Dynamic dielectric effect in liquids at low flow rates

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(Submitted 18 April 1991)
Zh. Eksp. Teor. Fiz **101**, 895–900 (March 1992)

A new dynamic dielectric effect has been observed, consisting of a strong dependence of the dielectric properties of liquids in the case of the transition from a motionless position to flow. Permittivity jumps have been observed amounting to $\approx 10^{-2}\%$ for nonpolar liquids, $\approx 1\%$ for alcohols, and $\approx 10\%$ for water. The accompanying flow rate was in the range of 0.1–10 mm/s. It is proposed that the nature of the effect is connected with the partial destruction of the hypermolecular structure of the liquid.

The properties of matter are determined by their molecular structure. Known dynamic effects, such as the Maxwell effect and the orientation effect in acoustic wave fields, are the result of the deformation of the liquid, produced by a gradient of the flow velocity in the given liquid.[1–4] The nature of these dynamic effects is connected with the tension and compression of the liquid in the corresponding directions, leading to a partial orientation of the molecules in such a fashion that their long axes tend to line up with the direction of the liquid flow.

In a number of our experiments, we observed a change in the dielectric properties of the liquids in their transition from the static (motionless) to the dynamic state and conversely, for small flow velocities (at which the Maxwell effect is still not observed by today's measurement methods). The given effect, which we can call the dynamic dielectric effect, is observed in all the liquids studied by us (nonpolar, polar, associated), and is apparently inherent in the liquid state.

The investigations were carried out with a high-resolution dielecometer.[4] This is basically a resonator method of measurement of the increases in the real ε' and imaginary ε'' components of the permittivity. As a measurement cell we used a double block of cavity resonators, one of which formed a reference channel and the other the measurement channel. The frequencies of the corresponding UHF generators are "tied" to the frequencies of these resonators by the help of automatic frequency control systems. Their difference frequency Δf is in fact the output signal of the ε' channel when $\Delta f \propto \Delta\varepsilon'$. The recording of $\Delta\varepsilon''$ is based on the absorption of the UHF energy in the resonator with the sample and the corresponding decrease in the voltage at the UHF detector. In the experiment different cells were used, based on H_{011} and E_{010} cavities whose volumes were partially filled with the investigated liquid. For this purpose, we used cuvettes made of fluoroplastic tubes, strictly aligned along the axes of the cavities. The liquid under study is fed from a vessel directly connected with the cuvette. The rate of flow of the liquid is set by a stopclock at the exit from the measurement cell. The working frequency of the dielecometer ≈ 10 GHz. The resolving powers in ε' and ε'' were $\approx 10^{-7}$ for nonpolar liquids and $\approx 10^{-4}$ for polar liquids.

Figure 1 shows the dependences of the increments $\Delta\varepsilon'$ and $\Delta\varepsilon''$ of a number of polar liquids on the outflow velocity v. The flow velocity of the liquids was determined by the number of drops per second (at a diameter of the tube of the cuvette ≈ 1 mm). These measurements were carried out with a cell based on a doubled block of resonators in the H_{001} mode.

We call attention to the fact that the $\Delta\varepsilon'(v)$ and $\Delta\varepsilon''(v)$ dependences either saturate or have a tendency to saturate at very small flow rates ($\gtrsim 3$ drops/s). Such a behavior of the permittivity differs qualitatively from the behavior of the permittivity predicted by the Maxwell effect. Essentially, the observed increments $\Delta\varepsilon'$ and $\Delta\varepsilon''$ significantly exceed the permittivity changes expected from orientation effect.

It is characteristic that, in the dependence of $\Delta\varepsilon'(v)$ of alcohols (only the dependence of the permittivity of methanol is shown in the graph) and water, the direction of the changes of the permittivity is contrary to the direction of the corresponding changes in the dependences of acetone and fluorobenzene. The same applies also to the increments $\Delta\varepsilon''(v)$ (with the exception of water). This lack of uniformity of behavior of $\Delta\varepsilon'(v)$ and $\Delta\varepsilon''(v)$ of liquids also distinguishes the observed effect from the well-known one. The quantitatively observed effect is minimal in unassociated liquids (of the type of fluorobenzene) amounts to $\approx 1\%$ in alcohols, and is maximal ($\approx 10\%$) in water. An exception in the alcohol series is ethanol, for which $\Delta\varepsilon'/\varepsilon' \lesssim 0.2\%$.

