MEASUREMENT OF THE COMPLEX DIELECTRIC PERMITTIVITY OF GLYCERINE AND ITS COMPLEX ETHERS

V. N. Khudaiberdyev, U. B. Khudayarov,
and M. U. Dzhanklich

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Experimental equipment is described and results presented from a study of dielectric permittivity and losses in glycerine, tributyrin, and tristearin in the liquid phase at frequencies from 40 Hz to 17 GHz.

Data on dielectric properties can provide information on the structure of liquids and the mechanisms of molecular processes with characteristic times to ~ 10^{-12} [1-3].

This study will describe experimental equipment developed to measure complex dielectric permittivity in liquid systems over the frequency range from 40 Hz to 17 GHz. The first results ever obtained over such a wide frequency range on dielectric permittivity and losses will be presented for the technologically important liquids glycerine $C_3H_5(OH)_3$ and its complex ethers tributyrin $C_3H_5(OOCC_3H_7)_3$ and tristearin $C_3H_5(OOCC_{17}H_{35})_3$. Interest in the study of dielectric characteristics of glycerine and its ethers has been stimulated by the possibility of their use as models for viscous liquids of various molecular mass μ_m and in the chemical industry [4].

For frequencies of 40 Hz-1 MHz a bridge circuit was used, the operation of which is described in detail in [2]. The complex bridge consists of a potentiometer bank, a dc amplifier, null indicator, precision resistance and capacitance boxes, with an oscillator for the electrical signal source. The specimen container was a molybdenum glass vessel ~ 15 ml in volume with variable distance between the stainless-steel plane-parallel capacitor plates which had a capacitance of 10 pF at a spacing of 0.5 cm. An advantage of this apparatus is its ability to measure chemically active liquids.

Values of ε^* were measured continuously over the frequency range f = 1-1250 MHz by a system for determination of complex transmission parameters which permitted automated measurement of dielectric parameters. The device, a block diagram of which is shown in Fig. 1a, operates on the principle of detecting reference and measurement signals which provide information on the dielectric parameters of the specimen studied. The signal from the measurement frequency oscillator 1 is applied to a frequency converter 2 where it is converted into two signals separated by 100 kHz. One of these signals passes through the uhf unit 3 to a measurement cell 4, approximately 10 ml in volume, after which uhf unit 3 produces signals proportional to the amplitude of the forward and reflected waves. These signals are applied to a mixer which uses the signal from converter 2 as a heterodyne. The signals are then fed to indicator circuit 5, which measures the standing wave ratio and uses a phase detector to determine the phase shift in the presence of the liquid. The values of η and Δ are recorded by chart recorder 6 for various positions of the shorting piston 7, which is reproducible to an accuracy of 10 μm.

The real and imaginary components of the complex dielectric permittivity can then be determined from the expressions

$$\varepsilon' = \left(\frac{\lambda_0}{\lambda_\varepsilon}\right)^2 - \frac{\varepsilon''\lambda_\varepsilon}{2\lambda_0}, \tag{1}$$

$$\varepsilon'' = \frac{\alpha\lambda_0^2}{\pi\lambda_\varepsilon}. \tag{2}$$

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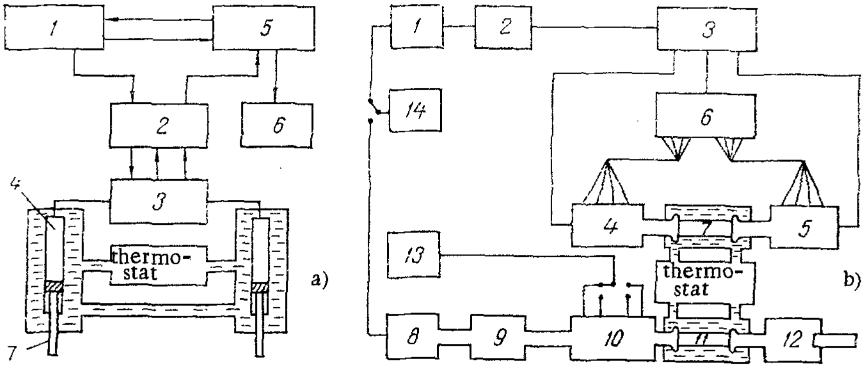

Fig. 1. Block diagrams of equipment for measuring ε' and ε" at frequencies 1-1250 MHz (a) and 3-7 GHz (b).

