A PULSE METHOD OF STUDYING THE THERMOACTIVITY
OF DIELECTRIC LIQUIDS

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A method is proposed here for measuring the thermoactivity of dielectric liquids and solutions. Experimental results are shown which have been obtained by thermoactivity measurements during the mixing of two dielectric liquids. The possibilities of using this method for a range of applications are discussed.

Measuring the thermoactivity of dielectric liquids ($\varepsilon = \sqrt{\rho c \lambda}$) is undoubtedly of great interest to chemical engineering and related research. Such measurements indicate the concentration of dielectric binary solutions, and they provide information about the kinetics of the reactions which are taking place. These measurements can also be useful for studying the kinetics of polymer transformations.

The gist of the method is as follows. Immersed in a dielectric is a thin-film transducing device in the form of a metal film ($\sim 0.1\ \mu$ thick) deposited on a dielectric substrate plate on which a constant heat flux (q = const) will appear when a square-wave electric current pulse is transmitted. The design and the technology of such transducers are discussed in [1]. At a pulse width of $100\ \mu\sec < \tau < 1000\ \mu\sec$ it is permissible to disregard the thermal capacity of the metal film and to consider the problem as one of a homogeneous medium. The solution to the heat conduction equation [3] for $x = 0$, where the metal film is located, will be

$$t = \frac{2q\sqrt{\tau}}{(\varepsilon_s + \varepsilon_0)\sqrt{\pi}},$$ (1)

with τ being the time of thermal flux action and t being the temperature rise above the initial level.

If through the film of the transducer is passed a train of identical pulses of width τ_0 and of such a frequency that the temperature of the substrate—liquid boundary surface becomes equal to the initial temperature t_0, then the temperatures t at the end of each pulse ($\tau = \tau_0$) will provide information about changes in the thermoactivity of the liquid volume contained within a thin boundary layer. Indeed, letting $\varepsilon = \varepsilon_0 + \Delta \varepsilon_\tau$, we have by the end of a single pulse a temperature rise due to the change in the thermoactivity of the liquid:

$$\Delta t = \frac{2q\sqrt{\tau_0}}{\sqrt{\pi}}\left(\frac{1}{\varepsilon_s + \varepsilon_0 + \Delta \varepsilon_\tau} - \frac{1}{\varepsilon_s + \varepsilon_0}\right).$$ (2)

The change in thermoactivity follows from (2):

$$\Delta \varepsilon_\tau = -\frac{\Delta t\,(\varepsilon_s + \varepsilon_0)^2}{\dfrac{2q\sqrt{\tau_0}}{\sqrt{\pi}} + \Delta t\,(\varepsilon_s + \varepsilon_0)}.$$ (3)

The surface temperatures are determined by measuring the resistance of the metal film and by converting changes in this resistance into electric signals. Let us analyze the electric measurement circuit. The test stand consists of a model G-5-2A pulse generator controlled by the plate current of the 6N5S triode. This set-up is described in [3]. The plate circuit includes a potentiometer bridge R_1, R_2, R_3, R_4 (Fig. 1)
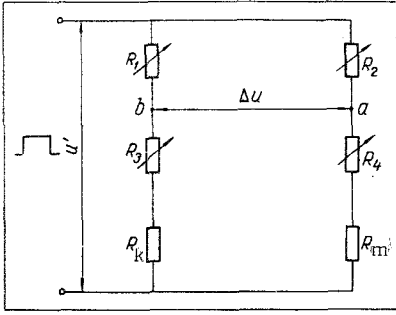
Fig. 1. Circuit diagram of the test bridge.

with two transducers R_k and R_m, each of the latter in one of the parallel arms of the bridge. Transducer R_k is located in air, transducer R_m is immersed in the dielectric liquid $\varepsilon = \varepsilon_0$. As electric pulses are applied, the metal films of both transducers heat up. Inasmuch as the temperature of both changes according to the same law $t \sim \sqrt{\tau}$ and their resistances also change in the same relation, there is a possibility that during the flow of current pulses the voltage between points a and b may become zero.

Signal balancing is achieved by means of potentiometers R_1, R_2, R_3, R_4. As a pulse train of frequency ~ 0.1 Hz is applied to the bridge, the change in thermoactivity ε_0 of the liquid produces an unbalance of the bridge and, as a result, a signal appears between points a and b.

