EFFECT OF ELECTRIC FIELD ON THE ULTRASONIC WAVE PROPAGATION VELOCITY IN OILS

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A dielectric liquid in an external electric field exhibits variations in its physical properties as a result of deformational polarisation and orientational polarisation. Moreover, it undergoes volume deformation due to electrostriction.

The present work represents an attempt at a quantitative description of ultrasonic wave propagation in a dielectric liquid acted on by a transversal electric field. Our search for a functional dependence between the propagation velocity c_E and the external field strength E was based on the change in free energy of the medium under the action of the field.

We derive general expressions valid with regard to polar as well as non-polar dielectrics for the square of the propagation velocity and compare them with our experimental results, obtained by the phase method for some selected oils.

Moreover, we determine the electrostrictional change in density of the medium in the external field for field strengths applied in experiments as well as for their maximal values close to breakdown.

Finally, we perform an analysis of our experimental results in face of the theoretical predictions and propose a new mechanism as responsible for the behaviour of the dielectric in the electric field.

W pracy podjęto próbę ilościowego opisu zjawiska propagacji fali ultradźwiękowej w cieczy dielektrycznej w obecności zewnętrznego poprzecznego pola elektrycznego. Poszukiwania funkcyjnej zależności między prędkością rozchodzenia się fali ultradźwiękowej w ciekłym dielektryku c_E a natężeniem przyłożonego pola E oparto na fakcie zmiany energii swobodnej badanego ośrodka pod wpływem zewnętrznego pola elektrycznego.

Wyprowadzono ogólne wyrażenia — słuszne dla dielektryków polarnych jak i niepolarnych — na kwadrat prędkości oraz porównano je z wynikami eksperymentalnymi otrzymanymi w wybranych olejach przy wykorzystaniu metody fazowej.

Ponadto wyznaczono elektrostrykcyjną zmianę gęstości ośrodka pod wpływem zewnętrznego pola elektrycznego, zarówno dla wartości natężeń stosowanych w doświadczeniach, jak i dla wartości maksymalnych równych wytrzymałości materiałowej.

W końcowej części pracy przeprowadzono analizę uzyskanych wyników doświadczalnych na tle przewidywań teoretycznych oraz przedstawiono inny możliwy mechanizm odpowiedzialny za obserwowane zachowanie się dielektryka w polu elektrycznym.

Theoretical

1. Relation between the propagation velocity of an ultrasonic wave in a liquid dielectric and the externally applied electric field strength

An external electric field applied to a liquid dielectric modifies the physical properties of the latter as a result of deformational polarisation and orientational polarisation. The ultrasonic propagation velocity also undergoes a modification due to its dependence on the field-sensitive properties. Our present considerations bear, in principle, on pure dielectric liquids free of impurities, random charge carriers (ions, free electrons), or gas bubbles. In order to find the relationship between the propagation velocity and the external field strength we made use of the following equation, well known in molecular acoustics [1, 11]:

$$c^2 = \frac{\gamma \cdot V^2}{M}\left[\frac{\partial^2 F}{\partial V^2}\right]_T, \tag{1}$$

with: c — the propagation velocity of the ultrasonic wave, $\gamma = c_p/c_v$ — the ratio of the specific heats at constant pressure and at constant volume, V — the molar volume, M — molecular mass, and F — molar Helmholtz free energy.
When the electric field E is applied to the liquid dielectric the free energy F increases according to the following equation:

$$F = \Delta F + V \cdot \frac{\varepsilon_r \cdot \varepsilon_0}{2} \cdot E^2, \tag{2}$$

where ΔF is the thermodynamical part of the free energy per one mole, ε_r — the relative electric permittivity of the liquid, and ε_0 — that of vacuum.
From Eq. (2) the general formulation (1) for the propagation velocity in the presence of an electric field takes the form:

$$c_E^2 = \frac{\gamma \cdot V^2}{M}\left[\frac{\partial^2\left(\Delta F + V \cdot \frac{\varepsilon_r \cdot \varepsilon_0}{2} \cdot E^2\right)}{\partial V^2}\right]_T \tag{3}$$

or:

$$c_E^2 = \frac{\gamma \cdot V^2}{M}\cdot\left[\frac{\partial^2 \Delta F}{\partial V^2}\right]_T + \frac{\gamma \cdot V^2 \cdot \varepsilon_0}{2 \cdot M}\cdot\left[\frac{\partial^2(V \cdot \varepsilon_r \cdot E^2)}{\partial V^2}\right]_T. \tag{4}$$

The second derivative $\left[\dfrac{\partial^2(\varepsilon_r \cdot V \cdot E^2)}{\partial V^2}\right]_T$ in (4) can be expressed in terms of the specific volume ϑ; after some transformations, we get:

$$\left[\frac{\partial^2(M \cdot \vartheta \cdot \varepsilon_r \cdot E^2)}{\partial(M \cdot \vartheta)^2}\right]_T = \frac{1}{M}\cdot\left[\frac{\partial(\varepsilon_r \cdot E^2)}{\partial\vartheta}\right]_T. \tag{5}$$

Eq. (5) inserted into (4) gives:

$$c_E^2 = \frac{\gamma \cdot V^2}{M} \cdot \left[\frac{\partial^2 \Delta F}{\partial V^2}\right]_T + \frac{\gamma \cdot \varepsilon_0 \cdot V^2}{2 \cdot M^2} \left[\frac{\partial(\varepsilon_r \cdot E^2)}{\partial \vartheta}\right]_T. \tag{6}$$

Since $\vartheta = \varrho^{-1}$, Eq. (6) goes over into the general expression:

$$c_E^2 = \frac{\gamma \cdot V^2}{M} \cdot \left[\frac{\partial^2 \Delta F}{\partial V^2}\right]_T - \frac{\gamma \cdot \varepsilon_0}{2} \cdot \left[\varepsilon_r \cdot \frac{\partial E^2}{\partial \varrho} + E^2 \frac{\partial \varepsilon_r}{\partial \varrho}\right]_T, \tag{7}$$

where ϱ is the density of the liquid dielectric.

The derivatives $\left[\dfrac{\partial \varepsilon_r}{\partial \varrho}\right]_T$ and $\left[\dfrac{\partial E^2}{\partial \varrho}\right]_T$ occurring in (7) are accessible to determination from expressions that result from the theory of dielectrics and from equations describing electrostriction.

The latter [2], which consists in a deformation under the action of an electric field, obeys the equation:

$$\frac{\Delta V}{V} = K \cdot E^2, \tag{8}$$

where $\Delta V/V$ is the relative deformation in volume and K the electrostriction constant, as well as the equation [3]:

$$p = \frac{\varepsilon_0 \cdot E^2}{2} \cdot \left(\frac{\partial \varepsilon_r}{\partial \varrho}\right)_T \cdot \varrho, \tag{9}$$

describing the pressure caused by the effect.

The last equation, on determination of the first derivative of the pressure with respect to the density, gives:

$$\left(\frac{dp}{d\varrho}\right)_T = \frac{\varepsilon_0 \cdot \varrho}{2} \cdot \frac{\partial \varepsilon_r}{\partial \varrho} \cdot \frac{\partial E^2}{\partial \varrho} + \frac{\varepsilon_0 \cdot E^2}{2} \cdot \frac{\partial \varepsilon_r}{\partial \varrho} + \frac{\varepsilon_0 \cdot E^2}{2} \cdot \varrho \cdot \frac{\partial^2 \varepsilon_r}{\partial \varrho^2}. \tag{10}$$

Taking into account the well known thermodynamical formula $\left(\dfrac{dp}{d\varrho}\right)_T = \dfrac{1}{\beta_T \cdot \varrho}$, where β_T denotes the isothermal compressibility of a fluid medium, we obtain:

$$\left(\frac{dE^2}{d\varrho}\right)_T = \left[\frac{2}{\beta_T \cdot \varrho^2 \cdot \dfrac{\partial \varepsilon_r}{\partial \varrho} \cdot \varepsilon_0} - \frac{E^2}{\varrho} - E^2 \cdot \frac{\dfrac{\partial^2 \varepsilon_r}{\partial \varrho^2}}{\dfrac{\partial \varepsilon_r}{\partial \varrho}}\right]_T \tag{11}$$

for the change in density of the dielectric under the action of the field.

