Spontaneous polarization in dilute polar-nonpolar solutions in the dielectric relaxation region

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Permittivity plots—temperature dependences of the real ε' and imaginary ε'' parts of the permittivity—for solutions of polar substances (acetonitrile, acetone, nitrobenzene, and butanol) in nonpolar solvents (heptane, hexane, cyclohexane) with concentrations of 2–10% were obtained at a frequency near 10 GHz. Anomalous behavior of the dielectric quantities ε' and ε'' was observed: The amplitudes of the obtained spectra are many times greater than the Debye relaxation contours. A doublet of peaks in ε' and ε'' was also observed in the dielectric spectrum: The peaks lie approximately symmetrically about the relaxation center and are displaced from it by 15–20 °C. One other relaxation region (near − 45 °C) was observed in a acetonitrile-hexane solution: It probably corresponds to the contribution of the longitudinal polarization. It is hypothesized that the dielectric spectrum is determined by fluctuations. The anomalous behavior of the relaxation contours $\varepsilon'(T)$ and $\varepsilon''(T)$ is associated with spontaneous polarization, which is determined by the correlation of the dipolar molecules under conditions of quasifree rotation. The satellite peaks in the dielectric spectrum are associated with pressure fluctuations and the acoustic phonons which arise under these conditions.

Studies of the dielectric properties of dilute solutions are mainly directed toward studying the intermolecular interactions as well as improving methods for measuring the dipole moments and the relaxation times of molecules.[1]

Measurements of molecular characteristics in extremely dilute solutions and in the regime of continuous recording of small changes in dielectric quantities have recently become possible.[2] This has given rise to the real possibility of obtaining (recording) and interpreting the Debye (dielectric) spectra as a function of the temperature. This approach was verified using a microwave dielectric recording instrument.[1,2] It was implemented with the help of a two-channel arrangement using a cell based on a twin assembly of H_{011} cavity resonators. The output signal in the ε' channel is formed in accordance with the relation $\Delta\varepsilon' = k'\Delta f$, where Δf is the instantaneous difference of the frequencies of the resonators, one of which is the measuring cavity and the other is the reference cavity; k' is the cell constant and is determined during calibration. The changes $\Delta\varepsilon'$ for the solution studied are converted automatically (continuously) into the quantity Δf, which is recorded with the help of a digital frequency meter and an automating plotter. The ε'' channel is formed in accordance with the relation $\Delta\varepsilon'' = k''\Delta u$, where Δu represents crystal microwave detector voltage changes associated with the microwave power absorbed by the sample, and k'' is the cell constant. The working frequency is ≈ 10 GHz. For given k' and k'' the resolution of the dielectric recording instrument with respect to ε' and ε'' ranged from 10^{-3} to 10^{-4}. Detection and recording can be conducted simultaneously in both channels ε' and ε''. The output information is represented in the form of permittivity temperature plots $\varepsilon'(T)$ and $\varepsilon''(T)$. The cells consisted of quartz tubes (with inner diameters 1.9 and 2.9 mm), secured along the axis of the corresponding cavities. To expand the range of the measurements, each cavity can be used as a measuring (or reference) cavity. The cell is placed in a special chamber of a serially produced TK-500 thermostat, controlled with the help of a temperature regulator and a programming setup. The cells are filled through teflon tubes passing through the top cover of the thermostat.

The dielectric recording instrument in this form acquires new functional possibilities which make it possible to record dielectric spectra. The idea of observing the spectra in the temperature domain is well known.[1,3] It is based on the fact that permittivity variance depends on both the frequency ω of the analyzing electromagnetic field and on the dielectric relaxation time τ, which both appear as the product $\omega\tau$ in the dispersion equation[4,5]

$$\varepsilon^*(\omega,T) - \varepsilon_{\mathrm{IR}} = \frac{\varepsilon_s - \varepsilon_{\mathrm{sm}}}{1 + i\omega\tau_D} + \frac{\varepsilon_{\mathrm{sm}} - \varepsilon_{\mathrm{IR}}}{1 + i\omega\tau_{\mathrm{rot}}}, \qquad (1)$$