As is well known

$$u_0 = \frac{u'R_1}{R_1 + R_3 + R_K} - \frac{u'R_2}{R_2 + R_4 + R_m} \,, \tag{4}$$

where u' is the voltage applied to the bridge. We will expand u into a series of terms in the variables R_k and R_m:

$$u = \left(\frac{u'R_1}{R_1 + R_3 + R_k} - \frac{u'R_2}{R_2 + R_4 + R_m} \right) - \frac{u'R_1 \Delta R_k}{(R_1 + R_3 + R_k)^2}$$

$$+ \frac{u'R_2 \Delta R_m}{(R_2 + R_4 + R_m)^2} + \frac{u'R_1 \Delta R_k^2}{(R_1 + R_3 + R_k)^3} - \frac{u'R_2 \Delta R_m^2}{(R_2 + R_4 + R_m)^3} + \ldots \tag{5}$$

As long as inequalities

$$\frac{\Delta R_k}{R_1 + R_3 + R_k} \ll 1, \tag{6a}$$

$$\frac{\Delta R_m}{R_2 + R_4 + R_m} \ll 1 \tag{6b}$$

hold true, one may break off the series (5) after the first four terms and write

$$\Delta u = u_0 + \left[\frac{u'R_2 \Delta R_m}{(R_2 + R_4 + R_m)^2} - \frac{u'R_1 \Delta R_k}{(R_1 + R_3 + R_k)^2} \right], \tag{7}$$

where u_0 is a small initial voltage due to imperfect bridge balance.

Since

$$\frac{u'R_2}{R_2 + R_4 + R_m} \simeq \frac{u'R_1}{R_1 + R_3 + R_k} \,,$$

hence

$$\Delta u = u_0 + \frac{u'R_2^2}{(R_2 + R_4 + R_m)^2} \left(\frac{\Delta R_m}{R_2} - \frac{\Delta R_k}{R_1} \right). \tag{8}$$

The condition for balance is that the second term on the right-hand side of (8) is equal to zero, or

$$\frac{\Delta R_m}{R_2} = \frac{\Delta R_k}{R_1} \,. \tag{9}$$

Substituting for ΔR_m and ΔR_k in (9) will yield the condition for balance

$$\frac{R_1 a_m R_m^2}{(\varepsilon_s + \varepsilon_0)(R_2 + R_4 + R_m)^2 S_m} = \frac{a_k R_k^2 R_2}{\varepsilon_s S_k (R_1 + R_2 + R_4)^2} \,. \tag{10}$$
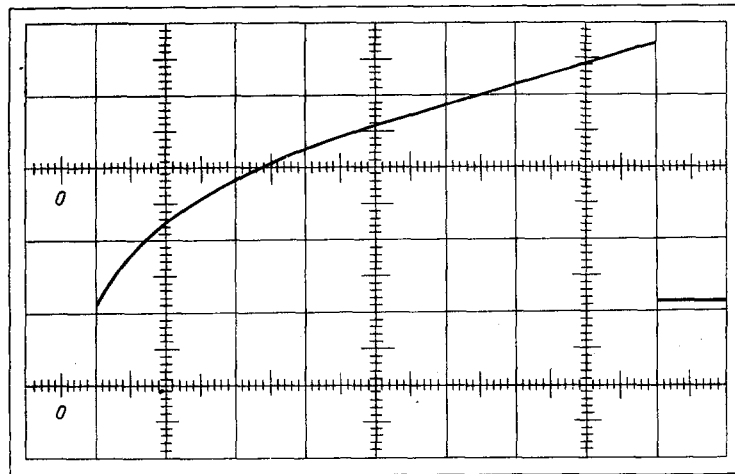
Fig. 2. Oscillogram of a signal produced by disturbing the
balance.

Since $\Delta R \propto \Delta t$ and $\Delta u \propto \Delta R$ when inequality (6b) holds true (this happens in all practical cases), then expression (3) can be rewritten as follows:

$$\Delta \varepsilon_\tau = - \frac{k \Delta u (\varepsilon_s + \varepsilon_0)^2}{\dfrac{2q v' \tau_0}{\sqrt{\pi}} + k \Delta u (\varepsilon_s + \varepsilon_0)}, \qquad (11)$$

where Δu is the incremental signal added to u_0 and k is the proportionality factor in $\Delta u = k \Delta t$. The value of k can be determined from expression (7).