Equations (11) involves moreover the first and second derivatives $\left(\dfrac{\partial \varepsilon_r}{\partial \varrho}\right)_T$ and $\left(\dfrac{\partial^2 \varepsilon_r}{\partial \varrho^2}\right)_T$, given by the theory of liquid dielectrics [4].

To determine the dependence of ε_r on the temperature T and density ϱ we have recourse to the theory appropriate for the given type of dielectric.

1.1. Liquids obeying the Debye law (non dipolar)

Thus, for non-dipolar liquids and dipolar ones obeying the Debye law one has:

$$\frac{\varepsilon_r - 1}{\varepsilon_r + 2} = A \cdot \varrho, \tag{12}$$

where

$$A = \frac{N_A}{3 \cdot \varepsilon_0 \cdot M} \cdot \left(\alpha + \frac{\mu_0^2}{3 \cdot k \cdot T} \right) \equiv \frac{1}{\varrho} \cdot \frac{\varepsilon_r - 1}{\varepsilon_r + 1}. \tag{13}$$

The above relations lead to:

$$\varepsilon_r = \frac{1 + 2 \cdot A \cdot \varrho}{1 - A \cdot \varrho}. \tag{14}$$

On calculating the first and second one obtains

$$\frac{\partial \varepsilon_r}{\partial \varrho} = \frac{3 \cdot A}{(1 - A \cdot \varrho)^2} \equiv \frac{(\varepsilon_r - 1) \cdot (\varepsilon_r + 2)}{3 \cdot \varrho} \tag{15}$$

and

$$\frac{\partial^2 \varepsilon_r}{\partial \varrho^2} = \frac{2 \cdot A}{1 - A \cdot \varrho} \cdot \frac{\partial \varepsilon_r}{\partial \varrho} \equiv \frac{2 \cdot (\varepsilon_r - 1)^2 \cdot (\varepsilon_r + 2)}{9 \cdot \varrho^2}. \tag{16}$$

On insertion of (15) and (16) into Eq. (11) and with regard to $c_0^2 = \gamma/(\beta_T \cdot \varrho)$ we obtain the following expression for the change in density of a non-dipolar liquid dielectric in an external electric field:

$$\left(\frac{\partial E^2}{\partial \varrho} \right)_T = \frac{6 \cdot c_0^2}{\gamma \cdot \varepsilon_0 (\varepsilon_r - 1)(\varepsilon_r + 2)} - (2\varepsilon_r + 1) \cdot \frac{E^2}{3 \cdot \varrho} \tag{17}$$

or

$$\left(\frac{\partial E^2}{\partial \varrho} \right)_T = \frac{2 \cdot c_0^2 \cdot (1 - A \cdot \varrho)^2}{3 \cdot A \cdot \gamma \cdot \varrho \cdot \varepsilon_0} - \frac{1 + A \cdot \varrho}{\varrho \cdot (1 - A \cdot \varrho)} \cdot E^2. \tag{18}$$

For the case of a non-dipolar liquid dielectric in an electric field we are now able to evaluate the change in density due to electrostriction. For the field strengths applied in our measurements and for a typical non-dipolar liquid dielectric:

$$c_0 = 1400 \ [\text{m/s}] \qquad \gamma = 1.4 \qquad \varrho = 900 \ [\text{kg/m}^3]$$
$$E = 3 \cdot 10^5 \ [\text{V/m}] \qquad \varepsilon_r = 2.2 \qquad \varepsilon_0 = 8.85 \cdot 10^{-12} \ [\text{F/m}]$$

on insertion into (17) we obtained:

$$\left|\frac{\partial E^2}{\partial \varrho}\right|_T = 1.88 \cdot 10^{17} - 5.5 \cdot 10^7 \cong 1.88 \cdot 10^{17} \ [V^2 \cdot m/kg],$$

meaning that at the above field strength the change in density amounts to:

$$\Delta\varrho = \frac{\Delta(E^2)}{\left(\dfrac{\partial E^2}{\partial \varrho}\right)_T} = 4.779 \cdot 10^{-7} \ [kg/m^3].$$

Thus, the relative change in density is:

$$\Delta\varrho/\varrho = 5.31 \cdot 10^{-10},$$

in good agreement with the literature [2,5].

Admitting a field of $E_{max} = 3 \cdot 10^7 \ [V/m]$ as the pre-breakdown limit, we find

$$\left|\frac{\partial (E^2)}{\partial \varrho}\right|_T = 1.88 \cdot 10^{17} - 1.8 \cdot 10^{12} \cong 1.88 \cdot 10^{17} \ [V^2 \cdot m/kg],$$

and the value of $\Delta\varrho$ corresponding to it as:

$$\Delta\varrho = \frac{\Delta(E^2)}{\left|\dfrac{\partial (E^2)}{\partial \varrho}\right|_T} = \frac{(3 \cdot 10^7)^2}{1.88 \cdot 10^{17}} = 4.78 \cdot 10^{-3} \ [kg/m^3].$$

The relative change in density of the non-dipolar dielectric due to electrostriction thus amounts to

$$\Delta\varrho/\varrho = 5.3 \cdot 10^{-6}.$$

Inserting in the general formula (7) the expressions for $(\partial \varepsilon_r/\partial \varrho)_T$, $(\partial^2 \varepsilon_r/\partial \varrho^2)_T$ and $(\partial E^2/\partial \varrho)_T$ determined for non-dipolar dielectrics, we finally arrive at the following formula expressing the phase velocity of ultrasonic waves in liquid non-dipolar media in the presence of an external constant electric field:

$$c_E^2 = \frac{\gamma \cdot V^2}{M} \cdot \left(\frac{\partial^2 (\Delta F)}{\partial V^2}\right)_T - \frac{3 \cdot \gamma \cdot \varepsilon_r}{\beta_T \cdot \varrho \cdot (\varepsilon_r - 1)(\varepsilon_r + 2)} + \frac{\gamma \cdot \varepsilon_0 \cdot E^2}{6 \cdot \varrho} \cdot (\varepsilon_r^2 + 2) \equiv \qquad (19)$$

$$\equiv \frac{\gamma \cdot V^2}{M} \cdot \left(\frac{\partial^2 (\Delta F)}{\partial V^2}\right)_T - \frac{\gamma \cdot (1 + 2A\varrho)(1 - A\varrho)}{3 \cdot A \cdot \beta_T \cdot \varrho^2} + \frac{\gamma \cdot \varepsilon_0 \cdot E^2 (2A^2 \varrho^2 + 1)}{2\varrho \cdot (1 - A\varrho)^2}. \qquad (20)$$

Obviously, by Eq. (20), if conditions are such that $A = \varrho^{-1}$, then $c_E \Rightarrow \infty$ and the situation comes to resemble what is referred to as "the Mossotti catastrophe" in the theory of dielectrics.

