EFFECT OF AN ELECTRIC FIELD ON THE DYNAMICAL VISCOSITY OF DIELECTRIC LIQUIDS

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UDC 532.13

Experimental results on the effect of an electric field on the dynamical viscosity of dielectric liquids are presented and the methods of measurement are described.

The direct action of an electric field is an important method of stimulating heat and mass exchange in dielectric liquids [1]. However, the lack of accurate models of these mechanisms, in particular, the effect of an electric field on the dynamical viscosity of a liquid, has prevented the wide application of numerous investigations in this field to the solution of practical problems.

Attempts at understanding the effect of an electric field on the flow of a dielectric liquid were initiated near the end of the last century and have continued to the present time [2-5]. The main deduction of the experimental results is that static and oscillating electric fields can lead to an increase in the resistance of the liquid to flow. According to most authors, this effect is explained by the rise of electroconvective motion in the liquid. The influence of the electric field on the molecular momentum transport is assumed to be negligibly small, and is not taken into account in treating the behavior of the liquid in a field.

On the other hand, there is the view that the field can lead to a perceptible change in the molecular transport coefficients of the liquid; in particular, the coefficient of dynamical viscosity. This view is supported by data on the effect of an electric field on heat conduction [6], since this is a molecular transport characteristic, as is the viscosity.

We describe an experimental study of the effect of static and oscillating 50-Hz electric fields on the dynamical viscosity of organic liquids. The dynamical viscosity was measured by means of capillary viscometry techniques together with interference methods of controlling the liquid flow. With the help of the latter, the image of a layer of liquid flowing through the capillary could be observed, and the deviation from laminar flow (the instant of onset of electroconvection) could accurately be determined.

The experimental set-up consisted of a measurement cell with overflow and measuring vessels, a thermostat, a device for measuring time intervals, a connecting valve with electrocontacts, a frequency-meter—chronometer, a high-voltage source with electric measuring devices, an optical interferometer (IAB-451) and a light source (optical quantum generator LG-75).

The measurement cell is shown schematically in Fig. 1. It is a modification of a capillary viscometer with a capillary of rectangular cross section formed by two hollow stainless steel plates 1, and two optical glass slides 2. The plates formed the electrodes of a capacitor; a high voltage was applied to one of the electrodes, and the other was grounded. The sample liquid was allowed to flow down through the capillary from above. The electric field vector was directed perpendicular to the flow. Plates 1 were given connecting tubes 3 for inflow and outflow of a thermostatic-control liquid.

Hollow metallic plates 4 were mounted to plates 1 from above with insulating screws 5. These plates formed the initial hydrodynamic flow stabilization section l_1 before entry into the test section l_2 formed by plates 1. The values of l_2 used in the experiments were 0.18825 and 0.13882 m, and l_1 was $5 \cdot 10^{-2}$ m. The capillary thickness 2h was varied between $0.492 \cdot 10^{-3}$ and $0.5 \cdot 10^{-3}$ m, and the width 2b was $8.5 \cdot 10^{-3}$ m.

Plates 1 were separated from plates 4 by insulating layers 6 of thickness 50 μm. Above and below the capillary were placed fluoroplastic covers 7. These were mounted to plates 1 and 4 by screws 8 and were provided with channels for the inflow and outflow of the sample liquid.

S. M. Kirov Chemical Engineering Institute, Kazansk. Translated from Inzhenerno-Fizicheskii Zhurnal, Vol. 45, No. 6, pp. 962-969, November, 1983. Original article submitted July 13, 1982.

