The results of investigating the dielectric properties of pyridine–benzene solutions at \( \lambda = 375 \) m, 3.21 cm, and 0.815 cm and the temperatures 10, 20, 30, and 40°C are set forth. The dielectric relaxation times and the enthalpies and entropies of activation of Brownian rotation were calculated for pyridine molecules. The time of Brownian rotation of the molecules in pure benzene was found. The magnitudes of concentration fluctuations in the first coordination sphere were calculated. It was shown that associated complexes of molecules are not formed in pyridine–benzene solutions. Experimental data agree quantitatively with theory if the latter takes into account the effect of concentration fluctuations on the dielectric properties of solutions in dc and high-frequency fields.

The benzene and pyridine molecules are similar in mass, size, and shape and are isoelectronic. In the pure liquids, benzene and pyridine, the mutual orientations of the molecules are distributed chaotically, and there is no association [1]. Acoustical investigations [2] and a study of light scattering [3] show that in pyridine–benzene solutions the mutual orientations of all types of molecules remain chaotic. However, pyridine–benzene solutions exhibit considerable positive deviations from ideality [4]. According to the molecular theory of solutions (see [5], pp. 378–387), this is explained by the fact that pyridine molecules are polar (\( \mu = 2.22 \) D), whereas benzene ones are nonpolar. Hence concentration fluctuations are relatively large in pyridine–benzene solutions. Thus such solutions are very convenient for studying the effect of concentration fluctuations on dielectric properties. We measured the dielectric constant \( \varepsilon_1 \) and dielectric loss \( \varepsilon_2 \) of these solutions in a broad interval of frequencies, temperatures, and compositions in order a) to obtain information on the molecular structure of solutions by independent methods of investigation, b) to consider the results of applying the theory of the dielectric properties of solutions, developed in [1], to this case, and c) to compare our conclusions regarding the structure of pyridine–benzene solutions with those reached by earlier methods of theoretical analysis [6].

The compounds used had the following properties: benzene, b. p. 80.1°/760 mm; m. p. 5.53°; pyridine, b. p. 115.0°/761 mm. Refractive indices \( n_D \) and densities \( d_4 \) are given in Table 1, together with our values of these constants for the solutions. Refractive index was determined with a Pulfrich refractometer. The method of measuring the dc dielectric constant \( \varepsilon_1 (\lambda = 375 \text{ m}) \), as well as \( \varepsilon_1 (\lambda = 3.21 \text{ and } 0.815 \text{ cm}) \), is described in [1]. The results are given in Table 2.

It follows from Table 2 that \( \varepsilon_1 \) is a linear function of \( 1/T \), where \( T \) is the temperature in °K in the interval studied (10–40° C). According to [1] and [7], this means that pyridine–benzene solutions consist of either molecules or stable (i. e., undissociated) molecular groups with chaotic distribution of mutual orientations. To answer the

<table>
<thead>
<tr>
<th>( \varphi )</th>
<th>( n_D^{20} )</th>
<th>( d_4^{20} )</th>
<th>( \varphi )</th>
<th>( n_D^{20} )</th>
<th>( d_4^{20} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.000</td>
<td>1.51004</td>
<td>0.9831</td>
<td>0.300</td>
<td>1.50480</td>
<td>0.9111</td>
</tr>
<tr>
<td>0.900</td>
<td>1.50948</td>
<td>0.9734</td>
<td>0.116</td>
<td>1.50255</td>
<td>0.8911</td>
</tr>
<tr>
<td>0.710</td>
<td>1.50811</td>
<td>0.9534</td>
<td>0.000</td>
<td>1.50106</td>
<td>0.8793</td>
</tr>
<tr>
<td>0.501</td>
<td>1.50636</td>
<td>0.9322</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

question as to the composition of structural units forming solutions, we shall consider the relation between \( \varepsilon_s \) and solution concentration. Let the subscript 1 denote the polar component and subscript 2 the nonpolar.