1.2. Liquids obeying Onsager's equation (dipolar)

In dealing with dipolar liquids fulfilling Onsager's equation we have to use an equation from which it results that the density of the dielectric is described by the following relation:

$$\varrho = \frac{9 \cdot \varepsilon_0 \cdot M \cdot k \cdot T}{N_A \cdot \mu_0^2} \cdot \frac{(2\varepsilon_r^2 - \varepsilon_r \cdot \varepsilon_\infty - \varepsilon_\infty^2)}{\varepsilon_r \cdot (\varepsilon_\infty + 2)^2}. \tag{21}$$

On calculating $(\partial\varrho/\partial\varepsilon_r)_T$ from (21) we get:

$$\left(\frac{\partial\varrho}{\partial\varepsilon_r}\right)_T = \frac{2 \cdot \varepsilon_r^2 + \varepsilon_\infty^2}{\varepsilon_r^2} \cdot \frac{9 \cdot \varepsilon_0 \cdot M \cdot k \cdot T}{(\varepsilon_\infty + 2)^2 \cdot N_A \cdot \mu_0^2} \equiv \frac{\varrho \cdot (2\varepsilon_r^2 + \varepsilon_\infty^2)}{\varepsilon_r \cdot (2\varepsilon_r^2 - \varepsilon_\infty \cdot \varepsilon_r - \varepsilon_\infty^2)}, \tag{22}$$

whence

$$\left(\frac{\partial\varepsilon_r}{\partial\varrho}\right)_T = \frac{\varepsilon_r^2(\varepsilon_\infty + 2)^2}{(2\varepsilon_r^2 + \varepsilon_\infty^2)} \cdot \frac{N_A \cdot \mu_0^2}{9 \cdot \varepsilon_0 \cdot M \cdot k \cdot T} \equiv \frac{\varepsilon_r(2\varepsilon_r^2 - \varepsilon_\infty \cdot \varepsilon_r - \varepsilon_\infty^2)}{\varrho(2\varepsilon_r^2 + \varepsilon_\infty^2)} \tag{23}$$

and

$$\left(\frac{\partial^2\varepsilon_r}{\partial\varrho^2}\right)_T = \frac{2 \cdot \varepsilon_r^3 \cdot \varepsilon_\infty^2}{(2 \cdot \varepsilon_r^2 + \varepsilon_\infty^2)^3} \left[\frac{(\varepsilon_\infty + 2)^2 N_A \cdot \mu_0^2}{9 \cdot \varepsilon_0 \cdot M \cdot k \cdot T}\right]^2 \equiv \tag{24}$$

$$\equiv \frac{2 \cdot \varepsilon_r \cdot \varepsilon_\infty^2 (2 \cdot \varepsilon_r^2 - \varepsilon_\infty \cdot \varepsilon_r - \varepsilon_\infty^2)^2}{\varrho^2 \cdot (2 \cdot \varepsilon_r^2 + \varepsilon_\infty^2)^3}.$$

On insertion of the preceding expressions into (11) we obtain the following equation for the change in density of a dipolar liquid dielectric in an electric field:

$$\left(\frac{\partial E^2}{\partial\varrho}\right)_T = \frac{2 \cdot \varepsilon_r^2 + \varepsilon_\infty^2}{\beta_T \cdot \varrho \cdot \varepsilon_0 \cdot \varepsilon_r (2\varepsilon_r^2 - \varepsilon_\infty \varepsilon_r - \varepsilon_\infty^2)} - \frac{E^2}{\varrho} \cdot \frac{4\varepsilon_r^4 + 8\varepsilon_r^2 \varepsilon_\infty^2 - 2\varepsilon_\infty^3 \varepsilon_r - \varepsilon_\infty^4}{(2\varepsilon_r^2 + \varepsilon_\infty^2)^2} \equiv$$

$$\equiv \frac{18(2\varepsilon_r^2 + \varepsilon_\infty^2) M \cdot k \cdot T}{\beta_T \varrho^2 \varepsilon_r^2 (\varepsilon_\infty + 2) N_A \mu_0^2} - \frac{E^2}{\varrho} \cdot \left[1 + \frac{2\varrho\varepsilon_r\varepsilon_\infty^2(\varepsilon_\infty + 2)^2 N_A \mu_0^2}{9\varepsilon_0(2\varepsilon_r^2 + \varepsilon_\infty^2)^2 M \cdot k \cdot T}\right]. \tag{25}$$

To determine the change in density for the field strengths applied in our measurements we assumed the following values for the synthetic oil FDO (bis-2-ethylohexylic phtalene):

$$c_0 = 1468.8 \text{ [m/s]}, \quad \text{at } T = 273 \text{ [K]},$$

$$\varrho = 945 \text{ [kg/m}^3], \quad \gamma = 1{,}3,$$

$$\varepsilon_r = 5.2 \quad \varepsilon_\infty = 2.24 \quad E = 3 \cdot 10^5 \text{ [V/m]}.$$

which, inserted into Eq. (25), gave

$$\left(\frac{\partial E^2}{\partial\varrho}\right)_T = 5.7 \cdot 10^{16} - 1.08 \cdot 10^8 \cong 5.7 \cdot 10^{16} \text{ [V}^2 \cdot \text{m/kg]}.$$

Hence, the relative change in density due to electrostriction amounts to

$$\frac{\Delta\varrho}{\varrho} = \frac{1}{\varrho} \cdot \frac{\Delta E^2}{\left(\dfrac{\partial E^2}{\partial\varrho}\right)_T} = \frac{1}{945} \cdot \frac{(3\cdot10^5)^2}{5.7\cdot10^{16}} = 1.67\cdot10^{-9}.$$

On the assumption that the maximum pre-breakdown field strength for oil is $E = 3\cdot10^7$ [V/m], Eq. (25) leads to

$$\left|\frac{\partial(E^2)}{\partial\varrho}\right|_T = 5.7\cdot10^{16} - 1.08\cdot10^{12} \cong 5.7\cdot10^{16} \ [V^2\cdot m/kg],$$

and the electrostrictional change in density $\Delta\varrho$ of the dipolar dielectric under consideration amounts to

$$\Delta\varrho = \frac{\Delta(E^2)}{\left|\dfrac{\partial E^2}{\partial\varrho}\right|_T} = \frac{(3\cdot10^7)^2}{5.7\cdot10^{16}} = 15.78\cdot10^{-3} \ [kg/m^3]$$

and the respective relative change in density to

$$\Delta\varrho/\varrho = 15.78\cdot10^{-3}/945 = 16.7\cdot10^{-6}.$$

On insertion of the quantities given by Eqs (23), (24) and (25) into (7) we obtain a general formula describing the propagation velocity of an ultrasonic wave in a dipolar liquid dielectric in the presence of an external static electric field:

$$c_E^2 = \frac{\gamma\cdot V^2}{M}\cdot\left[\frac{\partial^2(\Delta F)}{\partial V^2}\right]_T - \frac{\gamma\cdot(2\cdot\varepsilon_r^2+\varepsilon_\infty^2)}{2\cdot\beta_T\cdot\varrho\cdot(2\varepsilon_r^2-\varepsilon_r\cdot\varepsilon_\infty-\varepsilon_\infty^2)} +$$

$$+\frac{\gamma\cdot\varepsilon_0\cdot\varepsilon_r^2\cdot E^2}{2\cdot\varrho\cdot(2\varepsilon_r^2+\varepsilon_\infty^2)}\cdot(8\cdot\varepsilon_\infty\cdot\varepsilon_r-\varepsilon_\infty^2+2\varepsilon_r^2) \equiv \qquad (26)$$

$$\equiv \frac{\gamma\cdot V^2}{M}\cdot\left[\frac{\partial^2(\Delta F)}{\partial V^2}\right]_T - \frac{9\cdot\gamma\cdot\varepsilon_0(2\cdot\varepsilon_r^2+\varepsilon_\infty^2)\cdot M\cdot k\cdot T}{\beta_T\cdot\varrho^2\cdot\varepsilon_r\cdot(\varepsilon_\infty+2)^2\cdot N_A\cdot\mu_0^2} +$$

$$+E^2\cdot\left\{\frac{\gamma\cdot\varepsilon_0\cdot\varepsilon_r}{\varrho} + \frac{N_A\cdot\mu_0^2}{9\cdot M\cdot k\cdot T}\cdot\frac{\varepsilon_r\cdot(\varepsilon_\infty^2+2)}{(2\cdot\varepsilon_r^2+\varepsilon_\infty^2)}\cdot\left[1+\frac{\gamma\cdot\varepsilon_r\cdot\varepsilon_\infty^2}{2\cdot\varepsilon_r^2+\varepsilon_\infty^2}\right]\right\}.$$

The two forms of (26) determine the change in phase velocity of the wave in the macroscopic as well as the molecular approach.