0022-0841/83/4506- 1412$07.50

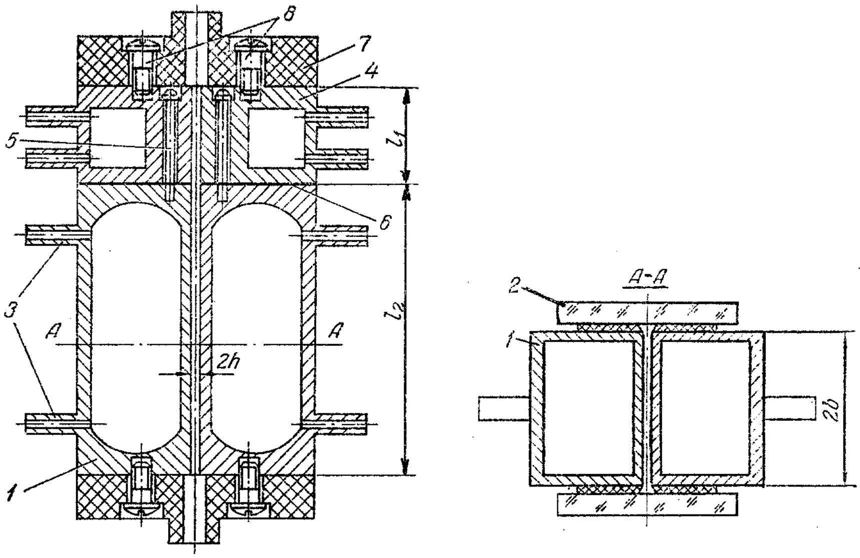

Fig. 1. Measurement cell.

The required high voltage was obtained by means of the constant voltage source B 5-24A and the transformer NOM-10.

The following organic liquids were chosen for the study: carbon tetrachloride, benzene, hexane, toluene, chlorobenzene, and acetone. The molecular dipole moments of these liquids are, respectively, 0, 0, 0, $1.67\cdot10^{-30}$, $5.20\cdot10^{-30}$, $9.47\cdot10^{30}$ C-m. The liquids were chemically purified, dehydrated with calcium chloride, filtered, and distilled at the boiling point. Their indices of refraction were then measured on the refractometer IRF-22. Deviations of the measured values from the accepted values [7] were less than $2\cdot10^{-4}$.

The dynamical viscosity was determined at temperature 293°K and atmospheric pressure. The static and oscillating electric field strengths were between $0.8\cdot10^{2}$ and $57\cdot10^{2}$ kV/m.

To test the rectangular cross section capillary in the measurement of dynamical viscosity, we performed preliminary experiments following the methods described in [8]. In these experiments, the correction to the kinetic energy of the liquid jet was determined, as was the so-called "entry" correction. The preliminary experiments showed that the liquid flow into the measurement cell was steady-state. This was as expected [9], because the capillary was such that $l_2/2h \approx 100$.

A flow Q of the sample liquid through the capillary was created by a constant drop ΔH between the levels of the liquid. The dynamical viscosity of the liquid in zero electric field was determined from the formula

$$\eta = 1.33\,(bh^3/Ql)\,\rho g \Delta H - 0.093\,(Qh/bl)\,\rho. \tag{1}$$

The values of the dynamical viscosity of the sample liquids in zero electric field differed from the accepted values of [10] by not more than 3.7%.

The electric field acted on the sample liquid only in section l_2 (the electric field was zero in section l_1). The dynamical viscosity of the liquid in the electric field was calculated from the formula

$$\eta^{el} = 1.33\,(bh^3/Q^{el} l_2)\,\rho g \Delta H - 0.093\,(Q^{el} h/bl_2)\,\rho - \eta l_1/l_2. \tag{2}$$

One of the principal factors that can distort the measurements of dynamical viscosity under the conditions of our experiment is electroconvection in the sample liquid. Therefore, in a preliminary experiment for each liquid, we determined the critical value of the electric field E_{cr}, above which electroconvection was observed.

Measurements of η and η^{el} were done under isothermal conditions for a liquid layer thickness of $2h \sim 0.5\cdot10^{-3}$ m. The image of the liquid layer in this case was uniformly bright. At a certain critical value E_{cr} (different for each liquid), an abrupt change in the size of the image was observed. This is evidently explained by electroconvection.