where ε_s is the quasistatic permittivity, $\varepsilon_{\mathrm{sm}}$ is the submillimeter component of the permittivity, $\varepsilon_{\mathrm{IR}}$ is the quasioptical permittivity, τ_D is the Debye relaxation time, and τ_{rot} is the relaxation time characterizing processes in the Poley region. It is well known that the relaxation time is a function of the temperature and, to a first approximation, it is described by an Arrhenius equation[1,6]

$$\tau = \frac{1}{\omega_m} = \tau_0 \exp\left(\frac{U}{RT}\right) \quad \text{or} \quad f_m = f_0 \exp\left(\frac{-U}{RT}\right), \qquad (2)$$

where $\tau = 1/2\pi f_m$ and f_m is the frequency corresponding to the maximum ε''_m of the absorption contour; U is the activation energy of the dielectric relaxation process; R is the gas constant; T is the temperature; and, $\tau_0 = 1/2\pi f_0$ is a preexponential factor. The exponential temperature dependence of the relaxation time makes it possible to tune effectively the frequency f_m of the dielectric contour relative to the fixed frequency f_w of the analyzing field. The temperature dependences $\varepsilon^*(T)$ so obtained make it possible to record the "temperature" dielectric spectra, which in the approximation (1) and (2) are equivalent to the dielectric spectra in the frequency domain.

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In the past widespread use of temperature spectroscopy was held up by the lack of data on τ (or f_m) of dilute and extremely dilute solutions. These difficulties have now been overcome in principle.[1] The temperature dependences $\varepsilon'(T)$ and $\varepsilon''(T)$ (permittivity vs temperature plots) have been obtained for a number of liquids and solutions with the help of the microwave dielectric recording instrument desribed above. They have confirmed the expected effectiveness of the dielectric method for studying dielectric relaxation processes. For a number of polar-nonpolar solutions, however, it has also been established that the temperature dependences $\varepsilon'(T)$ and $\varepsilon''(T)$ for them are anomalous, differing significantly from the Debye behavior (1). First, "resonance" behavior is observed not only in the dielectric losses $\varepsilon''(T)$ (as in the case of the Debye spectrum) but also in the real part of the permittivity $\varepsilon'(T)$. In addition, their maximum $\varepsilon'_m(T)$ and $\varepsilon''_m(T)$ occur at the same temperature T_m. Second, the amplitudes of the newly discovered spectra are many times greater (by 15–20 times) than the increments $\Delta\varepsilon'$ and $\Delta\varepsilon''$ for solutions corresponding to the usual Debye spectra. Finally, the dielectric spectrum contains satellite peaks, which are arranged symmetrically about the central line and are outwardly reminiscent of the Mandel'shtam-Brillouin doublet in the light-scattering spectrum. Moreover, another dielectric contour with a narrow band (of the order of several degrees) and relatively small amplitude (up to 1.5–2 units of ε') is observed at low temperatures (near 40–50 °C). This contour corresponds, in all probability, to the region of longitudinal oscillations of the polarizability.

A typical dielectric spectrum of a polar-nonpolar solution is presented in Fig. 1. The spectrum was constructed from the experimentally obtained temperature permittivity vs plots of dilute solutions of acetonitrile in hexane. The other solutions which we investigated (nitrobenzene, butanol, and acetone in paraffin hydrocarbons) have the same form, differing only by the width, amplitude, and position of the "line" on the temperature scale. The "lines" in the acetonitrile spectra with a width of about 15–20 °C and amplitude η up to 20 (we use here the reduced amplitude $\eta = \Delta\varepsilon_{\mathrm{obs}}/\Delta\varepsilon_{\mathrm{d}}$; $\Delta\varepsilon_{\mathrm{obs}}$ is the observed amplitude of the peak and $\Delta\varepsilon_g$ is the increment to the permittivity of the solution caused by the addition of the dipole substance) turned out to have the "highest Q." For the butanol-hexane solutions the width of the "line" increases to 30–50 °C, and the reduced amplitude decreases to $\eta = 2$–4 (with alcohol concentrations 20–30%).