1.3. Relation to experiments

In our measurements, we determined the absolute propagation velocity c_0 as well as the change in velocity Δc_E induced by the field E. The Eq. (19), which holds for

non-dipolar liquids, leads to the following relation:

$$c_E^2 - c_0^2 = \frac{\gamma \cdot \varepsilon_0 \cdot (\varepsilon_r^2 + 2)}{6 \cdot \varrho} \cdot E^2 \cong 2 \cdot c_0 \cdot \Delta c_E, \tag{27}$$

permitting the determination of Δc_E. The latter amounts to

$$\Delta c_E = \frac{\gamma \cdot \varepsilon_0 \cdot (\varepsilon_r^2 + 2)}{12 \cdot \varrho \cdot c_0} \cdot E^2. \tag{28}$$

Evaluations of Δc_E were carried out for the following values for non-dipolar mineral oil:

$$c_0 = 1508.67 \ [\text{m/s}] \quad \varrho = 863 \ [\text{kg/m}^3] \quad \gamma = 1.4$$

$$\varepsilon_r = 2.2 \quad E = 3 \cdot 10^5 \ [\text{V/m}] \quad \varepsilon_0 = 8.85 \cdot 10^{-12} \ [\text{F/m}],$$

which led to a change in velocity of

$$\Delta c_E = 4.88 \cdot 10^{-7} \ [\text{m/s}].$$

Assuming for mineral oil a maximal admissible field strength of $E_{\max} = 3 \cdot 10^7 \ [\text{V/m}]$ we obtained from (28) Δc_E as

$$\Delta c_E = \frac{1.4 \cdot 8.85 \cdot 10^{-12} \cdot (2.2^2 + 2)}{12 \cdot 863 \cdot 1508.67} \cdot (3 \cdot 10^7)^2 = 4.88 \cdot 10^{-3} \ [\text{m/s}].$$

For the case of dipolar dielectrics we had recourse to Eq. (26). Here, the change in velocity Δc_E is expressed by

$$\Delta c_E = \frac{\gamma \cdot \varepsilon_0 \cdot \varepsilon_r^2 \cdot (8 \cdot \varepsilon_\infty \cdot \varepsilon_r - \varepsilon_\infty^2 + 2 \cdot \varepsilon_r^2)}{4 \cdot c_0 \cdot \varrho \cdot (2 \cdot \varepsilon_r^2 + \varepsilon_\infty^2)^2} \cdot E^2. \tag{29}$$

We assumed the following values for the synthetic oil FDO — a dipolar liquid:

$$c_0 = 1468.8 \ [\text{m/s}] \quad \text{at} \ T = 273 \ [\text{K}]$$

$$\varrho = 945 \ [\text{kg/m}^3] \quad \varepsilon_r = 5.2 \quad \gamma = 1.3$$

$$\varepsilon_\infty = 2.24 \quad E = 3 \cdot 10^5 \ [\text{V/m}].$$

In this case, the theory predicts a field-induced change in velocity Δc_E equal to

$$\Delta c_E = 2.05 \cdot 10^{-7} \ [\text{m/s}].$$

On assuming as the highest admissible field strength $E_{\max} = 3 \cdot 10^7 \ [\text{V/m}]$, we obtained from Eq. (29) the following change in velocity Δc_E due to the increase in free energy:

$$\Delta c_E = \frac{1.3 \cdot 8.85 \cdot 10^{-12} \cdot 5.2^2 \cdot (8 \cdot 2.24 \cdot 5.2 - 2.24^2 + 2 \cdot 5.2^2)}{4 \cdot 1468.8 \cdot 945 \cdot (2 \cdot 5.2^2 + 2.24^2)^2} \cdot (3 \cdot 10^7)^2,$$

$$\Delta c_E = 2.05 \cdot 10^{-3} \ [\text{m/s}].$$

Experimental

2. Phase method for measurements of the ultrasonic wave propagation velocity and its variations in liquid dielectrics

Theoretical studies [6, 7] on the influence of a static electric field on the velocity of ultrasonic waves in liquid dielectrics predict but insignificant changes in velocity.

We accordingly had recourse to the phase method, which is one of the most sensitive experimental methods available. Owing to the use of a digital phase detector with very good parameters and computer technique of data processing we achieved a very high degree of accuracy in our measurements.

With (30), we determined the error on the measurement of the absolute value of the ultrasonic propagation velocity as given by:

$$\Delta(c_0) = \frac{f}{n} \cdot \Delta l + \frac{l \cdot f}{n^2} \cdot \Delta n + \frac{l}{n} \cdot \Delta f. \tag{29a}$$

On insertion of the following experimental data:

$$f = 1.6 \cdot 10^6 \text{ Hz} \qquad \Delta f = 1 \text{ Hz},$$
$$l = 0.248 \text{ m} \qquad \Delta l = 10^{-4} \text{ m},$$
$$n_0 = 257 \qquad \Delta n = \Delta\Phi/2\Pi = 5.57 \cdot 10^{-4},$$
$$\Delta\Phi_{min} = 3.35 \cdot 10^{-3} \text{ rad} \qquad c_0 = 1544 \text{ m/s}$$

into (29a), we obtained:

$$\Delta(c_0) = 0.65 + 0.00335 + 0.00097 = 0.63442 \text{ m/s}.$$

The accuracy of our phase measurements amounted to

$$\Delta\Phi_{min} = 3.5 \cdot 10^{-3} \text{ rad},$$

permitting the recording of the change in propagation velocity, in conformity with Eq. (31), as amounting to $3.35 \cdot 10^{-3}$ m/s.

On the other hand, the relative change in propagation velocity of the ultrasonic wave is determined from Eq. (29b):

$$\frac{\Delta c}{c_0} = \frac{-\Delta\Phi \cdot l \cdot f \cdot n_0}{2 \cdot \Pi \cdot n_0^2 \cdot l \cdot f} = \frac{-\Delta\Phi}{2 \cdot \Pi \cdot n_0} = -\frac{\Delta\Phi}{\Phi_0} = 2.17 \cdot 10^{-6}. \tag{29b}$$

By (29b), the relative change in propagation velocity is independent of the length of the measuring vessel and frequency, and is dependent on the phase alone.