In order to test this assumption and refine the values of E_{cr}, we carried out additional experiments with a gap between the electrodes of 2h = 0.96 mm. Visualization of the inter-

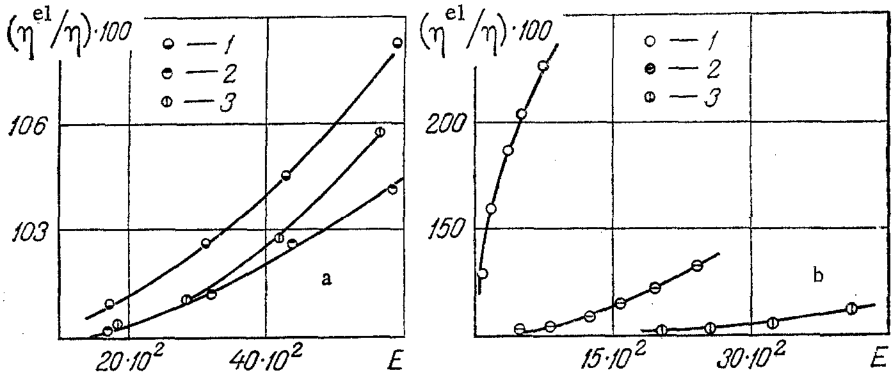

Fig. 2. Dependence of $\eta^{el}/\eta\cdot 100\%$ on E (in kV/m) for a static electric field. (a): hexane (curve 1), carbon tetrachloride (curve 2), benzene (curve 3), (b): acetone (curve 1), chlorobenzene (curve 2), toluene (curve 3).

ference pattern was accomplished by thermostatic control of the walls of the capillary at different temperatures ($\Delta t \sim 0.2-0.4°K$). Three to five interference fringes were seen in the image of the moving liquid layer. In the test section of the capillary they were parallel to each other, which corresponds to steady-state laminar flow of the liquid. For an applied electric field with $E < E_{cr}$, the interference pattern of the moving liquid layer did not change; this indicates no electroconvection. For $E \geqslant E_{cr}$, the interference pattern abruptly changed. The interference fringes in the image vanished, and its size changed. Turbulent motion of the liquid was observed, which indicated the onset of electroconvection.

The values of E_{cr} of the sample liquids, measured under isothermal conditions and with $2h = 0.5\cdot 10^{-3}$ m, agreed (within $\pm 0.5\cdot 10^{2}$ kV/m) with the values obtained for $2h = 0.96\cdot 10^{-3}$ m and $\Delta t \sim 0.2-0.4°K$, and ranged from $8\cdot 10^{2}$ to $57\cdot 10^{2}$ kV/m. The dynamical viscosity was not measured for $E \geqslant E_{cr}$.

The experiment was performed in the following sequence. The value of η for the sample liquid in zero electric field was measured. Then the value η^{el} in the electric field was determined. The effect of the electric field on the dynamical viscosity of the liquid is given by the ratio η^{el}/η. The elapsed times τ, τ^{el} for a certain volume of liquid V to flow through the capillary were measured. The flow rates $Q = V/\tau$ and $Q^{el} = V/\tau^{el}$ were determined and the values of η and η^{el} were calculated according to (1) and (2). In the calculation of η and η^{el}, we used the arithmetic average of values for τ and τ^{el} obtained over many measurements for a given series of experiments.

For the calculation of η^{el} in (2) there appears the density of the liquid ρ. It is well known that electrostriction occurs in a dielectric liquid in an applied electric field. The liquid experiences a pressure, and hence the density changes. However, according to [11], the change in ρ for an incompressible liquid can be ignored.

In a static or oscillating 50-Hz electric field, Joule heating of the dielectric liquid can occur. However, the preliminary experiments described above showed that the interference pattern of the moving liquid layer did not change in the applied field for $E < E_{cr}$, and so Joule heating was not significant.

The experimental results are shown in Fig. 2 and Fig. 3. It can be seen that the electric field leads to an increase in the dynamical viscosity both for nonpolar liquids (Figs. 2a and 3a) and for polar liquids (Figs. 2b, 3b). The relative change of viscosity is much larger for the polar liquids, and increases with increasing applied electric field and molecular dipole moment. For the maximum electric field used in the experiment, the dynamical viscosity of the most polar liquid (acetone) increased by a factor greater than its absolute magnitude in the absence of the field. The absolute magnitude of the change in viscosity in a static electric field was qualitatively similar to that observed in an oscillating field of 50 Hz.