The characteristic attributes of the dielectric spectra remain unchanged in a rather wide range of concentrations. For example, Fig. 2 shows the temperature dependences $\varepsilon'(T)$ and $\varepsilon''(T)$ for nitrobenzene-hexane solutions with different concentrations of the dipolar component.

We begin our analysis of the observed effect with the fluctuation nature of the dielectric constant. The fact that the dielectric properties of substances are determined by thermal fluctuations is inherent in the initial equation of the theory of polarization:[7,8]

$$\varepsilon-1=\frac{4\pi\varepsilon\langle M^2\rangle_0}{(2\varepsilon+1)VkT}, \tag{3}$$

where ε is the permittivity, k is Boltzmann's constant, T is the temperature, V is the volume of the dielectric, and $\langle M^2\rangle_0$ is the mean-square of the fluctuation electric moment. The quantity $\langle M^2\rangle_0$ characterizes the intensity of the polarization fluctuations produced in the system by density and (or) concentration fluctuations. All of them, in turn, ultimately depend on the character and intensity of intermolecular interactions.

In the general case the molecular interaction energy u in a solution can be represented as the sum[9]

$$U=U_{11}+U_{12}+U_{22}, \tag{4}$$

where U_{11} and U_{22} are the molecular interaction energies of the solvent and the (dipolar) solute, respectively, and U_{12} is the interaction energy between molecules of different kinds. The fact that the energies U_{11} and U_{12} contain only dispersion and induction components, which are not temperature dependent, must be taken into account here. They affect only the mobility of dipolar molecules and the initial permittivity. The energy U_{22} is the dipole–dipole interaction energy; it depends on the intermolecular separation r and the mutual angular orientation as[10,11]

$$U_{or}=-\frac{p^2}{r^3}(3\cos^2\theta-1), \tag{5}$$

where θ is the angle between the directions of the dipoles p which are separated by a distance r.

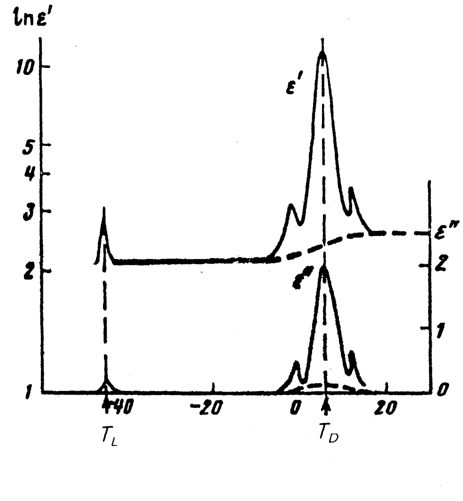

FIG. 1. Dielectric spectrum (ε' and ε'') as a function of temperature for a dilute solution of acetonitrile (10%) in hexane. The dashed curves are the expected Debye curves $\varepsilon'(T)$ and $\varepsilon''(T)$.

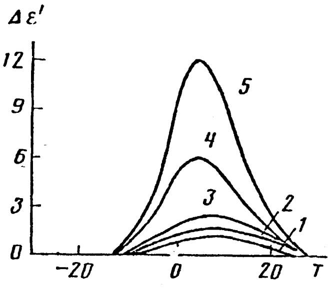

FIG. 2. Dielectric contours $\varepsilon'(T)$ of a solution of nitrobenzene in hexane with different volume concentrations: 2% (1), 3% (2), 4% (3), 5% (4), and 10% (5).

According to Eq. (5) the strength of the interaction depends on the intensity of the electric field E generated by one molecule at the location of the second molecule, so that the energy of the molecules is determined by the product pE. At distances (of the order of 1 nm) corresponding to the solution concentrations chosen in the experiment, this energy gives rise to an appreciable correlation of the molecules. Taking into account the disordering effect of the temperature, the degree of correlation of the molecules can be estimated with the help of the effective dipole moment[3]

$$p_{\text{eff}} = p\mathscr{L}\left(\frac{pE}{kT}\right), \tag{6}$$

where $\mathscr{L}(\ldots)$ is the Langevin function.