The block diagram of our device is shown in Fig. 1. The measuring vessel exhibits two paths along which beams of continuous ultrasonic waves propagate: the one is the reference path and the other the measuring path.
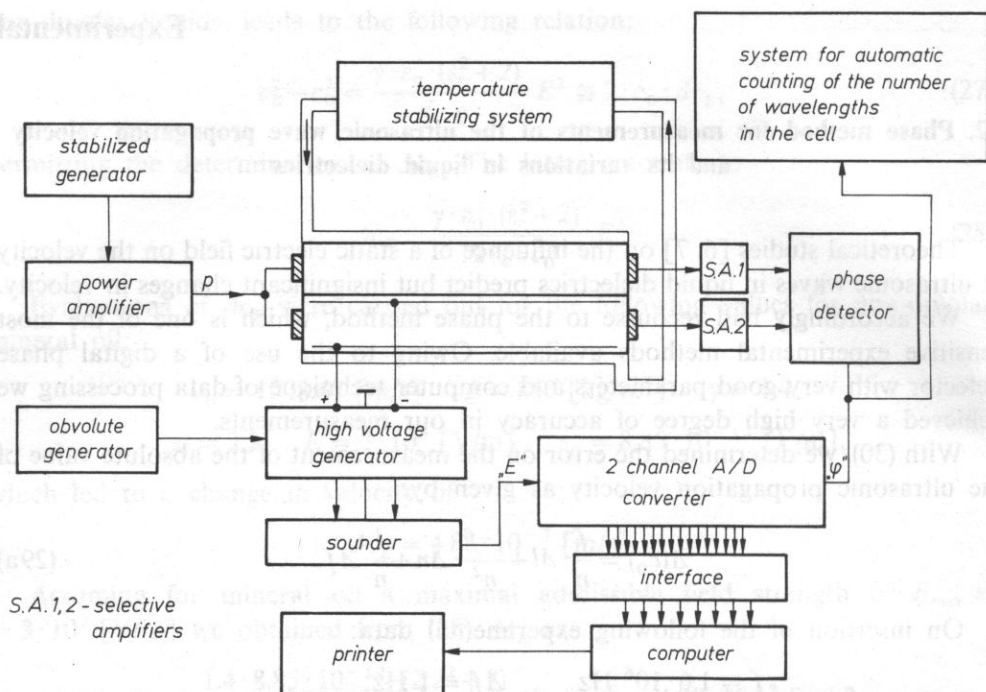
FIG. 1. Block diagram of the measuring setup for measurements of the influence of an electric field on the propagation velocity of an ultrasonic wave in a liquid dielectric

This construction of the vessel was dictated by the need for thermal compensation of the system in order to exclude effects other than that of the external electric field. The vessel holding the liquid was thermostatized by means of a cryostat. The emitter and receiver transducers were distant by $l = 0.248$ [m], whereas the distance between the field electrodes amounted to $l_1 = 26$ [mm].

The temperature stability achieved after several hours of operation of the cryostat amounted to 0.05 K, whereas the absolute values of the ultrasonic propagation velocities were determined for different temperatures (Tables 1 and 2) stabilized to within 0.2 K.

When checking for an effect of the external electric field on the temperature of the oil we used a high accuracy quartz thermometer, permitting measurements of the momentary temperature to within 0.001 K. For the duration of this test (Fig. 3), the cryostat was switched off.

To provide for zero potential (necessary for the safety of the experimenter and to ensure proper cooperation with the electronic appliances) the two electrodes introducing the external electric field were connected to a supply of bipolar symmetric voltage. The one electrode was at positive and the other at negative voltage with respect to the housing. In this way we achieved an enhancement of the electric field homogeneity throughout the liquid dielectric.

Our device permitted the measurement of the absolute propagation velocity of ultrasonic waves in liquids as well as its small variations; the relevant formulae are these [7]:

$$c_0 = \frac{l \cdot f}{n},$$ (30)

and

$$\Delta c = -\frac{\Delta \Phi \cdot l \cdot f}{2 \cdot \Pi \cdot n_0^2},$$ (31)

with: l — the distance between the transducers ($l = 0.248$ m), f — the frequency of the ultrasonic wave ($f = 1.6$ MHz), n_0 — the number of wavelengths in the measuring vessel ($n_0 = l/\lambda_0$), $\Delta \Phi$ — the change in phase, measured in radions.

In principle, the formulae (30) and (31) are valid for running waves only. If reflections of the continuous sine wave between the transducers are insignificant, (30) and (31) can be used to determine the phase velocity of the ultrasonic wave and its variations.

In the case of multiple reflections, the shift in phase Φ of a continuous sine wave at the end of a segment of length l is given by Eq. (32) [8]:

$$\Phi = \beta \cdot l + \text{arctg} \left[\frac{k_1 \cdot k_2 \cdot \exp(-2 \cdot \alpha \cdot l) \cdot \sin(2 \cdot \beta \cdot l)}{1 - k_1 \cdot k_2 \cdot \exp(-2 \cdot \alpha \cdot l) \cdot \cos(2 \cdot \beta \cdot l)} \right],$$ (32)

where $\beta = 2 \cdot \Pi \cdot f/c = 2 \cdot \Pi/\lambda$ — is the wave number, k_1, k_2 — amplitude reflection coefficients at the two ends of l, and α — amplitude damping coefficient per unit length.

The first term of (32) represents the shift in phase on a single traversal of the path l whereas the second term is related with the phase shift due to multiple reflections. One notes that as $\alpha \cdot l$ increases the effect of multiple reflections decreases. Since the vessel was relatively long and the oils studied were characterized by high damping coefficients for ultrasonic waves, we assumed $\Phi \cong 2 \cdot \Pi \cdot l/\lambda$.

In order to check our assumption we performed an evaluation of the second term of (32) for paraffin oil. The shape of $f(l)$ thus obtained is shown in Fig. 2, where

$$f(l) = \Phi - \beta \cdot l = \text{arctg} \left[\frac{k_1 \cdot k_2 \cdot \exp(-2 \cdot \alpha \cdot l) \cdot \sin(2 \cdot \beta \cdot l)}{1 - k_1 \cdot k_2 \cdot \exp(-2 \cdot \alpha \cdot l) \cdot \cos(2 \cdot \beta \cdot l)} \right].$$

The quantity plotted in Fig. 2 determins the shift in phase due to multiple reflections of the wave as a function of the length of the measuring vessel.

The first term of (32) is a linearly growing function with the following slope coefficient:

$$\beta = 2\Pi/\lambda = 2\Pi f/c = 6.7 \cdot 10^3 \text{ rad/m} = 67 \text{ rad/cm}.$$

For the whole vessel $l = 0.248$ m,

$$\frac{2\Pi}{\lambda} \cdot l = 1660 \text{ rad},$$

whence

$$\frac{2\Pi}{\lambda} \cdot l \gg f(l).$$

A comparison of the two phase terms for the oil under investigation and paraffin oil (Fig. 2) leads to similar results with regard to the great similarity of the acoustic properties of the two oils.
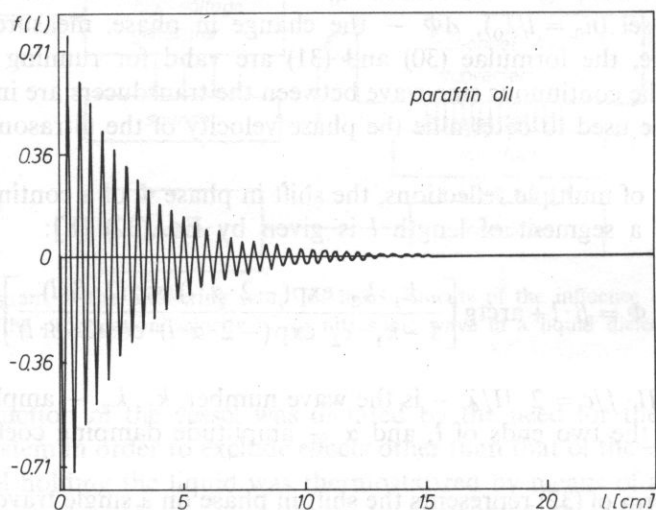

FIG. 2. The phase shift $\Phi(x)$ of the continuous wave arising in multiple reflections as a function of the length of the measuring vessel, for paraffin oil

3. Experimental results for selected liquid dielectrics

Our measurements were carried out in the following oils: mineral condenser oil, and the synthetic aromatic hydrocarbon AKB and FDO, at field strengths from 0 to 308 [kV/m] and temperatures from 253 to 303 [K]. The oils were carefully purified by various physicochemical methods [9]. Moreover, to check whether the external electric field caused a perceptible rise in temperature of the dielectric (Joule heat), we carried out tests in which, among others, we took accurate recordings of the temperature prior to and after switching the field on.

