Complex permittivity of organic solvents at microwave frequencies

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Abstract. The complex electrical permittivity of industrially produced organic solvents of several classes with different abilities to form hydrogen bonds, such as ketones (acetone, 2-butanoctane), alcohols (ethyl alcohol, isopropyl alcohol), acetic esters (ethyl acetate, propyl acetate, butyl acetate), hydrocarbon solvents (toluene, ortho-xylene, heptane, solvent Nefras), chlorine-containing solvents (carbon tetrachloride, tetrachloroethylene), as well as a mixed solvent based on acetone, butyl acetate and ortho-xylene of brand R-5A, were studied. The frequency dependences of permittivity were measured by the coaxial probe method in a wide frequency range from 200 MHz to 20 GHz. It is shown that the chemical nature of solvents has a significant effect on their permittivity. It was found that solvents with weak hydrogen bonds (hydrocarbons and chlorine-containing solvents) have low values of the permittivity (not higher than 2.6) and negligible dielectric losses. Solvents with moderately strong bonds (acetic acid esters and ketones) have high values of permittivity with pronounced frequency dispersion, noticeable dielectric losses and Debye relaxation frequency above 20 GHz. Strong hydrogen bonded solvents (alcohols) are characterized by high values of the permittivity with significant frequency dispersion and Debye relaxation frequency below 1.5 GHz.

1. Introduction

Currently, organic solvents are widely used in many industries: in the manufacture of polymer composite materials, including glass and carbon plastics, during the organic synthesis of substances, in paint and varnish industry, etc. The choice of solvents largely depends on their application and properties, necessary for any technological process. As a rule, to solve a specific problem, the desired solvent is selected based on the following characteristics: dissolving ability, volatility, viscosity, electrical conductivity, fire hazard, explosion hazard, etc. However, in some areas of industrial application, for example, for the manufacture of coatings by electrostatic deposition [1], the production of nanofibers and fibrous materials by the method of electroforming [2], the synthesis of various substances, the electromagnetic properties of solvents, namely, the values of their electrical permittivity are the most important.

A lot of scientific papers have been devoted to the research of the electromagnetic properties of widely used organic solvents [3–6]. A significant drawback of most works is that the data (calculated or experimental) on the permittivity of solvents are given either at one allocated (fixed) frequency or in a rather narrow frequency band. Moreover, in the literature data, as a rule, the research results of a wide class of solvents are not presented.
The study of the dielectric properties of solvents is also important in the aspect that, in the manufacture of many polymer composite materials and non-metallic structural materials (glass, carbon fiber), to ensure good material impregnation, uniform distribution of the filler in the matrix, solvents are used to reduce the viscosity of the binder, which after the manufacturing process remain in the volume of the material – residual solvents. Residual solvents, in turn, affect the radiophysical characteristics of the resulting polymer composite materials. In this regard, having information on the dielectric properties of solvents in a wide frequency band, it is possible to create methods for determining residual solvents in polymer composite materials, which will allow conducting an output control of products from such materials by radiophysical parameters.

Thus, the study of the frequency dependences of the complex permittivity of organic solvents in a wide frequency range is an urgent task of modern materials science.

2. Objects of the research and measurement technique

Widely used, industrially-produced organic solvents of several classes with different ability to form hydrogen bonds were selected as objects of research:

- alcohols – ethyl alcohol, isopropyl alcohol;
- esters of acetic acid – ethyl acetate, n-propyl acetate, butyl acetate;
- ketones – acetone (propanone), methyl ethyl ketone (butanone);
- hydrocarbons – toluene, ortho-xylene, heptane, solvent Nefras;
- chlorine-containing solvents – carbon tetrachloride, tetrachlorethylene;
- mixed solvent R-5A (acetone: butyl acetate: ortho-xylene in a ratio of 3:3:4).

Table 1 shows some characteristics of the studied solvents [5–8]. All selected solvents are chemically pure qualifications.

The values of the complex permittivity of the indicated solvents were measured by the coaxial probe method. This method relates to non-destructive testing and is well suited for determining the dielectric properties of non-magnetic materials, the magnetic permeability of which is equal to one. An open-input coaxial probe is essentially a transmission line with a slice at one end. The measurement of complex permittivity occurs by immersing the probe in a liquid. The field created at the open end of the probe penetrates the material, using the vector network analyzer (VNA), the complex reflection coefficient (S11) of the transmission line is measured and the value of permittivity is calculated from the measured value of S11 [9]. Figure 1 shows a typical measuring system that implements the coaxial probe technique, which consists of a VNA, software for calculating the complex permittivity, coaxial probe, probe holder and microwave cable.

![Figure 1. Diagram of microwave permittivity measurements by the coaxial probe technique.](image)
In this article, DAK (Dielectric Assessment Kit) software and hardware complex, coupled with the Rohde & Schwarz ZVA24 VNA, acted as a ready-made technical solution for measuring the dielectric properties of solvents. DAK complex is the optimal solution for measuring the dielectric parameters of liquids. The special geometric shape of the probes ensures high measurement accuracy. The advantages of DAK complex are its high measurement speed, portable design, a wide frequency range (from 10 MHz to 67 GHz, depending on the types of probes used), as well as ease of calibration and work with software.