For characteristic values $p \approx 3D$, $E \approx 2\cdot 10^6$ V/cm, and $\mathscr{L} \approx 0.7$–0.8 the value of p_{eff} is five to six orders of magnitude greater than the average "isotropic" dipole moment

$$\langle p \rangle = pE_a/kT, \tag{7}$$

where E_a is the intensity of the analyzing field. This means that in dilute solutions dipolar molecules actually acquire a new state, qualitatively different from the "natural" disordered state characteristic for individual liquids. There arises a situation that is characteristic for order-disorder phase transitions, when the force field of the dipole–dipole interaction strives to counter the thermal energy by transforming the system into a new state in which the dipolar molecules are aligned in a predominant direction. The strength of the field acting on each molecule can be estimated with the help of the relation (5). For axisymmetric molecules (which dipolar molecules are) the interactions are localized near the poles of the molecules and they are oriented along the axis of the dipolar molecules. Since the field of a separate molecule has a predominant direction, the mutual orientation of the molecules also has a predominant orientation. As a result, the molecules strive to align themselves head-to-tail in a chain. For such a model, each molecule lies between the poles of its neighbors, and their interaction energy is thus determined by twice the quantity U_{or} given by Eq. (5). Under the condition that the molecules are correlated ($\cos\theta = 1$), for the most characteristic values $p \approx 3D$ and $r = 1$ nm ($N = 10^{21}$ cm^{-3}), we obtain $U_{22} \approx 4\cdot 10^{-14}$ erg, which is close, in order of magnitude, to the thermal energy kT.

The fact that the intermolecular interaction energy is equal to the thermal energy is very revealing. The point is that these energies must be equal in order for spontaneous polarization to arise in ferroelectrics.[12] An analogous effect should also occur in solutions. In this case the dielectric properties of the solutions must satisfy the Curie–Weiss law[12]

$$\varepsilon - 1 = \frac{c}{T - T_c}, \tag{8}$$

where c is a constant and T_c is the critical temperature.

In the case of dilute solutions the condition for the formation of spontaneous polarization according to Eq. (8) is the energy balance $kT = U_{22}$ realized in the temperature dependence of the permittivity at $T = T_c$. The overall model of dipole correlation of the molecules, which was proposed above, corresponds to the Ising model (its electrical variant), which explains fairly well the mechanism of spontaneous polarization of ferroelectrics.[12]

In contrast to solid ferroelectrics, for which domain formation is a characteristic feature, apparently only mobile short-lived clusters distributed randomly in the volume in can form in solutions, and for this reason in the absence of a field they do not exhibit any macroscopic manifestations. In an external electric field such dynamical domains acquire a corresponding orientation which ensures formation of an increased macroscopic electric moment.

The model of dynamical domains is very close to the model of sybotactic groups (swarms), which Frenkel took into account in his analysis of the properties of liquids in electric and magnetic fields (Ref. 13, p. 349). Frenkel started from the assumption that a "swarm" consisting of g molecules behaves in an external field as a single gigantic molecule with moment pg''. From the fundamental standpoint, this idea is in full agreement with the mechanism of spontaneous polarization. A specific feature of dilute solutions is that the energies kT and U_{22} remain approximately the same in a wide temperature range.

Another characteristic feature of dilute solutons is that the dipole–dipole interaction energy U_{22}, which operates against the background of the relatively large energy U_{12} [see Eq. (4)], is small. The correlation becomes more effective as U_{12} decreases; the effect of this energy is to limit the angular mobility of the molecules.

Thus the strongest ferroelectric effect should be expected for solvents with the lowest activation energy U_a directly related with the energy U_{12}. In this respect, methane solutions and insulating matrices based on noble gases are promising. On the other hand, it has been established that in benzene solutions (for which the activation energy is approximately two times larger than in the hydrocarbons employed) the effect is no longer appreciable.

This explains why the dielectric properties of individual liquids do not exhibit any anomalies with respect to the Debye behavior in the region of dielectric relaxation. In liquids, the energy of the central interaction forces is significantly greater than the dipole–dipole interaction energy, and for this reason it suppresses the rotational motion of the molecules and this weakens the correlation of the dipoles. This result is in full agreement with the relatively small g factor (not more than 3–4) in liquids, which characterizes the associating capability of the molecules (the factor g is the parameter in Kirkwood's theory[1,7]).