The time-evolution of temperature in the mineral oil, as shown in Fig. 3, points to
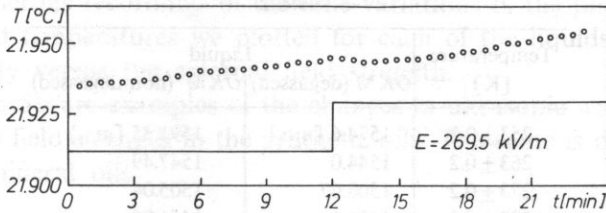
FIG. 3. Time evolution of the changes in temperature in mineral oil (condenser degassed oil) prior to and after application of the electric field

a very high grade of purity, since except for an insignificant creep in temperature (thermostat switched off), the characteristic exhibited no upward trend typical for conducting liquids on application of an electric field.

In the phase method used by us, we first determined (at a given temperature) the absolute value c_0 of the ultrasonic propagation velocity by measuring the delay in phase originating in the liquid between the emitter and receiver transducers.

Next, voltage was applied to the electrodes thus producing an electric field of strength E in the liquid dielectric. Simultaneously, we recorded in the memory of the computer the change in the phase from the moment the field was switched on until $\Delta\Phi$ attained a constant value. It was then possible to re-switch on a field of different strength. In this way we obtained recording of the change in phase with time on switching on the field, for 10 different field strengths, at a well determined temperature.

Table 1 shows the absolute values of c_0 for the synthetic condenser oils at the frequency $f = 1.6$ MHz and different temperatures.

Table 1

| Temperature [K]	Liquid		
	FDO	AKB (degassed)	AKBn (non-degassed)
253±0.2	1550 [m/s]	1600 [m/s]	1596.42 [m/s]
262±0.2	1503.1	1562.2	1555.27
273±0.2	1468.8	1520.3	1514.12
283±0.2	1437.7	1486.1	1477.04
293±0.2	1397.2	1448.2	1439.97
303±0.2	1322.7	—	—

Table 2 shows the ultrasonic propagation velocities in the mineral condenser oils determined experimentally under the same conditions and frequency.

As examples, we give in Figs. 4a and 4b the time-evolutions of the change in phase, and thus the changes in propagation velocity, for different field strengths and constant temperature.

Table 2

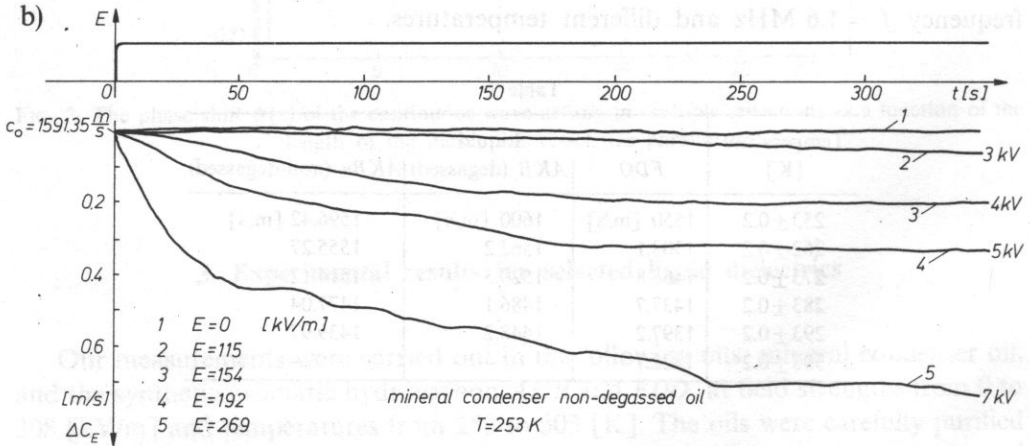| Temperature	Liquid	
[K]	OKM (degassed)	OKM (non-degassed)
253 ± 0.2	1574.6 [m/s]	1591.35 [m/s]
263 ± 0.2	1544.0	1547.49
273 ± 0.2	1508.67	1505.04
283 ± 0.2	1470.1	1466.05
293 ± 0.2	1432.56	1430.05
303 ± 0.2	1397.2	—

a)
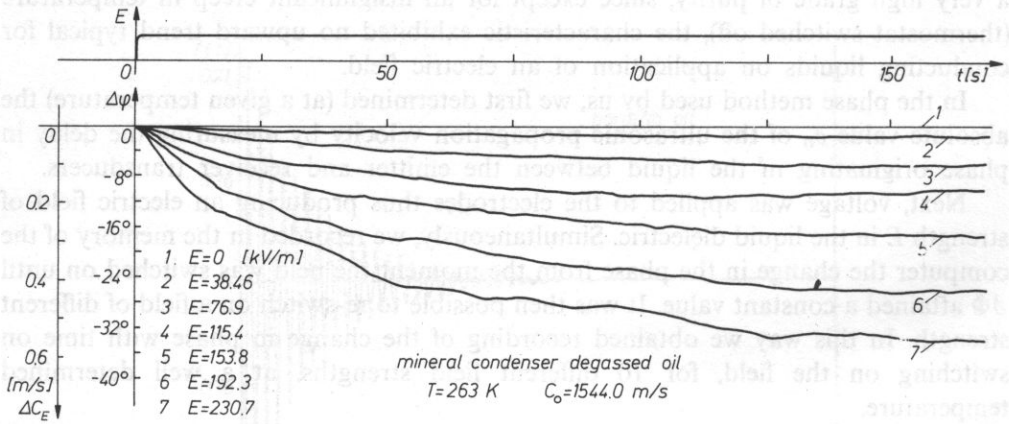
b)

FIG. 4. Time evolution of the changes in phase $\Delta\Phi$ and ultrasonic wave propagation Δc on application of an electric field at constant temperature ($T = 263$ K): a — in mineral (condenser) oil, b — in synthetic (aromatic hydrocarbon) oil

From our numerous recordings of the time-variations of the phase for different field strengths and temperatures we plotted for each of the liquids, graphs of the changes in velocity versus the external field strength.

Figures 5a and 5b are examples of the changes in ultrasonic wave propagation velocity *versus* the field strength in the synthetic oils. The same is done in Figs. 6a and 6b for the mineral oils.
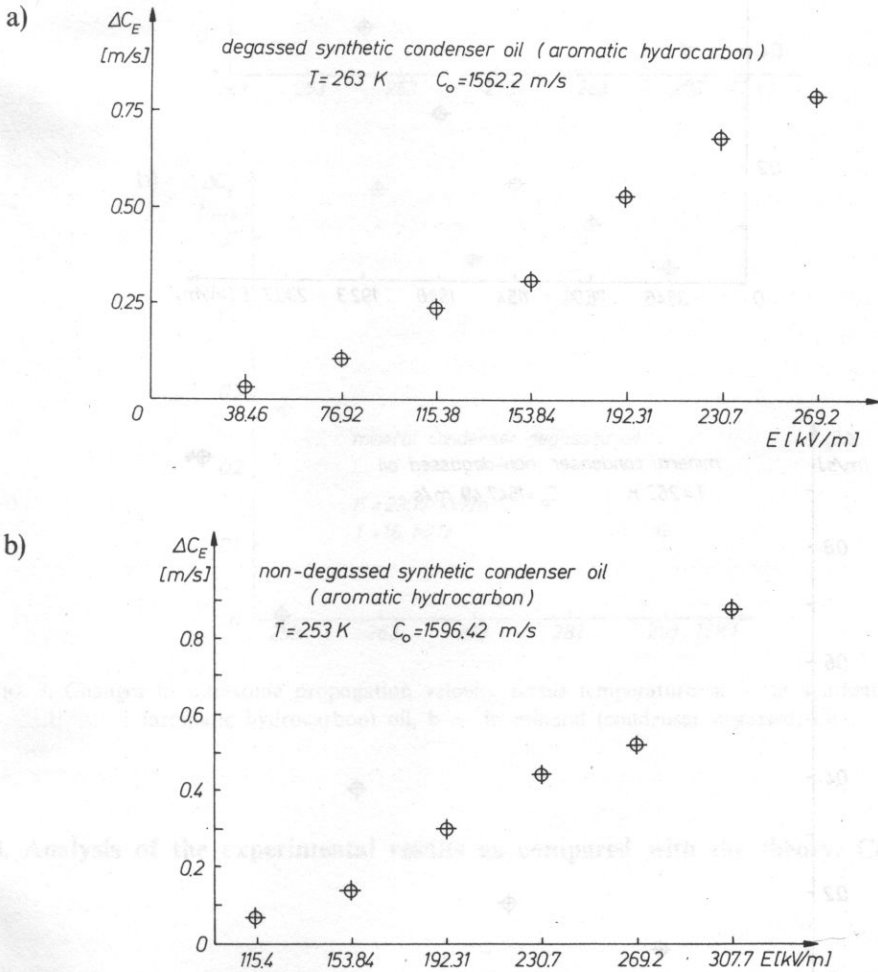
a)

b)

