position of compensation is of the form

$$U_{\mathrm{m}} = \frac{\delta R_{\mathrm{m}} U_0}{4R_1}, \tag{17}$$

where U_0 is the voltage of the power source, and the resistance increment of the pickup δR_{m} in a linear approximation is determined by the formula

$$\delta R_{\mathrm{m}} = \alpha_{\mathrm{m}} R_{\mathrm{m}0}\, \delta T_{\mathrm{m}} \,. \tag{18}$$

(α_{m} is the temperature coefficient of resistance of the heating element of the pickup.)

The temperature increment of a plane pickup is

$$\delta T_{\mathrm{m}} = R_{\mathrm{m}} \left(\frac{U_0}{2R_1} \right)^2 \frac{\sqrt{t}}{S\varepsilon \sqrt{\pi}} \,. \tag{19}$$

Substituting expressions (18) and (19) into formula (17) and assuming that $\delta R_{\mathrm{m}} << R_{0\mathrm{m}}$, we arrive at

$$U_{\mathrm{m}} = \frac{\alpha_{\mathrm{m}} R_{\mathrm{m}0}^2 U_0^3 \sqrt{t}}{16 \sqrt{\pi}\, \varepsilon S R_1^3} \,. \tag{20}$$

The instrumental accuracy of the experimental setup in measurements by means of a bridge circuit can be evaluated by the ratio of the useful signal (20) to the oscillograph sensitivity δU, i.e., the minimum change in the signal (in voltage) recorded by the differential input of the oscillograph:

$$\frac{U_{\mathrm{m}}}{\delta U} = \frac{\alpha_{\mathrm{m}} R_{\mathrm{m}0}^2 U_0^3 \sqrt{t}}{16 \sqrt{\pi}\, \varepsilon S R_1^3 \delta U} \,. \tag{21}$$

In the measurements use was made of a pickup with resistive paths arranged as shown in Fig. 1 (the path width was about 0.5 mm; its thickness was 500 Å; the total length of the path was about 20 cm; the material used was aluminum sprayed on a lavsan film of thickness 30 μm). At $S = 10^{-4}$ m^2, $R_1 = 700$ Ω, $R_{0\mathrm{m}} = 220$ Ω, $\varepsilon = 2000$ W·sec$^{1/2}$/(m^2·K), $t = 10^{-1}$ sec, $\alpha_{\mathrm{m}} = 5 \cdot 10^{-3}$, $U_0 = 300$ V, $\delta U = 10^{-5}$ V, the instrumental accuracy calculated by formula (21) was about 10^5, which exceeded the methodological accuracy determined previously by an order of magnitude.

Evaluation of thermal noise by the Nyquist criterion [8, p. 7] showed that in the measuring element it begins to manifest itself at a sensitivity of the zero indicator of about a microvolt. This is one-two orders of magnitude below the typical sensitivity of an oscillograph and therefore can be neglected.

From formula (21) it follows that the voltage of the power source and the pickup resistance are the dominant factors that increase the sensitivity of the measuring circuit.

In the final analysis, recording of limitingly small changes in the thermal activity of liquids is determined by the sensitivity of the zero indicator, and quantitative measurement of these changes is made with an error equal to the methodological one.

Indeed, if with a field applied to the substance investigated or with a change in its temperature a small deviation of the thermal activity occurs, then the curve on the screen characterizing the useful signal changes slightly both in shape and in position. The possibility of noting this deviation is determined by precisely the instrumental error. Having noticed a change in the curve compared to its initial position and paying no attention to noise entering the confidence interval, the operator can return the signal observed on the screen to the previous form by changing the resistances in the bridge arms. The accuracy of this operation is again mainly attributable to the instrumental error.

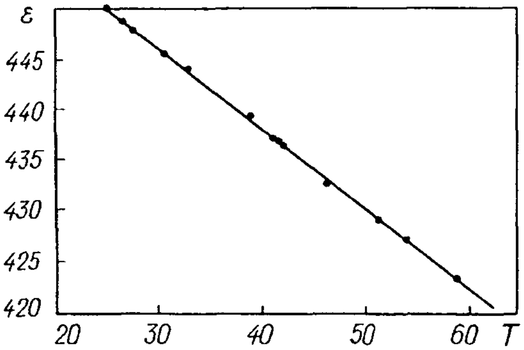

Fig. 4. Thermal activity of a 5% solution of polystyrene in toluene.

6. Experiments. It is obvious that the possibility of detecting deviations of the measured quantity following the second scheme (see Sec. 1) at the level $\delta\varepsilon/\varepsilon \sim 10^{-4}-10^{-5}$ corresponds to an accuracy of 10^4-10^6 for measurement by the first scheme. This is related to the fact that the minimally recorded change $\delta\varepsilon$ in the measured quantity also serves as an estimate of the uncertainty interval that enters the expression for accuracy [3].

Therefore, knowing $\delta\varepsilon$ in the second of the enumerated schemes of experiment, we can judge the accuracy of the method using first scheme and, vice versa, by the accuracy attained in the first scheme of experiment one can judge the minimum change in the quantity measured that can be recorded on the setup used.

A series of experiments was conducted on measurement of the thermal activity of solutions of polystyrene in toluene at different concentrations (the first scheme of experiment). Figure 4 reproduces the result of one of these experiments (a 5% solution of polystyrene in toluene at a degree of polystyrene transformation of about 90%). The solid line smooths out the experimental data. The standard deviation is about 0.05 $\mathrm{W \cdot sec^{1/2}/(m^2 \cdot K)}$ or approximately 0.01% of the absolute value of the quantity measured and corresponds to a minimum accuracy of $\sim 10^4$. This accuracy provides the possibility of recording minimum changes in the thermal activity not exceeding 10^{-4} in absolute value, which has been confirmed: the setup turned out to be sensitive to changes in the thermal activity equal to 0.05 $\mathrm{W \cdot sec^{1/2}/(m^2 \cdot K)}$, which corresponds to a temperature increment of approximately 0.1°.

NOTATION

C_p, specific heat of the liquid at constant pressure; L, width of the resistive path; ρ, liquid density; S, area of the resistive element of the plane pickup; t, duration of the heating pulse; the symbol δ denotes the uncertainty interval of the physical quantity ($\delta\varepsilon$, δU) and the variation of the physical parameter (δR_1 and so on) in specified cases; the symbol Δ denotes the partial contribution of some factor to the uncertainty of the quantity measured ($\Delta\varepsilon$). Subscripts: m, measuring pickup; c, compensation pickup; s, substrate; res, resistive element of the pickup; m.e, methodological error; 0, initial value of the physical quantity.

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