Light scattering studies also confirm the fact that fluctuations are manifested significantly more strongly in solutions than in liquids.[4]

Thus the spontaneous polarization arising under conditions of quasifree rotation of dipolar molecules is responsible for the resonance character of the temperature dependence $\varepsilon'(T)$ and the anomalously high amplitudes of the relaxational contours $\varepsilon'(T)$ and $\varepsilon''(T)$ of dilute polar-nonpolar solutions. Evidently, this effect cannot be studied without taking into account its relation to the frequency behavior of the dielectric properties of solutions. According to the activation mechanisms of dielectric polarization in solutions, two regions of dielectric relaxation are present in the behavior of the dielectric constant (1) as a function of the frequency: the Debye and Poley regions.[4,5] The frequencies $f_L = 1/2\pi\tau_D$ and $f_U = 1/2\pi\tau_{\text{rot}}$ are the centers of the corresponding relaxation regions. The interaction of the analyzing field with the dipolar molecules is strongest at these frequencies. For a given strength of the source of the field, however, this means nothing more than maximum field–matter interaction time. The interaction time, in turn, predetermines over the effectiveness of the orientation of the dynamical "domains" and, correspondingly, the magnitude of the effective electric moment and therefore also the solution permittivity itself. Here the field is an ordering factor, which orients "domains" predominately in the direction of the analyzing field.

At "resonance" $\omega\tau_D = 1$ the period of the electromagnetic wave is equal to the average translational diffusion time, and for $\omega\tau_{\rm rot} = 1$ the period of the electromagnetic wave is equal to the average rotational (angular) diffusion time.[5]

Polarization in dilute polar–nonpolar solutions is distinguished from the "standard" polarization by the fact that the former is formed by molecular clusters (which are produced by molecular correlation) whose electric moments are significantly larger than the statistical dipole moments $\langle p \rangle$ of separate molecules. This mechanism of dielectric polarization in solutions is confirmed by the fact that the observed effect decreases systematically as the solution concentration decreases (see Fig. 2). It follows from Eq. (1) that the dispersion behavior of $\varepsilon^*(\omega,T)$ depends, to the same degree, on both the frequency ω and the relaxation time τ. The dependences $\varepsilon^*(\omega)$ and $\varepsilon^*(T)$ form the basis for the known methods of studying dielectric relaxation.[1] A corresponding measurement apparatus has been developed in order to implement these methods, namely dielectric spectrometry in the frequency and temperature domains, respectively.[1,2] Unfortunately, this apparatus does not completely satisfy the requirements which it must meet for applications in studies of dielectric spectra of dilute and extremely dilute solutions. The apparatus described above (microwave dielectric recording instrument) has made such studies possible. For dilute solutions the temperature dependences $\varepsilon^*(T)$ obtained with its help are typical dielectric spectra.

We now estimate the frequency f_m of the corresponding "resonance" temperatures T_D and T_L of the dielectric spectrum (Fig. 1). For this, we write Eq. (2) for the "resonance" temperature T_m, to which correspond the maxima of the contours $\varepsilon'(T)$ or $\varepsilon''(T)$ of a dilute solution at the frequency f_w of the analyzing field,

$$\ln\frac{\nu_m}{f_w} = \frac{U}{RT_m}\left(1-\frac{T_m}{T}\right), \qquad (9)$$

where ν_w is the frequency corresponding to the relaxation time τ at temperature T, $\tau = 1/2\pi\nu_w$, U is the activation energy, and R is the gas constant.

Substituting into Eq. (9) the values $U \approx 20$–25 kJ/mole, $T = 298$ K, $T_m = T_D = 275$–280 K, and $\tau = 4$ psec for acetonitrile solution gives in order of magnitude $\nu_w/\nu_m \approx 4$. Hence $\nu_w \approx 10$ GHz, which corresponds to the working frequency f_w.