FIG. 5. Changes in propagation velocity *versus* electric field strength, at constant temperature: a — in degassed synthetic oil, b — in non-degassed synthetic oil

On the other hand, in Figs. 7a and 7b we give the changes in velocity *versus* temperature, for a well determined strength of the static electric field.

The electric fields strength $E = U/l_1$ was measured with an accuracy of about 1.4%.
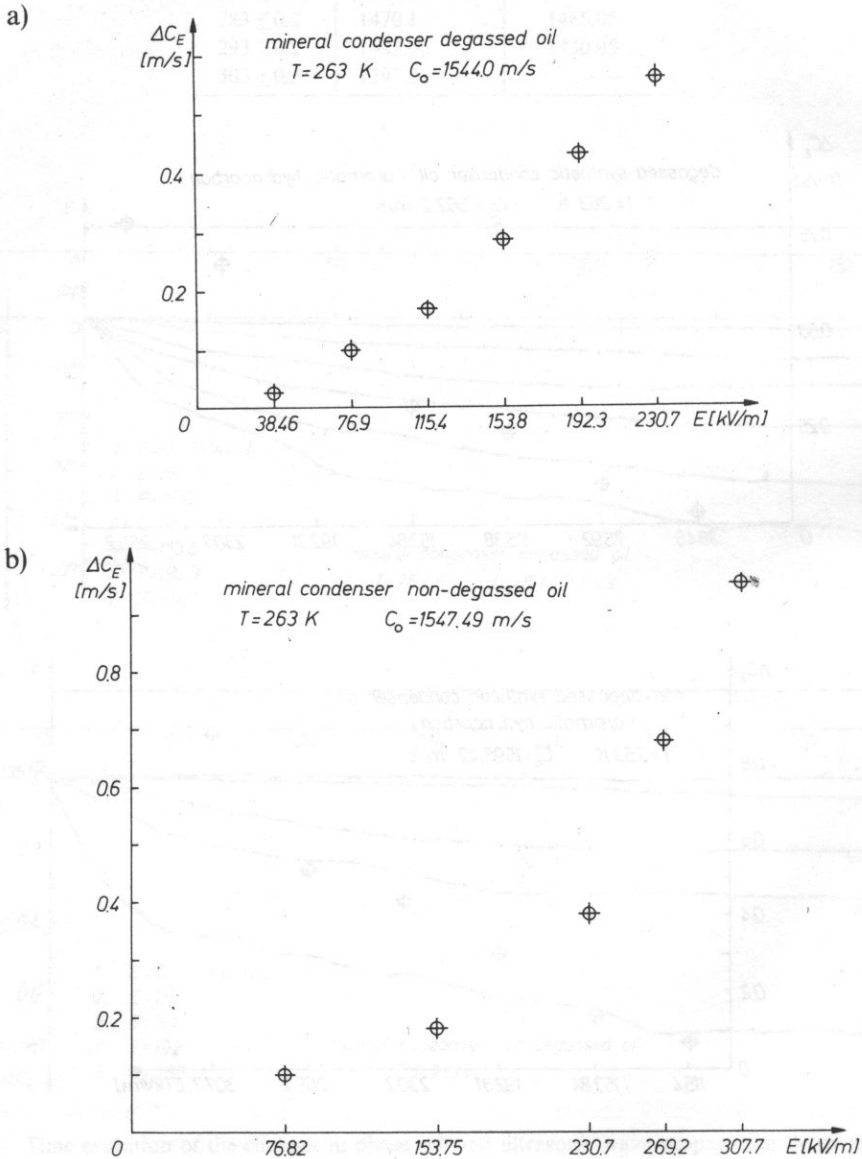
a)

b)

FIG. 6. Changes in propagation velocity *versus* electric field strength, at constant temperature: a — in degassed condenser oil, b — in non-degassed condenser oil
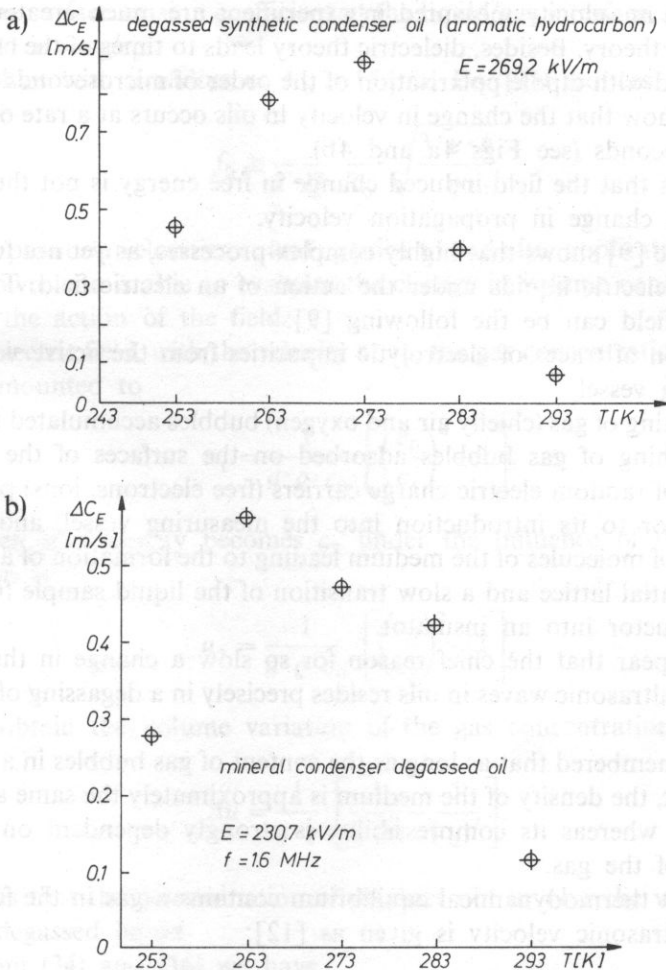
FIG. 7. Changes in ultrasonic propagation velocity *versus* temperature: a — in synthetic condenser (aromatic hydrocarbon) oil, b — in mineral (condenser degassed) oil

4. Analysis of the experimental results as compared with the theory. Conclusions

Our experiments show that an increase in strength of the externally applied electric field causes a well measurable rise in propagation velocity of the ultrasonic wave. However, a comparison of our experimental values for the field-induced changes in velocity of the wave and the values predicted by our theoretical considerations (of the formulae (28) and (29)) reveals important discrepancies.

The changes in velocity measured in experiment are much greater than those predicted by the theory. Besides, dielectric theory leads to times of the change in free energy connected with dipole polarisation of the order of microseconds whereas our measurements show that the change in velocity in oils occurs at a rate of as much as some tens of seconds (see Figs 4a and 4b).

This suggests that the field-induced change in free energy is not the only factor determining the change in propagation velocity.