TABLE 1. Mean Relative Uncertainty in Measurements of ε' and ε", and Some Results of Control Measurements at 293°K

f, MHz	Δε', %	Δε", %	Liquid	f, MHz	ε'	ε"
0,00004—1,0	0,5	1,0	C_6H_6	$\frac{0,010}{0,010}$	$\frac{2,26}{2,26}$	$\frac{0,001}{0,001}$
			C_6H_6	$\frac{0,50}{0,50}$	$\frac{2,26}{2,26}$	$\frac{0,001}{0,001}$
			C_6H_6	$\frac{1,0}{1,0}$	$\frac{2,25}{2,25}$	$\frac{0,001}{0,001}$
1—1250	1,5	3,0	C_6H_6	$\frac{100}{100}$	$\frac{2,24}{2,24}$	$\frac{0,015}{0,015}$
			C_6H_6	$\frac{500}{500}$	$\frac{2,24}{2,24}$	$\frac{0,010}{0,010}$
			C_6H_6	$\frac{1000}{1000}$	$\frac{2,23}{2,23}$	$\frac{0,01}{0,01}$
3000—7000	1,0	2,0	C_3H_6O	$\frac{4000}{3120}$	$\frac{20,9}{21,1}$	$\frac{1,76}{1,32}$
11000—17000	1,5	3,0	C_3H_6O	$\frac{15000}{-}$	$\frac{16,4}{-}$	$\frac{3,02}{-}$

Note: Numerator of fraction indicates experimental data; denominator, results of [1].

For low attenuation, $\alpha = 1/2\ell \ln (\eta + 1)/(\eta - 1)$, and in simplified form, for large $\alpha = 1/\ell \ln 2/(\eta + 1)^2$.

To measure ε' and ε" of liquids in the range 3-7 GHz a device was developed based on waves traveling toward each other. Waves are transmitted in opposite directions through the liquid being studied through elements with known attenuation. This eliminates the effect of uhf signal power level and transfer coefficient of the measurement lines on experimental accuracy.

In this circuit (Fig. 1b) a uhf signal from oscillator 1 passes through amplifier 2 to switching circuit 3. Circuit 3 then passes the uhf signals through semiconductor attenuator alternately to power level sensors 4 and 5. Indicator circuit 6 accepts signals from four power level sensors corresponding to signals transmitted through or reflected from the system under study 7. By performing a subtraction indicator 6 produces attenuation coefficients, measured over approximately 1.5 min.

Simultaneously a uhf signal from generator 8 passes through uhf signal gate 9 to a power level sensor 10, then to cell 11, where it is reflected by shorting element 12, the position

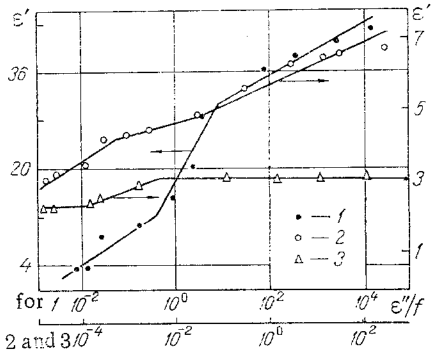

Fig. 2. Values of ε' and ε''/f vs frequency for glycerine (1) and tributyrin (2) at 283°K and tristearin (3) at 353°K. f, MHz.

of which is reproducable to an accuracy of 1 μm, and applied to measurement amplifier 13. The wavelength within the liquid λ_ε in this case corresponds to the distance between maxima or minima. The frequencies of uhf generators 1 and 8 is measured by frequency counter 14.

The values of ε' and ε'' are determined from the expressions

$$\varepsilon' = \left(\frac{\lambda_0}{\lambda_\varepsilon}\right)^2 + \left(\frac{\lambda_0}{\lambda_{cr}}\right)^2 - \left(\frac{\varepsilon''\lambda_\varepsilon}{2\lambda_0}\right)^2, \tag{3}$$

$$\varepsilon'' = K\,\frac{(A - A_0)^2\,\lambda_0^2}{\lambda_\varepsilon}\,. \tag{4}$$

Here, K = 3.77 cm^{-1} is the cell constant. The attenuation coefficient is recorded automatically, and the volume of liquid studied is approximately 20 ml.

At frequencies of 12-17 GHz ε' and ε'' were measured with equipment using automated measurement in waveguide channels.