The form of the "statics $\rightleftarrows$ dynamics" transitions of polar liquids is shown in Figs. 2a and 2b. The measurements were carried out on the basis of experimental dielectrograms. For different liquids, the only variation is the time to

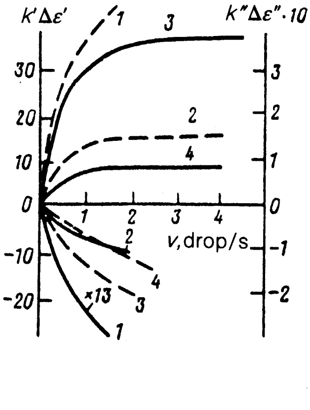

FIG. 1. Plots of $\Delta\varepsilon'(v)$ (solid curve) and $\Delta\varepsilon''(v)$ (dashed curve) of polar liquids: water (*1*), methanol (*2*), acetone (*3*), fluorobenzene (*4*). $k' = 70$ kHz, $k'' = 2$ V.

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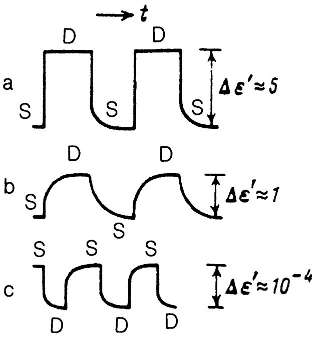

FIG. 2. Form of the "static(S) ⇄ dynamic(D)" transitions for a) water, b) methanol, c) hexane.

reach the "plateau." As a rule, the transition from static to dynamic takes place significantly more rapidly (not less than an order of magnitude) in comparison with the reverse transition from dynamic to static. Of all the liquids investigated by us, the smallest transition time was for water, the determination of which was limited by the inertia of the motion of the carriage of the recorder. Incidentally, the "inertia-free" nature of the "statics ⇄ dynamics" transition process can also suggest the use of the non-thermal nature of the effect.

It can be assumed that the observed behavior of $\Delta\varepsilon'(v)$ and $\Delta\varepsilon''(v)$ of dipolar liquids (Fig. 1) is due to the simultaneous action of several factors: a) the orientation effect, which is connected with the presence of a gradient of the liquid flow velocity; b) the caloric effect; c) the hydrostatic effect; d) the structural effect. We now estimate the contributions to $\Delta\varepsilon'/v$ from the enumerated factors.

The Maxwell effect can be estimated from the well-known relation[3]

$$\Delta n = G\eta D. \qquad (1)$$

where Δn is the difference in the index of refraction of the liquid in mutually perpendicular directions, G is the gradient of the flow velocity, η the coefficient of viscosity, and D the dynamo-optical constant.

Unfortunately, there are no data in the literature on $\Delta\varepsilon'(v)$, and as an approximation, one must make use of the Maxwell relation $\varepsilon \approx n^2$, which yields the increment $\Delta\varepsilon = 2\Delta n$. Substitution (in order of magnitude) of the known data $D \approx 10^{-10}$ Pa^{-1}, $\eta = 0.1$ P, and also of our experimental data $G \lesssim 10$ s^{-1} gives $\Delta n \approx 10^{-10}$. And, even if we take into account the incorrectness of the application of the relation $\Delta\varepsilon = 2\Delta n$, this still does not give us agreement between the result expected from (1) and experiment. Here, of course, we see the unusual nature of the result, when, even at very small liquid flow velocities, relatively large changes in the permittivity (up to 1–10%) are observed.

With the aim of establishing the influence of the caloric effect, we determined the temperature coefficients for several of the more characteristic liquids. For this purpose, we determined the dependence of the quantities $\Delta\varepsilon'$ and $\Delta\varepsilon''$ on the level of the power P damped in the measurement cell. In the given experiment, the linearity of the dependences $\Delta\varepsilon'(P)$ and $\Delta\varepsilon''(P)$ was established. The sign of the change $\Delta\varepsilon'(P)$ was shown to be negative, which agrees in natural fashion with the negative temperature coefficients of the permittivities in liquids. In each specific case, the correction for the caloric effect can be determined and then taken into account in the resulting quantity $\Delta\varepsilon'$. The correction for the caloric effect is introduced in connection with the permittivity difference of the liquid in the equilibrium state and in the dynamic state.

A hydrostatic effect can result from the change in the level of the liquid in the cuvette in the process of measurement. It can appear as the result of the change in the density and the permittivity of the liquid in the cell upon change in the level of this liquid; the hydrostatic coefficients of the liquids have the order of 10^{-2}–10^{-3} mPa^{-1} (Ref. 4), while the fall in the pressure in the experiment did not exceed 10^{-3} mPa; therefore, the hydrostatic effect does not exceed $\Delta\varepsilon'_h = 10^{-5}$–$10^{-6}$. In comparison with the observed effect in polar liquids, the corrections $\Delta\varepsilon'_h$ can be neglected.