The literature [9] shows that highly complex processes, as yet not fully clarified, take place in dielectric liquids under the action of an electric field. The processes caused by the field can be the following [9]:

1. elimination of traces of electrolytic impurities from the active volume of the measuring vessel,
2. the vanishing of gas (chiefly air and oxygen) bubbles accumulated in the liquid,
3. the vanishing of gas bubbles adsorbed on the surfaces of the electrodes,
4. removal of random electric charge carriers (free electrons, ions) present in the liquid prior to its introduction into the measuring vessel, and
5. ordering of molecules of the medium leading to the formation of a pseudocrystalline spatial lattice and a slow transition of the liquid sample from a donor semiconductor into an insulator.

It would appear that the chief reason for so slow a change in the velocity of propagation of ultrasonic waves in oils resides precisely in a degassing of the medium by the field.

It will be remembered that as long as the content of gas bubbles in a liquid is not excessively great, the density of the medium is approximately the same as that of the degassed liquid whereas its compressibility is strongly dependent on the volume concentration of the gas.

If a liquid at thermodynamical equilibrium contains a gas in the form of small bubbles, the ultrasonic velocity is given as [12]:

$$c_A = \frac{c_0}{\sqrt{1 + g \cdot u \cdot \varrho \cdot c_0^2}}, \tag{33}$$

with: c_A — the ultrasonic propagation velocity in the liquid with gas bubbles, c_0 — that in the liquid with no bubbles, ϱ — the density of the liquid, u — the volume concentration of the gas in the liquid, and

$$g = \frac{3}{4 \cdot \Pi^2 \cdot \varrho \cdot R_0^2 \cdot f_0^2}. \tag{34}$$

In (34), f_0 is the resonance frequency of bubbles of radius R_0 given by

$$f_0 = \frac{1}{2 \cdot \Pi \cdot R_0} \cdot \sqrt{\frac{3 \cdot \varkappa}{\varrho} \cdot \left(p + \frac{2 \cdot \sigma}{R_0}\right)}, \tag{35}$$

where σ is the surface tension coefficient at the liquid/gas interface, ϱ the hydrostatic pressure, and $\varkappa = c_p/c_v$.

For bubbles with a radius of $R_0 > 15$ μm, Eq. (35) reduces to

$$f_0 \cong \frac{1}{2 \cdot \Pi \cdot R_0} \cdot \sqrt{\frac{3 \cdot \varkappa \cdot p}{\varrho}}. \qquad (36)$$

If the propagation velocities c_1 and c_2 prior to and after application of the electric field are known, one is able to evaluate the change in volume concentration of the gas due to the action of the field.

At zero electric field, with the velocity at c_1, the gas concentration u_1 determined from (33) amounted to

$$u_1 = \frac{1}{g \cdot \varrho \cdot c_0} \cdot \left[\left(\frac{c_0}{c_1} \right)^2 - 1 \right], \qquad (37)$$

whereas when the velocity becomes c_2 under the influence of the field the gas concentration is

$$u_2 = \frac{1}{g \cdot \varrho \cdot c_0} \cdot \left[\left(\frac{c_0}{c_2} \right)^2 - 1 \right], \qquad (38)$$

whence we obtain the volume variation of the gas concentration $\Delta u = u_1 - u_2$

$$\Delta u = \frac{1}{g \cdot \varrho} \cdot \left[\frac{1}{(c_1)^2} - \frac{1}{(c_2)^2} \right]. \qquad (39)$$

One notes that the determination of Δu does not involve the velocity c_0 in the completely degassed liquid.

Since from (34) and (36) we have

$$g = \frac{1}{\varkappa \cdot p}, \qquad (40)$$

Δu finally takes the form

$$\Delta u = \frac{\varkappa \cdot p}{\varrho} \cdot \frac{(c_2 + c_1) \cdot (c_2 - c_1)}{c_1^2 \cdot c_2^2}. \qquad (41)$$

For the mineral oil with $\varrho = 900$ [kg/m³], for which our measurements gave $c_1 = 1544$ [m/s], $c_2 = 1544.55$ [m/s] and $\varkappa = 1.43$, $p = 9.81 \cdot 10^4$ [N/m²], the change in volume concentration Δu evaluated from Eq. (41) amounts to

$$\Delta u = 4.655 \cdot 10^{-8}.$$

The mobility of the gas bubbles in the electric field is also accessible to determination from the experimental data. This quantity is defined as the ratio of the velocity of displacement of gas bubbles u_0 and the electric field strength E:

$$\frac{u_0}{E} = \frac{\Delta l}{\tau \cdot E'}$$ (42)

with Δl — the distance between the electrodes in the measuring vessel, and τ — the time constant of the change in propagation velocity of the wave.

On the assumption of values currently applied in such studies, we evaluated the mobility of the gas bubbles as

$$\frac{\Delta l}{\tau \cdot E} = \frac{2.6 \cdot 10^{-2} \, [\text{m}]}{100 \, [\text{s}] \cdot 2.7 \cdot 10^5 \, [\text{V/m}]} = 9.6 \cdot 10^{-10} \left[\frac{\text{m}^2}{\text{V} \cdot \text{s}} \right],$$

a value in good agreement with the literature [9].

When, however, comparing the changes in propagation velocity measured for the same field strength but different temperatures, we found a maximum to appear at a well defined value of the temperature (see Figs 7a and 7b). Now, the dynamic viscosity of a liquid is known to vary strongly with temperature — the lower the temperature the greater is the viscosity. Obviously, at decreasing temperature, the dynamic viscosity coefficient of the liquid increases making the displacement of the gas bubbles more and more difficult.

For a given field strength we thus observe smaller and smaller changes of the ultrasonic propagation velocity. Along these lines one would expect the latter to grow monotonically with growing temperature. However, this is by no means the case.

As the temperature increases (and notwithstanding the fact that the viscosity then decreases) the thermal vibrations of the molecules increase thus preventing the displacement of the bubbles in the oil. Presumably, both these effects are responsible for the maximum of Δc_E versus temperature.

It is also noteworthy that the change in propagation velocity occurs much more rapidly in CCl_4 [10] than in oils. This, too, may hinge on the viscosity. It will be remembered that the two kinds of liquid differ very considerably as to their coefficients of dynamic viscosity (by a factor of about 100).

We are further confirmed in our conviction that the change in ultrasonic propagation velocity is due essentially to degassing by the fact that preliminary studies carried out by us in AC fields failed to detect any perceptible, measurable changes in c_E in liquid dielectrics.

Moreover, the theoretical expressions show that in the field strength range $(0 \div E_{max})$ the magnitude of $(\partial E^2 / \partial \varrho)_T$ is practically field-independent, i.e., that the electrostrictive change in density of the medium is proportional to the square of the electric field strength.

Conclusions

1. With growing field strength, the ultrasonic propagation velocity increases; however, the interpretation of the process is still incomplete.

2. The theoretical magnitudes of the electric field-induced variations in ultrasonic velocity are much smaller than those recorded in experiment.

3. Dielectrics theory leads to times of the change in free energy connected with dipole polarisation of the order of microseconds whereas our measurements for oils show the propagation velocity to vary with times of as much as some tens of seconds. This suggests that the electric field modifies the ultrasonic velocity both by affecting the free energy and by way of some other mechanism. The reason for these slow variations in Δc_E in oils is presumed to reside in degassing of the medium by the electric field.

4. The experimentally determined changes in ultrasonic velocity due to the electric field acting on the viscous medium permit the evaluation of the change in volume gas concentration in the liquid dielectric.

5. The change in ultrasonic propagation velocity measured as a function of temperature at constant field strength is found to exhibit a maximum.

6. Tests with an AC electric field failed to detect any measurable change in ultrasonic velocity.

7. The theoretical formulae lead to $(\partial E^2/\partial \varrho)_T$ — values practically independent of the electric field strength in the range $(0 \div E_{\max})$, i.e., the electrostrictive change in density is directly proportional to $(E)^2$.

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