A similar situation obtains for the temperature T_L of the second relaxation region ($T_L \approx 230$ K). The expected change in the frequency ν_m can be estimated from Eq. (9). Under the assumption that the low-temperature relaxation region is of a rotational nature $U_a = U_{\rm rot} \approx kT$,[5] we obtain $\nu_L \approx 1.3 f_w$. Of course, however, with such a small tuning slope $\Delta f/\Delta T$ the frequency ν_m cannot be transferred from the submillimeter range into the microwave range. The result is thus significant, since it confirms the experimental fact that the position of the Poley absorption contour is virtually temperature independent.

The assumption that longitudinal oscillations of the polarization with frequency $1/\tau_L = (1/\tau_D)(\varepsilon_s/\varepsilon_{\rm IR})$ are present in the solution is more plausible.[15] In this case $U_a \approx U_D \approx 20$ kJ/mole, and the tuning slope of the frequency ν_m becomes large, so that for the parameters of the low-temperature relaxation region $\nu_m \approx 10 f_w$. This is in complete agreement with existing ideas about the nature of longitudinal oscillations of the polarization.[15]

Two circumstances are important for the formation of the observed dielectric spectrum. The first is associated with the high correlation of the dipoles, which results in an anomalous increase of the amplitude of the dielectric contours $\varepsilon'(T)$ and $\varepsilon''(T)$. The second one is associated with the strong interaction of dipolar molecules with the electromagnetic field in the region of the dielectric relaxation; they determine one another and together produce the observed effect, i.e., an additional (spontaneous) polarization, associated with the high correlation of dipolar molecules in solution, is superposed on the "usual" mechanism of dispersion of the permittivity according to (1). This contribution to the permittivity is much greater than the drop in ε' and ε'' expected according to Eq. (1), equal to $(\varepsilon_s - \varepsilon_{\rm sm})/2$ (at $\omega\tau = 1$).

It is interesting that the dielectric spectra are very similar to the light-scattering spectra. The dielecric spectrum (see Fig. 1), like the light-scattering spectrum, had a doublet of lines, approximately symmetrically arranged about the central peak (similarly to the Mandel'shtam–Brillouin doublet formed by isentropic pressure fluctuations[11,14]). It is well known that adiabatic pressure fluctuations in a fluid propagate in the form of undamped waves with the speed of sound. Owing to the wave character of the propagation of acoustic disturbances, the behavior of the pressure fluctuations is correlated even at distances which are large compared with intermolecular distances.[16] The pressure fluctuations, in turn, modulate the permittivity of the solution, which can be recorded. In an undamped sound wave (acoustic phonon) the relation between the frequency Ω and the wave vector q is $\Omega^2 = v^2 q^2$. Correspondingly, the spectral resolution of the correlation function of the pressure fluctuations (and thereby also the corresponding permittivity fluctuations) will contain two lines with frequencies[16]

$$\Omega = \pm vq, \qquad (10)$$

which is what predicts the presence of a doublet of lines in the dielectric spectrum.

To a given direction of the electric field (achieved by the adopted orientation of the cell in the resonator) there correspond acoustic phonons, with frequency Ω and wave vector q, which coincide with this direction. For this reason, frequencies shifted upwards and downwards with respect to the radiation frequency ω, i.e., $\omega \pm \Omega$, appear in the direction of the electric field as a result of modulation of the permittivity of the solution. The separation of a given orientation of the phonons gives apparently rise to the vertical temperature gradient arising in the cavity.

The presence of fluctuation sound waves in the solution can be described by a corresponding Lorentzian,[17] introduced into the material equation of the dielectric polarization

$$\varepsilon''(\omega)\sim\varepsilon''(T)\sim\mathscr{L}(\omega_0\pm vk-\omega)$$

$$=\frac{1}{\pi}\frac{\Gamma k^2}{(\omega_0\pm vk-\omega)^2+(\Gamma k^2)^2}, \tag{11}$$

where ω_0 is the angular frequency of the analyzing field, v is the speed of sound waves in the solution, k is the wave vector, and Γ is the effective mass diffusion coefficient for sound waves in the medium. The Lorentzian $\mathscr{L}(\cdots)$ describes the frequency (or temperature) behavior of the permittivity of the solution, owing to pressure fluctuations at constant entropy, which in turn results in propagation of sound waves with speed v. This process is characterized by a damping with time constant $1/\Gamma k^2$.