The principle of ε* measurement is based on separate detection of signals proportional to their power. This is accomplished by two directional couplers connected in series. One of these is oriented toward the incident wave; the other, toward the reflected. The incident wave coupler is connected through a decoupling attenuator to a uhf generator. A waveguide isolator is used to eliminate low-frequency interference. The output of the reflected wave coupler is connected to the specimens to be studied. To measure ε' and ε'' of the liquids in the cell a shorting piston with position reproducable to 1 μm is used. The measurement portion of the cell with the liquid under study (approximately 5 ml) is separated from the empty part by a Teflon film 1 μm thick.

By measuring the thickness of the liquid, maxima (or minima) in the amplitude of the total reflected wave are determined. The ratio of η values for various positions of the maxima (minima) is expressed by

$$\frac{\eta_m}{\eta_n} = \frac{\operatorname{th}\left(\pi n \operatorname{tg}\frac{\Delta}{2}\right)}{\operatorname{th}\left(\pi m \operatorname{tg}\frac{\Delta}{2}\right)}\,. \tag{5}$$

From Eq. (5) we can obtain expressions for calculation of ε' and ε'' [1];

$$\varepsilon' = \left(\frac{\lambda_0}{\lambda_\varepsilon}\right)^2 + \left(\frac{\lambda_0}{\lambda_{cr}}\right)\left(1 - \operatorname{tg}^2\frac{\Delta}{2}\right), \tag{6}$$

$$\varepsilon'' = 2\left(\frac{\lambda_0}{\lambda_\varepsilon}\right)^2 \operatorname{tg}\frac{\Delta}{2}\,. \tag{7}$$

For high stability uhf power levels (within 0.02 dB) the real and imaginary components of ε* can be determined from expressions similar to Eqs. (3), (4). It should be noted that the given equipment permits measurement of ε' and ε'' over a wide range of values, with highest accuracy obtained for $10^{-2} < \varepsilon''/\varepsilon' < 1$.

In all the apparatus used the specimen was thermally stabilized to within 0.1°K in the temperature range 220-420°K. Analysis of systemic and random error together with control measurements of the complex dielectric permittivity of acetone and benzol, some of which are presented in Table 1, indicate that the uncertainty in ε' determination is 1%, and for $\varepsilon'' \sim 2\%$.

The experimental complex was used to study the dielectric properties of glycerine and its complex ethers tributyrin and tristearin in the liquid phase at temperatures from 280 to 370°K. The dielectric permittivity ε' and loss ε'' in glycerine and tristearin had been measured previously for a narrow frequency and temperature range [3, 5].

The liquids to be studied were first vacuum distilled and degasified. The purity of the specimens was determined by gas–liquid chromatography and monitored before and after the experiments by measuring density and index of refraction. The impurity content did not exceed 0.3%, and the value of ρ_{277}^{293} was 1261.1 kg/m^3 for glycerine and 1034.6 kg/m^3 for tributyrin, while for tristearin $\rho_{277}^{353} = 869$ kg/m^3.

The measurements of ε' and ε'' in glycerine and its ethers revealed dielectric relaxation over practically the entire frequency interval. Considering the finite number of dielectric relaxation times τ_{di} characterizing i relaxation processes, we have

$$\varepsilon' = \sum_{i\geqslant 1} \frac{(\varepsilon_{si} - \varepsilon_{\infty i})\, b_{di}}{1 + \omega^2 \tau_{di}^2} + \varepsilon_\infty, \tag{8}$$

$$\varepsilon'' = \sum_{i\geqslant 1} \frac{(\varepsilon_{si} - \varepsilon_{\infty i})\, b_{di}\omega\tau_{di}}{1 + \omega^2 \tau_{di}^2}. \tag{9}$$

A computer program was developed to determine the relaxation parameters from Eqs. (8), (9). Results of ε' and ε'' calculations in the liquids studied showed that within the limits of experimental uncertainty, the results agreed with Eqs. (8), (9) using three dielectric relaxation times. To illustrate the dependence of dielectric properties on f and μ_m, Fig. 2 presents data for glycerine and its ethers, the straight segments corresponding to dispersion regions. For glycerine, in the first region the dielectric relaxation time $\tau_{d1} \sim 10^{-6}$ sec, in the second, $\tau_{d2} \sim 10^{-9}$ sec, and in the third $\tau_{d3} \sim 10^{-10}$ sec, while for tributyrin and tristearin $\tau_{d1} \sim 10^{-7}$ sec, $\tau_{d2} \sim 10^{-10}$ sec, and $\tau_{d3} \sim 10^{-11}$ sec. We note that in glycerine at frequencies f > 10 GHz there is a falloff of ε', indicating the presence of a fourth relaxation process with time $\tau_{d4} \lesssim 10^{-11}$ sec. With increase in temperature, in the materials studied τ_{di}, b_{di}, and $(\varepsilon_{si} - \varepsilon_{\infty i})$ decrease. With increase in μ_m there is a reduction in ε' and ε'', so that the quantities τ_{di}, b_{di}, and $(\varepsilon_{si} - \varepsilon_{\infty i})$ decrease correspondingly.