The transient thermoactivity was determined experimentally as follows: a drop of alcohol was placed on the surface of transducer R_m and the signal was then balanced out. Generally ($u_0 \neq 0$) a balanced signal is a step voltage and during the time of recording it, this time being much longer than the pulse width, its top contracts into a point. After balancing, a pulse train of a certain frequency was sent through the transducer and the oscilloscope sweep was triggered. At the same time, a drop of water was added to the drop of alcohol. As the two liquids mixed within the volume adjacent to the metal film, a change in the thermoactivity was taking place and a signal Δu appeared as a result (Fig. 2). Inasmuch as $\tau_m \ll \tau$, the signal degenerated into a vertical line segment. The oscillogram shown in Fig. 3 depicts the process of water and alcohol mixing. Here the time base of the sweep is 1 sec and the applied pulse frequency is ~50 Hz. From this oscillogram one can extract data pertaining to the changes in concentration.

Indeed, $\Delta u \propto \varepsilon(\text{liq})$, where $\varepsilon(\text{liq}) = \varepsilon(C)$, C is the alcohol concentration in water.

As the concentration changes, heat of mixing is released simultaneously, and this causes a shift of the initial signal level. Using for this measurement a calibrated curve will make it possible to assess not only the changes in concentration but also the changes in temperature at the substrate—liquid boundary.

Typical curves of temperature and concentration changes in the layer of the solution adjacent to its boundary with the substrate plate are shown in Fig. 4. In this particular case the temperature of the water drop was slightly lower than that of the alcohol drop and, therefore, one observes an initial temperature decrease followed by a temperature increase due to the released heat of mixing. The thin layer of alcohol remaining on the surface becomes heated up, its temperature increases, the diffusion of water into this layer becomes appreciable, and a signal appears which corresponds to the decrease in alcohol concentration.

We will now estimate the frequency of applied pulses which determines the frequency of thermoactivity changes recordable by this method. The limiting frequency depends on the substrate—liquid interface cooling time. For the purpose of this estimate, let us consider first the following problem:

$$\frac{\partial t}{\partial \tau} = a \frac{\partial^2 t}{\partial x^2}, \qquad t \geqslant 0, \quad x \geqslant 0 \qquad (12)$$
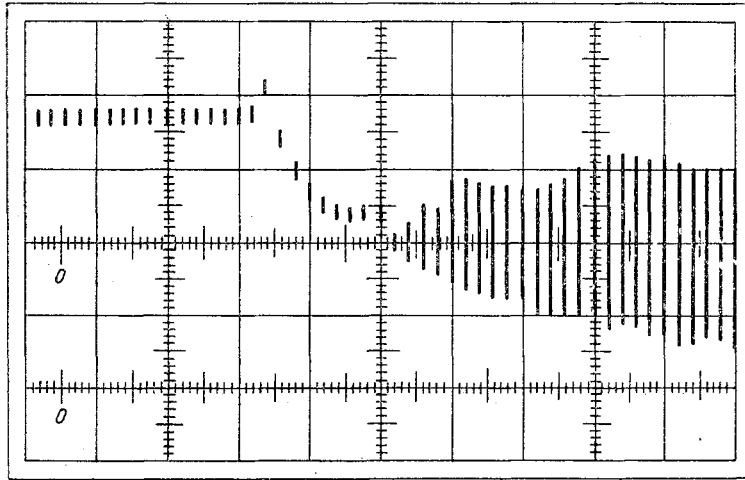
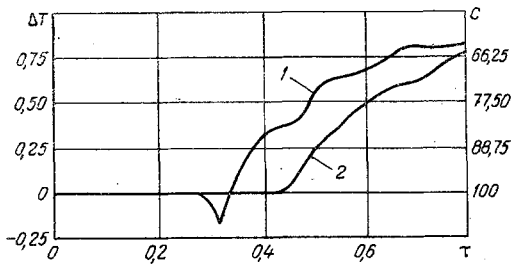Fig. 3. Oscillogram of the water and alcohol mixing process.

Fig. 4. Curves of temperature (1) and concentration (2) percent changes in a layer of solution adjacent to the surface of the substrate plate, when alcohol and water are mixed on it; τ is in seconds.

with the boundary conditions

$$t\big|_{x=0}=0,$$
$$t\big|_{x=\infty}=0$$

and the initial condition

$$t(x,\ 0) = \frac{2q\sqrt{\tau_0}}{\varepsilon}\ \mathrm{ierfc}\ \frac{x}{2\sqrt{a\tau_0}}.$$

The result for x = 0 is

$$t(0,\ \tau) = \frac{2g\sqrt{\tau_0}}{\varepsilon\sqrt{\pi}} \left(\sqrt{\frac{\tau}{\tau_0}+1} - \sqrt{\frac{\tau}{\tau_0}} \right). \tag{13}$$