Table 1. Characteristics of organic solvents at a temperature of 25 °C.

| Name of a solvent     | Density (g/cm³) | Electrical conductivity (Ohm⁻¹·cm⁻¹) | Permittivity at a frequency of 10⁶ Hz |
|-----------------------|-----------------|--------------------------------------|-------------------------------------|
| **Solvents with weak hydrogen bonds** |                 |                                      |                                     |
| toluene               | 0.87            | <10⁻¹⁴ (19.5 °C)¹                  | 2.4                                 |
| ortho-xylene          | 0.88            | 10⁻¹⁵ (19.5 °C)²                  | 2.5                                 |
| solvent Nefras        | 0.86            | –                                    | –                                   |
| heptane               | 0.68            | <10⁻¹³ (19.5 °C)²                  | 1.9                                 |
| carbon tetrachloride  | 1.54            | 4·10⁻¹⁸ (18 °C)³                  | 2.3 (0 °C)³                         |
| tetrachlorethylene    | 1.62            | –                                    | 2.2                                 |
| **Solvents with moderately strong hydrogen bonds** |                 |                                      |                                     |
| ethyl acetate         | 0.90            | 10⁻⁹                                | 6.0                                 |
| propyl acetate        | 0.84            | –                                    | –                                   |
| butyl acetate         | 0.88            | –                                    | 4.9 (30 °C)¹                        |
| solvent R-5A          | 0.85            | –                                    | –                                   |
| methyl ethyl ketone   | 0.81            | 10⁷ (19.5 °C)³                    | 18.5 (20 °C)³                       |
| (butanone)            |                 |                                      |                                     |
| acetone               | 0.79            | 6·10⁻⁸                              | 20.7                                |
| **Solvents with strong hydrogen bonds** |                 |                                      |                                     |
| isopropyl alcohol     | 0.79            | 3.5·10⁻⁶                           | 18.3                                |
| ethyl alcohol         | 0.79            | 1.3·10⁻⁹                           | 25.2                                |

¹ The value of a different temperature for the indicated reference values is given in parentheses.

The dielectric spectra of the studied solvents were measured in a continuous frequency band from 0.2 to 20 GHz with a step of 10 MHz at room temperature 23 °C.

3. Measured results and discussion
Figures 2 and 3 show the measured frequency dependences of the real and imaginary parts of the complex permittivity of non-polar solvents: heptane, toluene, ortho-xylene, carbon tetrachloride, tetrachlorethylene, and solvent Nefras.
It can be seen from the measurement results shown in figures 2 and 3 that for solvents with weak hydrogen bonds (hydrocarbons and chlorine-containing solvents), the real part of the permittivity $\varepsilon'$ is practically independent of the frequency in the bandwidth from 200 MHz to 20 GHz, in contrast to the imaginary part of permittivity $\varepsilon''$, the nature of the frequency dispersion of which varies depending on the type of solvent. So for solvents that do not have dipole moments in the molecules (carbon tetrachloride, carbon tetrachlorethylene, heptane, toluene), $\varepsilon''$ decreases to almost zero in the frequency range from 0.2 to 10 GHz. However, for an aromatic hydrocarbon with a very small dipole moment, in which substituents CH$_3$- in the benzene ring are in the ortho position – ortho-xylene and
the solvent Nefras, which consists of a mixture of alkylbenzenes and has weak dipole moments, $\varepsilon''$ increases with increasing frequency throughout the studied bandwidth. In general, for all the hydrocarbons studied, the real part of the permittivity is in the range from 1.8 to 2.6, while the dielectric losses of $\varepsilon''$ does not exceed 0.15.

Table 2 shows the real and imaginary parts of the permittivity of the solvents studied in this work at fixed frequencies of 0.2, 1, and 20 GHz.

Table 2. Measured values of the complex permittivity of various solvents at fixed frequencies.