η^{el} was measured for $E < E_{cr}$. When $E \geqslant E_{cr}$, we observed a further increase in the "viscosity" of the liquid. This effect was evidently caused by both molecular and electroconvective momentum transport. Hence from the experimental results, it follows that the effect of an electric field on the flow of a dielectric liquid can be related to an increase in the dynamical viscosity for $E < E_{cr}$, and to electroconvective flow for $E \geqslant E_{cr}$.

TABLE 1. Values of η, ΔG_η, ΔH_η, $\bar{\varepsilon}^P$, $\bar{z}_1$, $\bar{z}_\eta$ for Acetone, Chlorobenzene, and Hexane

Liquid	$\eta\cdot 10^3$, Pa·sec	$\Delta G_\eta\cdot 10^{-3}$, J/mole	$\Delta H_\eta\cdot 10^{-3}$, J/mole	$\bar{\varepsilon}^P\cdot 10^{22}$, J	$\bar{z}_1$	$\bar{z}_\eta$
Acetone	0,32	9,92	8,92	30,52	7,53	9,7
Chlorobenzene	0,83	13,05	12,40	20,66	7,45	19,7
Hexane	0,30	11,18	10,22	10,07	7,56	33,6

TABLE 2. Values of η^{el}, η^{el}/η, ΔG_η^{el}, ΔH_η^{el}, and $\bar{z}_\eta^{el}$ for Acetone, Chlorobenzene, and Hexane for Various Values of the Electric Field

Liquid	$E\cdot 10^{-2}$, kV/m	$\eta^{el}\cdot 10^3$, Pa·sec	$\eta^{el}/\eta\cdot$ 100 %	$\Delta G_\eta^{el}\cdot 10^{-3}$, J/mole	$\Delta H_\eta^{el}\cdot 10^{-3}$, J/mole	$\bar{z}_\eta^{el}$
Acetone	7,84	0,72	226	11,93	10,92	11,8
Chlorobenzene	20,33	1,00	121	13,52	12,87	20,6
Hexane	58,82	0,32	108	11,37	10,41	34,3

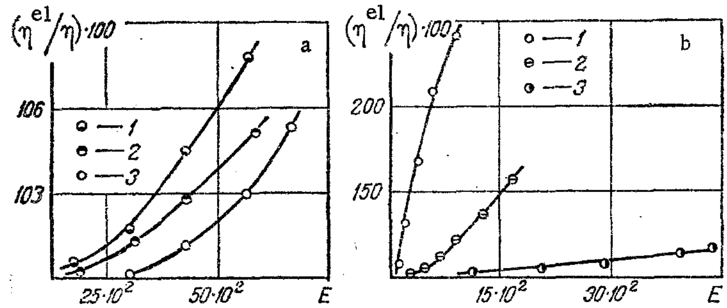

Fig. 3. Dependence of $\eta^{el}/\eta\cdot 100\%$ on E (in kV/m) for an oscillating field of frequency 50 Hz. The notation is the same as in Fig. 2.

The theory of molecular transport processes in liquids (such as momentum transport) has not been completely worked out. Therefore, we give a qualitative interpretation of the experimental results using some essential assumptions about the mechanism of viscous flow and the intermolecular interactions in a liquid. In particular, we start from the expression for the dynamical viscosity given in [12]:

$$\eta = (hN/V_M)\exp(\Delta G_\eta/RT) = A\exp(\Delta G_\eta/RT). \tag{3}$$

For our experiment T = const, $A = hN/V_M$ and R is a constant. Therefore the effect of the field on the viscosity must be due to the change in ΔG_η:

$$\eta^{el} = A\exp(\Delta G_\eta^{el}/RT). \tag{4}$$

From experiment $\eta^{el} > \eta$ and hence $\Delta G_\eta^{el} > \Delta G_\eta = \Delta H_\eta - T\Delta S_\eta$. The latter can be interpreted as the effect of the field on ΔH_η and ΔS_η.