Thus, the factors enumerated cannot explain the changes in the permittivities observed in liquids in the region of small flow velocities.

On the other hand, the very fact of the liquid flow suggests a change in the hypermolecular structure, while the differnce in the viscosities in the classes of liquids is a reflection of the singularities of their intermolecular interactions. In this connection we can assume that the observed permittivity effect is due to the partial disruption (or establishment) of hypermolecular structure of the liquid in its transition to the flow (or equilibrium) state. It is understood that the "structural" contribution to $\Delta\varepsilon'$ will depend on the level of "organization" of the hypermolecular structure. The experimental data on $\Delta\varepsilon'$ and $\Delta\varepsilon''$ confirm the presence of such a connection.

For example, in alcohols and water, $\Delta\varepsilon'$ is negative. That is, the alcohols and water belong to the class of associated liquids. They make the largest "structural" contribution, which is not only compensated by a positive contribution from the caloric effect but is also guaranteed by a definite appearance of a negative "remainder." It should be noted that, in the alcohols, a negative sign is also possessed by $\Delta\varepsilon''$. This result is in complete agreement with the assumption of partial disruption of the structure of the liquid. Actually, in the transition of the alcohol to the fluid state, part of the association is disrupted, and the monomeric molecules formed in this case have a smaller relaxation time and therefore make a small contribution to the dielectric losses.

In acetone and water, the structure is simple and they almost do not form associates; therefore, the "structural" contribution is minimal, and the observed values of $\Delta\varepsilon'$ are connected primarily with the caloric effect. In this connection, the liquid in the cell should have during its motion a somewhat lower temperature than the liquid at equilibrium. Since the temperature coefficients of the permittivity are negative in liquids, the transition to the dynamic state decreases ΔT and, by the same token, increases $\Delta\varepsilon'$. The increment $\Delta\varepsilon' \approx 0.4$ observed for acetone, were it due to the thermal effect, should change in the temperature of the acetone by about 0.02 °C (the temperature coefficient of the permittivity is equal to 0.002 deg^{-1}). This value is in complete agreement with the UFH energy dispersed in the resonator in this case (about 1–2 mW). This means that the dielectric jump $\Delta\varepsilon'$ and $\Delta\varepsilon''$ of acetone are due essentially to the caloric effect. The approximately uniform character of the "static

$\rightleftarrows$dynamic" transition fronts also supports this idea.

Water occupies a special place among the liquids studied. The quantity $\Delta\varepsilon'$ is negative in it, while $\Delta\varepsilon''$ is positive. This fact can be explained since, in water, in comparison with the alcohols at the operating frequency, the numerical values of ε' and ε'' are very large. Therefore, the observed increments $\Delta\varepsilon'(v)$ and $\Delta\varepsilon''(v)$ turn out to be significant (they reach 10%). So far as the sign of $\Delta\varepsilon''$ is concerned, it can be explained by the fact that, in water, the processes of disruption and the formation of hydrogen bonds make a much greater contribution to the absorption of energy of the UFH field than do the alcohols.[5] In the dynamic state, their number increases and, by the same token, this explains the increase in $\Delta\varepsilon''$. The jumps $\Delta\varepsilon'$ and $\Delta\varepsilon''$ formed by the "static$\rightleftarrows$dynamic" transition turn out to be the greatest among the liquids we studied. These are furthermore reproducible both in magnitude and in shape. This result also agrees with the assumption of the "structural" nature of the observed dynamodielectric effect. Actually, water has the most pronounced structurization (i.e., most of the molecules take part in the structural organization). Therefore, the disruption of this structure is accompanied by participation of the maximum number of molecules. The monomeric molecules released as a result of the frequent disruption of the structure make a significantly smaller contribution to the permittivity in comparison with their "lattice" contribution.

In addition to polar liquids, we also studied the dielectric properties of a number of nonpolar liquids. The measurements were carried out on the same dielcometer,[4] but with E_{010}-mode block resonators. Each of the resonators included a cuvette (made of a fluoroplastic tube of diameter 4 mm) aligned along its axis. In such a combination, the apparatus possessed a sensitivity in ε' and ε'' to within 10^{-7}.

The measurements made on the dependence of the permittivity on the flow velocity of hydrocarbons (pentane, heptane, hexane *et al.*), benzene, and carbon tetrachloride. In all these liquids, the $\Delta\varepsilon'(v)$ dependence was reliably established. In the region of small shear stresses (at a flow rate up to $v \approx 1$–2 drops/s) these dependences are linear. Upon increase in the flow rate (to 2–3 drops/s) the dependence of $\Delta\varepsilon'$ begins to depart rapidly from linearity and then changes sign. Upon further increase in the rate ($v = 4$–5 drops/s), the dependence can completely change sign. For most of the liquids studied, the $\Delta\varepsilon'(v)$ dependences are *S*-shaped. Here the scale of change of the permittivity in these dependences was about 10^{-4}.