| Name of a solvent                  | Permittivity at a fixed frequency |
|------------------------------------|----------------------------------|
|                                    | 200 MHz  | 1 GHz   | 20 GHz  |
|                                    | $\varepsilon'$ | $\varepsilon''$ | $\varepsilon'$ | $\varepsilon''$ | $\varepsilon'$ | $\varepsilon''$ |
| toluene                            | 2.40     | 0.10    | 2.30    | 0.11    | 2.35    | <0.01     |
| ortho-xylene                       | 2.61     | 0.10    | 2.50    | 0.06    | 2.39    | 0.07      |
| solvent Nefras                     | 2.49     | <0.01   | 2.50    | 0.05    | 2.39    | 0.09      |
| heptane                            | 1.92     | 0.04    | 1.86    | 0.04    | 1.91    | <0.01     |
| carbon tetrachloride               | 2.31     | <0.01   | 2.26    | 0.06    | 2.27    | <0.01     |
| tetrachlorethylene                 | 2.26     | <0.01   | 2.24    | 0.07    | 2.25    | <0.01     |
| ethyl acetate                      | 6.24     | 0.01    | 6.08    | 0.30    | 5.11    | 1.39      |
| propyl acetate                     | 5.38     | <0.01   | 5.37    | 0.09    | 4.36    | 1.18      |
| butyl acetate                      | 4.97     | 0.02    | 4.91    | 0.15    | 3.82    | 0.98      |
| solvent R-5A                       | 7.86     | 0.20    | 7.41    | 0.45    | 6.23    | 1.81      |
| methyl ethyl ketone (butanone)     | 18.18    | 0.47    | 17.34   | 1.10    | 13.67   | 6.38      |
| acetone                            | 20.93    | 0.38    | 19.93   | 1.06    | 17.95   | 5.82      |
| isopropyl alcohol                  | 16.64    | 6.58    | 5.50    | 5.39    | 3.06    | 0.56      |
| ethyl alcohol                      | 26.46    | 4.07    | 17.22   | 10.46   | 4.16    | 1.79      |

Figures 4 and 5 show the measured frequency dependences of the permittivity of solvents with moderately strong hydrogen bonds: esters of acetic acid in the homologous series – ethyl acetate, propyl acetate, butyl acetate; ketones in the homologous series are 2-propanone (acetone), 2-butanol (methyl ethyl ketone) and a mixed solvent R-5A, consisting of acetone, butyl acetate and ortho-xylene in a ratio of 3:3:4.

The measurement results show that solvents with moderately strong hydrogen bonds with an increase in frequency from 200 MHz to 20 GHz are characterized by an almost linear decrease in the values of the real part of the permittivity with a simultaneous increase in dielectric losses.

It should be noted that for the solvents, with an increase in the length of the hydrocarbon chain in the homologous series of these classes, the permittivity decreases. For example, for esters of acetic acid at a frequency of 8 GHz, the real part of the permittivity $\varepsilon'$ for ethyl acetate is 5.7, propyl acetate is 5.0, butyl acetate is 4.4. For the ketone class, respectively, $\varepsilon'$ at a frequency of 8 GHz takes the value 19.1 for 2-propanone (acetone) and 16.1 for 2-butanol (methyl ethyl ketone). It must be clarified that with a decrease in the permittivity in the homologous series of esters and ketones, their dissolving ability with respect to polar substances decreases, but at the same time, their dissolving ability to less polar substances increases.
As noted above, solvent R-5A is a mixture of several components. Since this mixture is physical, i.e. individual components do not enter into a chemical reaction with each other, its permittivity can be described by the Lichtenekker’s model [10]:

\[
\ln \varepsilon_\Sigma = \sum_i C_i \ln \varepsilon_i ,
\]

where \( \varepsilon_\Sigma \) is an effective permittivity of the mixture, and \( \varepsilon_i \) and \( C_i \) are permittivity and volume concentration of \( i \) component, respectively.

Figure 4 also shows the calculated frequency dependences of the complex permittivity of solvent R-5A, which, as the comparison shows, are in fairly good agreement with the obtained experimental data.

In addition to the measured dielectric spectra of ketones, figure 5 shows the experimental frequency dependences of the permittivity of solvents with strong hydrogen bonds – alcohols.

The dielectric spectra of ethyl and isopropyl alcohols have a form that differs significantly from the frequency dependences of the complex permittivity of solvents with weak and moderately strong hydrogen bonds. The graphs presented in figure 5 demonstrate that the permittivity of alcohols is characterized by a pronounced frequency dispersion, which has the form of a Debye relaxation [11] with a relaxation frequency below 1.5 GHz.
4. Conclusion
In the course of studies of the permittivity spectra of organic solvents at microwave frequencies, it was found that the coaxial probe method allows effectively studying the dielectric properties of organic solvents in the frequency range from 200 MHz to 20 GHz. The limiting static values of the permittivity of the solvents are in good agreement with the previously known data at a frequency of 1 MHz, shown in table 1. The measurement results indicate that the chemical nature of the solvent and its ability to form hydrogen bonds has a significant effect on the frequency spectrum of the complex permittivity. Solvents with weak hydrogen bonds have low values of permittivity (not higher than 2.6) and negligible dielectric losses. Solvents with moderately strong bonds (acetic acid esters and ketones) have high values of permittivity with pronounced frequency dispersion, noticeable dielectric losses and Debye relaxation frequency above 20 GHz. Strong hydrogen bonded solvents (alcohols) are characterized by high values of permittivity with significant frequency dispersion and Debye relaxation frequency below 1.5 GHz. The results of calculations and experiments show that the measured values of the complex permittivity of the mixed solvent R-5A, consisting of acetone, butyl acetate and ortho-xylene in a ratio of 3:3:4, are in good agreement with Lichtenacker’s law for the effective permittivity of a mixture of several components.

Thus, the obtained data of the complex permittivity of industrially produced organic solvents in the frequency range from 200 MHz to 20 GHz allow expanding their application in various fields of materials science.

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