This happens to be the solution to the one-dimensional cooling problem for the case of a substrate surface heated by a constant heat flux (q_0 = const) which acts on that surface during the time τ_0. It was assumed that the substrate is in air and that the heat lost through dissipation is negligible. Since the substrate is in a liquid, however, hence, assuming the thermal properties of the liquid to be the same as those of the substrate, it becomes necessary to divide expression (13) by two. Taking also into account the spatial distribution of heat, expression (13) must be rewritten — with sufficient accuracy — as follows:

$$t(0,\ \tau) = \frac{q\sqrt{\tau_0}}{\varepsilon\sqrt{\pi}} \left(\sqrt{\frac{\tau}{\tau_0}+1} - \sqrt{\frac{\tau}{\tau_0}} \right) \mathrm{erf}\ \frac{1}{\sqrt{2\mathrm{Fo}_y}}\ \mathrm{erf}\ \frac{1}{\sqrt{2\mathrm{Fo}_z}}, \tag{14}$$

where

$$\mathrm{Fo}_y = \frac{a\tau}{L_y^2}, \quad \mathrm{Fo}_z = \frac{a\tau}{L_z^2},$$

L_y and L_z are respectively the width and the length of the metal film.

Now we must satisfy the inequality

$$\frac{q\sqrt{\tau}}{\sqrt{\pi}\,\varepsilon} \left(\sqrt{\frac{\tau}{\tau_0}+1} - \sqrt{\frac{\tau}{\tau_0}} \right) \mathrm{erf}\ \frac{1}{\sqrt{2\mathrm{Fo}_y}}\ \mathrm{erf}\ \frac{1}{\sqrt{2\mathrm{Fo}_z}} < 0.01, \tag{15}$$

where the figure 0.01 is taken from a calculated estimate that the heat stored up in the substrate after passage of a prior pulse will not affect the amplitude of the subsequent temperature increment pulse beginning after τ_0.

The next task is to determine the time interval between consecutive pulses and, by the same token, the pulse frequency.

If $q\sqrt{\tau_0}/\sqrt{\pi\varepsilon} = 1°C$ with $\tau_0 = 200\ \mu sec$ while $L_y = 1$ mm and $L_z = 4$ mm, for instance, then the incoming pulse frequency must be $f \leq 200$ Hz.

In practice the incoming pulse frequency may be as high as 500 Hz.

In order to estimate the sensitivity of this method, we substitute

$$\Delta R_m = R_m\,\alpha_2\Delta t = R_m\ \alpha_2\ \frac{2q\sqrt{\tau_0}}{\sqrt{\pi}(\varepsilon_s + \varepsilon_0)} = \frac{R_m^2\,\alpha_2 \cdot 2 \cdot u'^2\sqrt{\tau_0}}{\sqrt{\pi}(\varepsilon_s + \varepsilon_0)S_2(R_2+R_4+R_m)^2}$$

into (7) and differentiate the latter with respect to ε, which gives

$$\frac{\partial u}{\partial \varepsilon} = \frac{2u'^3 R_2 R_m^2\,\alpha_2\sqrt{\tau_0}}{\sqrt{\pi}\,S_2(R_2+R_4+R_m)^4(\varepsilon_s+\varepsilon_0)^2}. \tag{16}$$

With the transducer parameters and the electric circuit used in this study, the sensitivity amounted to about 0.1 mV/J/m$^2 \cdot$ deg $\cdot$ sec$^{1/2}$.

The measurement precision depends on the amplitude of signal Δu: at an amplitude of 30-50 mm it is 2-4%.

NOTATION

ε	is the thermoactivity coefficient;
q	is the heat flux;
t	is the temperature;
τ	is the time;
u	is the potential difference;
R	is the ohmic resistance;
α	is the temperature coefficient of resistance;
S	is the area;
C	is the concentration;
a	is the thermal diffusivity;
$Fo = a\tau/x^2$	is the Fourier criterion;
f	is the frequency;
liq	is the liquid.

Subscripts

s	denotes the substrate;
0	denotes the initial value of parameters.

LITERATURE CITED

1. Yu. A. Polyakov, Physical Gas Dynamics, Heat Transfer, and Thermodynamics of High-Temperature Gases [in Russian], Izd. AN SSSR, Moscow (1962).
2. A. V. Lykov, Theory of Heat Conduction [in Russian], Izd. Vysshaya Shkola, Moscow (1967).
3. Yu. A. Polyakov and G. G. Spirin, Inzh.-Fiz. Zh., 16, No. 2 (1969).