We shall assume further that the mutual orientations of the molecules are distributed chaotically (i.e., no complexes are present) and neglect the effect of concentration fluctuations. According to Onsager's theory [8], developed for solutions on just such assumptions (in this case the experimental constant of the solutions is equal to the average local dielectric constant [1]: \( \varepsilon_s = \varepsilon_{sl} \)), the relation between \( \bar{\varepsilon}_{sl} \) for the solution and the dc dielectric constants of the individual liquid components has the form *:

\[
\bar{\varepsilon}_{sl} \approx \varepsilon_{sl} \phi + \varepsilon_{st} (1 - \phi) .
\]  

(1)

Comparison of values of \( \bar{\varepsilon}_{sl} \) for solutions, calculated by Eq. (1) (Table 3), with experimental values of \( \varepsilon_s \) (Table 2) shows that the difference \( \varepsilon_{sl} - \varepsilon_s \) is positive throughout the concentration interval and reaches a maximum at \( \phi = 0.6 \). The results of calculation for 20° are given in Table 3. For other temperatures from 10 to 40° the shape of the \( \varepsilon_s \) isotherms remains unchanged, but the difference \( \bar{\varepsilon}_{sl} - \varepsilon_s \) decreases slightly with rising temperature. We shall assume that the difference between \( \varepsilon_s \) values calculated by Eq. (1) and experimental \( \varepsilon_s \) values is due to the effect of solution inhomogeneity caused by small-scale concentration fluctuations. Then this difference should agree with values of \( \varepsilon_{sl} - \varepsilon_s \) calculated by the following equation (see [1], p. 150):

\[
\delta \varepsilon = \frac{\varepsilon_{sl} - \varepsilon_s}{\partial \varepsilon_s / \partial \phi} .
\]  

(2)

Calculations by Eq. (2) for solutions at 20° and \( \phi = 0.50 \) and 0.710 give \( \Delta \varepsilon_s = \bar{\varepsilon}_{sl} - \varepsilon_s = 0.9 \pm 0.5 \) and 0.8 \pm 0.5, respectively. The differences \( \Delta \varepsilon_s \), calculated from the \( \bar{\varepsilon}_{sl} \) and \( \varepsilon_s \) values listed in Tables 2 and 3, are equal to 0.42 and 0.75. The discrepancies between the \( \Delta \varepsilon_s \) values lie within the limits of experimental and computational error. The formula

\[
(\Delta \phi)^2 = \frac{(\bar{\varepsilon}_{sl} - \varepsilon_s) 3\varepsilon_s}{(\varepsilon_{sl} - \varepsilon_s)^2}
\]  

(3)

was used to calculate the statistical-average small-scale concentration fluctuations (Table 3). These values pass through a maximum when the volume fraction of pyridine \( \phi \) is about 0.6. According to [1] (see p. 146), it follows from this that in the first coordination sphere of molecules, \( |\Delta \phi| \approx 0.4 \) on the average. Hence if \( Z = 12 \), the first coordination sphere of the pyridine molecule contains an average of 10 such molecules when \( \phi = 0.6 \). When the centers of mass of the molecules are distributed chaotically (ideal solution), this number should be 7 at \( \phi = 0.6 \).

Using values of \( \varepsilon_s, \varepsilon_{sl}, \) and \( \varepsilon_{st} \) from Table 2, one may plot diagrams of complex dielectric constant (Argand diagrams). The centers of the arcs \( \varepsilon_2 = f(\varepsilon_1) \) lie very close to the \( \varepsilon_1 \) axis. Hence \( \varepsilon \) for pyridine–benzene solutions, as well as pure pyridine [1], almost exactly follows the equation

*The equation derived by Onsager is actually much more cumbersome (see formula 13.5 in [1]), but it leads practically to the same relation as our Eq. (1). The results of calculating \( \varepsilon_{sl} \) for pyridine–benzene solutions at 20° by Eq. (1) and the equation derived directly by Onsager are compared in Table 3.