By applying the principles of thermodynamics of irreversible processes to the dielectric data effective values of the enthalpy $\Delta H^{\neq}_{\varepsilon i}$ of the relaxation processes were calculated. The uncertainty in their determination is ~ 8%. For glycerine $\Delta H^{\neq}_{\varepsilon 1} = 35$ kJ/mole, $\Delta H^{\neq}_{\varepsilon 2} = 25$ kJ/mole, and $\Delta H^{\neq}_{\varepsilon 3} = 9$ kJ/mole, while for tributyrin and tristearin the corresponding $\Delta H^{\neq}_{\varepsilon i}$ values are ~ 5 kJ/mole lower.

Thus, the equipment developed permits determination of dielectric permittivity ε' and dielectric losses ε'' with an uncertainty of ~ 0.5-1.5% and ~ 1-3%, respectively, over the frequency range 40 Hz-17 GHz at temperatures from 220 to 420°K. Comparison of time and thermodynamic parameters for each dielectric relaxation region to corresponding characteristics of glycerine, tributyrin, and tristearin obtained by acoustical spectroscopy methods (for example, [6]) indicates the common nature of the mechanisms of molecular processes observed by the various methods.

NOTATION

ε^*, complex dielectric permittivity; ε', dielectric permittivity; ε'', dielectric loss; f, frequency; $\omega = 2\pi f$; μ_m, molecular mass; uhf, ultrahigh frequency; η, standing wave ratio; η_m and η_n, values of η at maxima m and n; Δ, phase shift; λ_0, radio signal wavelength; λ_ε, height of liquid; λ_{cr}, critical wavelength; ℓ, height of liquid column; α, radio signal absorption; A and A_0, attenuation coefficients with and without liquid; $\Delta\varepsilon'$ and $\Delta\varepsilon''$, mean relative uncertainty in ε' and ε'' determination; T, temperature; ρ_{277}, density; τ_{di}, dielectric relaxation time; b_{di}, relative relaxation force of relaxation process i; ε_{si} and $\varepsilon_{\infty i}$, low frequency and high frequency values of ε' for dielectric relaxation region i; $\Delta H^{\neq}_{\varepsilon i}$, enthalpy of activation of process i.

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TEMPERATURE RESISTANCE COEFFICIENT OF COMPOSITE RESISTIVE MATERIALS IN THE MIXED-STRUCTURE APPROXIMATION

O. A. Vasilenko, A. A. Maier,
V. A. Chashchin, E. N. Gulaeva,
and V. I. Bus'ko

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A method of calculating the temperature resistance coefficient and its temperature dependence for resistive materials in the approximation of a matrix–statistical structure is outlined.

Recently, the traditional empirical selection of optimal compositions of composite structures has been gradually replaced by a calculation based on the approximation of real heterogeneous systems by hypothetical structural models: The matrix model (with isolated inclusions of one phase in the other); the statistical model (with interpenetrating phases forming continuous three-dimensional "networks"); and the mixed model, which is a combination of the matrix and statistical models [1, 2].

Resistive cermet materials may be adequately represented by the two latter models, corresponding to the two conduction mechanisms discussed in the literature [3]: the contact mechanism (statistical structure) and the tunnel–barrier mechanism (mixed structure).

The most effective method of reducing the temperature resistance coefficient (TRC) of composite resistors is to use the thermocompensation effect [4], when the conducting subsystem consists (as a minimum) of two phases with opposite types of temperature dependence of the electrical conduction; semiconducting and metallic.

To realize the statistical method in practice, it is necessary to have monodisperse filler powders with identical particle materials. In constructing resistive materials with a matrix–statistical structure, no such difficulties are observed.

The aim of the present work is to calculate the TRC of resistive materials in the approximation of a matrix–statistical structure, which may be represented in the form of a heterogeneous system consisting of two subsystems: The conducting subsystem and the dielectric subsystem. The conducting subsystem is of matrix type and consists either of a semiconductor dispersed in a metallic matrix, or of a metal dispersed in a semiconducting matrix.

First, consider the calculation of the electrical conductivity of the conducting subsystem, in the form of a metallic matrix with inclusions of spherical semiconducting particles.

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