Such a complicated character of the $\Delta\varepsilon'(v)$ is explained by the simultaneous action of all the factors previously enumerated (caloric, orientational, hydrostatic, and structural). It can be assumed that the structural contribution to $\Delta\varepsilon'(v)$ is very small in nonpolar liquids. The smallness of the observed increments $\Delta\varepsilon'$ testifies to this. At this level of observation of the permittivity, the effect of each of the possible factors turns out to be significant. Hence the complicated character of the behavior of $\Delta\varepsilon'(v)$. Besides, no $\varepsilon''(v)$ dependence in the studied liquids, at the level of sensitivity $\approx 2\times10^{-7}$ in ε'' has been observed.

The transitions "static$\rightleftarrows$dynamic" at constant rate (1 drop/s) have the "usual" shape (see Fig. 2b). The transition time from one state to another is sufficiently large (about 1–2 minutes) that it is connected with the inertia of the accompanying DDE of the thermal processes.

To establish stronger regularities in the behavior of the dynamic properties of nonpolar liquids in the region of small shear stresses, it is necessary to guarantee the conditions of viscous flow of the liquid, and also to set and control the temperature, pressure, and flow rate of the liquid. The regular connection between the value of $\Delta\varepsilon'$ (with allowance for corrections for the caloric effect) and the level of hypermolecular organization of the liquid is traced. For simple liquids (acetone, fluorobenzene) the relative changes of the permittivity $\Delta\varepsilon'/\varepsilon'$ are minimal, for alcohols, they increase to 1–2%, and for water they are maximal. In particular, water is the least structured, in agreement with the very large jumps in the permittivity $\Delta\varepsilon'$.

The Maxwell orientational effect is connected with the fact that the shear stresses produce a directed electric moment. But, along with this, the shear stresses also lead to a disruption of the hypermolecular structure if such exists. The fact is that the properties of liquids are consequences of the disruption of their structure at small stresses. This is in fact the cause of the disruption of the structure of the liquid. On the other hand, the structure predetermines the physical properties, in particular, the dielectric properties. The connection of the permittivity with the structure can be represented in the general form[4]

$$F(\varepsilon) = gp^2/3kT. \tag{2}$$

where $F(\varepsilon)$ is the dielectric functions, p the dipole moment, k Boltzmann's constant, T the temperature, and g the Kirkwood factor. The value of g characterizes the spatial correlation between the molecules, and is represented in the form

$$g = 1 + Z\langle\cos\theta_{ij}\rangle, \tag{3}$$

where Z is the number of nearest neighbor molecules; θ_{ij} is the angle between the orientations of the ith and the jth dipoles, and

$$\langle\cos\theta_{ij}\rangle = \int \cos\theta_{ij}\exp\left(-\frac{u}{kT}\right)d\Omega_i\,d\Omega_j \Big/ \int \exp\left(-\frac{u}{kT}\right)d\Omega_i\,d\Omega_j, \tag{4}$$

where Ω_i and Ω_j are the orientationc oordinates of the ith and jth molecules, and u is the energy of the intermolecular interaction, averaged over the positions and orientations. Equations (2)–(4) allow us to explain and describe the observed effect. Here g is the index of the intensity of the dynamic dielectric effect. According to (3), for $g \approx 1$ (when only the molecular structure exists) the permittivity effect is insignificant. The departure of g from unity testifies to the presence of some hypermolecular structure, formed by some group of the z molecules. Of all the liquids we have studied, the g factor for water is the smallest. For this reason, in water, almost all the molecules ($\approx 90\%$) participate in the formation of the quasilattice. Therefore, the DDE in water is very large.

Equations (3) and (4) suggest that the "static$\rightleftarrows$dynamic" transition should lead to a decrease in the number Z of bonds but also to a decrease in the mean statistical angle θ_{ij}, which should inevitably produce a corresponding decrease in the dielectric properties of the liquid, in accordance with Eq. (2); this is in fact confirmed by experiment.

On the other hand, Eqs. (2)–(4) are the initial conditions for confirmation of the dynamic-dielectric method as the method of investigating the hypermolecular structure of the liquid, when, on the basis of the experimental values of $\Delta\varepsilon'$ and $\Delta\varepsilon''$, it should be possible to obtain information on the character of the intermolecular bonds.

The authors expresses his gratitude to S. V. Livantsov, S. A. Lovtsov, and A. V. Filippov for help in carrying out the experiment.

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Translated by R. Beyer