It can be shown that an increase in ΔG_η in the electric field is fundamentally connected with the increase in ΔH_η, and

$$\eta^{el} = A\exp[(\Delta H_\eta^{el} - T\Delta S_\eta)/RT]. \tag{5}$$

The quantities ΔG_η^{el} and ΔH_η^{el} are calculated from the formulas:

$$\Delta G_\eta^{el} = RT\ln(V_M\eta^{el}/hN), \tag{6}$$

$$\Delta H_\eta^{el} = RT[\ln(V_M\eta^{el}/hN) - (T/V_M)\,\partial V_M/\partial T]. \tag{7}$$

Values of these quantities and others for the liquids used in the experiment are shown in Tables 1 and 2.

In [13] the assumption was made that ΔH_η is a certain fraction of the total intermolecular interaction energy. Therefore we attempt to relate ΔH_η to the intermolecular interaction energy of the liquid, and consider the possible causes of a change in ΔH_η in an electric field.

The calculation of the intermolecular interaction energy in a liquid is a complicated problem, and it can be done only approximately. We estimate the molecular interaction energy with the first coordinate sphere of the liquids under study using a potential of the London–Debye–Keesom type assumed in [14]

$$\bar{\varepsilon}_1 = \bar{z}_1 \bar{\varepsilon}^{\mathrm{P}} = \bar{z}_1 \{(1/\bar{r}_1^6)\,[(3/4)\,(J\alpha^2) + 2\mu^2\alpha + 2\mu^4/3kT]\}, \tag{8}$$

where $\bar{z}_1$ and $\bar{r}_1$ are the number of molecules and radius of the first coordinate sphere, averaged over the volume of the liquid. In (8), with the help of the term $\bar{z}_1$, the collective molecular interaction is taken into account (the additivity of molecular interactions is assumed).

Comparison showed that $\Delta H_\eta > \bar{\varepsilon}_M = \bar{z}_1\bar{\varepsilon}^p N/2$ (the intermolecular interaction energy of the liquid per mole with molecular interaction correlations taken into account within the first coordinate sphere) or $\Delta H_\eta/\bar{\varepsilon}_M = k_\eta$.

The shear stress in the liquid in laminar flow is apparently not high enough to change molecular characteristics such as μ, α, J, and hence also $\bar{\varepsilon}^p$. On the other hand, in the process of flow a certain deformation of the "supermolecular structure" of the liquid [15] (short-range structure) must occur. Therefore, we write

$$\Delta H_\eta = k_\eta \bar{z}_1 \bar{\varepsilon}^{\mathrm{P}} N/2 = \bar{z}_\eta \bar{\varepsilon}^{\mathrm{P}} N/2 = \bar{\varepsilon}_\eta N/2, \tag{9}$$

where $\bar{z}_\eta = k_\eta \bar{z}_1$ and $\bar{\varepsilon}_\eta = \bar{z}_\eta \bar{\varepsilon}^p$ is the average number of molecules with interaction correlations in flow and their energy, respectively. We have from (9)

$$\bar{z}_\eta = \Delta H_\eta/(\bar{\varepsilon}^{\mathrm{P}} N/2) = \Delta H_\eta/\bar{\varepsilon}_N^{\mathrm{P}}, \tag{10}$$

where $\bar{\varepsilon}_N^p = \bar{\varepsilon}^p N/2$. For the liquids in our experiment, $\bar{z}_\eta > \bar{z}_1$ (see Table 1) and $\bar{\varepsilon}_\eta > \bar{\varepsilon}_1$, so that in flow an increase in the short-range molecular correlations and an increase in the interaction energy in comparison with that for a liquid at rest occurs. We then rewrite (3) in the form

$$\eta = A \exp[(\bar{z}_\eta \bar{\varepsilon}_N^{\mathrm{p}} - T\Delta S_\eta)/RT]. \tag{11}$$