The poles $\pm vk$ determine the positions of the satellites on the frequency scale and, taking Eq. (2) into account, also on the temperature scale. Since the system is actually in the region of the "diffuse" phase transition, the accompanying significant increase in the fluctuations permits experimental observation of the satellites $\omega\pm\Omega$ in the dielectric spectrum with the help of existing measurement apparatus. For this reason, an equation similar to (11) can also be written for the real part of the permittivity.

The experimentally obtained satellite frequencies $\Omega/2\pi$ in the dielectric spectrum [given by the data on the corresponding temperatures of the spectrum according to Eq. (2)] agree in order of magnitude (10^9-10^{10} Hz) with the frequencies of the Mandel'shtam-Brillouin lines in the light-scattering spectrum.[11–17] The intensity of the satellites in the dielectric spectra of the solutions studied is significantly weaker than for the central peak, but sufficient to record them reliably: Their amplitudes reach $\Delta\varepsilon'_a\approx1.5$ and $\Delta\varepsilon''_a\approx0.1$ (with instrumental resolution $\Delta\Delta\varepsilon'\approx10^{-3}$ and $\Delta\Delta\varepsilon''\approx10^{-4}$).

We now make some quantitative estimates on the basis of the experimental data. First, we determine Ω from Eq. (9), substituting into this equation the known quantities $U\approx20$–25 kJ/mole, $T\approx280$ K, and $\Delta T\approx15$–20 K. We use the obtained frequency $\Omega/2\pi\approx5\cdot10^9$ Hz to calculate the wave number of the sound wave from Eq. (10), using $v\approx10^5$ cm/sec. We obtain the value $q\approx3\cdot10^5$ cm^{-1}, which agrees, in order of magnitude, with the experimental data on light scattering;[17] this can serve as a confirmation of the "sound" origin of the doublet of lines in the dielectric spectrum. Comparison of the experimental data on the width of these lines with the calculations also gives the same result. The width is determined by the mass diffusion coefficient (Γ) for sound waves according to the relation[18]

$$\Delta\Omega_\Gamma/2\pi=\Gamma q^2. \tag{12}$$

Substituting into Eq. (9) the known quantities $\Delta T_\Gamma\approx(7$–$10)$ K, $T\approx280$ K, and $f_w\approx10^{10}$ Hz gives $\Delta\Omega_\Gamma/2\pi\approx10^9$ Hz. Next, substituting $\Delta\Omega_\Gamma$ into Eq. (12), we obtain $\Gamma\approx10^{-2}$ cm^2/sec, which also agrees in order of magnitude with existing data.[17] The strong fluctuations inherent only in solutions (concentration fluctuations) were a decisive factor for observing the "anomalous" dielectric spectrum. Fluctuations in liquids (density fluctuations) are significantly weaker, though they remain finite and they can theoretically be predicted in the dielectric spectrum. This supposition was confirmed experimentally. Quasiresonance contours $\varepsilon'(T)$ and $\varepsilon''(T)$ in nonanol, which are indicative of fluctuation processes, were observed with the help of the same apparatus (described above). Their amplitudes $\varepsilon'_m\approx0.5$ and $\varepsilon''_m\approx0.1$ are significantly smaller than for the "resonance" spectra of solutions, and the position of the contours ε' and ε'' on the temperature scale was found to be above "room" temperature ($T_m\approx350$ K). The "resonance" observed in nonanol apparently lies in the first relaxation region, which corresponds to relaxation time $\tau\approx2$ ns.[19] For this reason, at room temperature the frequency ν_m of the relaxation contour lies significantly below the working frequency f_w. In order to observe resonance $\nu_m=f_w$ the temperature of the solution must be increased. The low amplitude of the contours $\varepsilon'(T)$ and $\varepsilon''(T)$ in nonanol can be explained by the relatively weak correlation of the dipolar alcohol molecules.[6,19]

Spontaneous polarization has thus been observed in dilute polar-nonpolar solutions. The effect consists of an anomalous increase in the dielectric quantities in the region of Debye relaxation of solutions at concentrations corresponding to high correlation of dipolar molecules and the appearance of a doublet of lines arranged symmetrically about the central relaxational contour.

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