An applied electric field will lead to an increase in the dipole moment of the molecule $\mu^{el} = \mu + [\alpha + \mu^2/3kT]E$ and therefore to an increase in $\bar{\varepsilon}^p$. However, for the fields used in the experiment, the change in $\bar{\varepsilon}^p$ did not exceed 0.5% for our liquids, and this can be ignored. Hence one can assume that the increase in the viscosity in an electric field is due principally to an increase in short-range molecular correlations (increase in $\bar{z}_\eta$ and $\bar{\varepsilon}_\eta$). In analogy to (9), (10), and (11) we write

$$\Delta H_\eta^{\mathrm{el}} = \bar{z}_\eta^{\mathrm{el}} \bar{\varepsilon}^{\mathrm{p}} N/2, \tag{12}$$

$$\bar{z}_\eta^{\mathrm{el}} = \Delta H_\eta^{\mathrm{el}} / \bar{\varepsilon}_N^{\mathrm{p}}, \tag{13}$$

$$\eta = A \exp[(\bar{z}_\eta^{\mathrm{el}} \bar{\varepsilon}_N^{\mathrm{p}} - T\Delta S_\eta)/RT], \tag{14}$$

where $\bar{z}_\eta^{el}$ is the average number of molecules for which interaction correlations occur for flow in an electric field. It is seen from Tables 1 and 2 that $\bar{z}_\eta^{el} > \bar{z}_\eta$ and thus $\bar{\varepsilon}_\eta^{el} > \bar{\varepsilon}_\eta$. Hence, according to our assumptions, the increase in viscosity in an electric field is due to an increase in short-range molecular correlations and a corresponding increase in the interaction energy in comparison to that in the absence of the field.

NOTATION

2h and 2b, thickness and width of the capillary, m; l_1, l_2, and $l = l_1 + l_2$, length of the hydrodynamical stabilization section, test section, and total length of the capillary, respectively, m; η, dynamical viscosity, Pa·sec; T, absolute temperature, °K; E, electric field strength, kV/m; ΔG_η, ΔH_η, ΔS_η, free enthalpy, enthalpy, and entropy of flow activation, J/mole; $h = 6.6748 \cdot 10^{-34}$, Plank's constant, J·sec; $k = 1.3805 \cdot 10^{-23}$, Boltzmann constant, $\mathrm{J \cdot deg^{-1}}$; R = 8.3144, gas constant, J/mole-deg; $N = 6.0225 \cdot 10^{26}$, Avogadro number, $\mathrm{kmole^{-1}}$; V_M, molar volume, $\mathrm{m^3}$; J, ionization potential, J; α, polarizability of the molecule, $\mathrm{C \cdot m^2/V}$; μ, molecular dipole moment, C·m; $\bar{\varepsilon}^p$, average intermolecular pair interaction energy, J; ρ, density, $\mathrm{kg/m^3}$; g, acceleration of gravity, $\mathrm{m/sec^2}$; Q, flow rate, $\mathrm{m^3/sec}$; Subscripts: el and η, quantities in the electric field and in free flow, respectively; cr, critical value.

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LAWS FOR THE HEAT CAPACITY OF ELEMENTS OF THE PERIODIC SYSTEM

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UDC 536.63:546

We show a correlation between the derivative of the heat capacity with respect to the reduced temperature of elements and their group number at temperatures above the Debye temperature. We derive a relation which reflects the character of the variation of the heat capacity of the elements as a function of the characteristics of their electron structure.

For a long time the fundamental rule for the heat capacity of elements at high temperatures ($T > \theta_D$) was the empirical Dulong and Petit law. According to this law the molar heat capacities of monatomic solids at temperatures of the order of 300°K are approximately 25 J/mole·°K. However, experimental data at higher temperatures showed that deviations from the Dulong and Petit law in a number of cases increase to tens of percent [1]. It has been noted by many authors [2, 3, etc.] that the heat capacity of elements varies periodically with their atomic number. All this urgently required explanation. Since there is no single reliably theory, it is evident that answers to the questions posed can most likely be obtained by seeking new more general empirical relations.

Actually, by correlating accumulated experimental data Ivanova [4] showed that the Dulong and Petit law is a special case of a more general law: the molar heat capacities of

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Translated from Inzhenerno-Fizicheskii Zhurnal, Vol. 45, No. 6, pp. 969-974, December, 1983. Original article submitted June 29, 1982.