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Infrared and Dielectric Spectroscopy—A Useful Marriage for Exploration of Hydrogen-Bonded Systems

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Abstract: The paper presents our experience in the combined use of vibrational spectroscopy and dielectric methods in the investigation of molecular structure and interactions in hydrogen-bonded systems. Here, we show three selected examples obtained by our research groups. The first example concerns examination of the mixture of propionic acid with triethylamine. It has been found the presence of the pronounced maxima of dielectric permittivity and conductivity at some acid-amine molar ratio. This observation suggests that the mixture has properties of both the ionic and dipolar liquids. In the next work, we have elucidated the mechanism of the dissociation of 1-octanol and 3-octanol associates in solutions and in the pure liquid phase. It has been evidenced that at first dissociate the terminal alcohol molecules. These studies also have shown that the tendency of formation of the cyclic associates increases from 1-octanol to 3-octanol. The last example concerns an examination of 1-hexanol in n-hexane. Our results suggest that in the solutions the most populated species are the cyclic trimers. It is contrary to numerous previous studies claiming that cyclic tetramers are the most abundant species. Of particular importance is the observation that the peak due to the free OH is contributed mainly by the absorption from the monomers. This suggests that the band from the free terminal O-H groups in the linear associates is obscured by a broad absorption from the hydrogen-bonded O-H groups. Based on our results, it is possible to conclude that simultaneous use of vibrational spectroscopy and dielectric methods allows to get deeper insight into molecular structure with higher confidence and to draw conclusions not available from separate application of each method.

Keywords: NIR/IR spectroscopy; dipole moment; nonlinear dielectric effect; alcohol; association; hydrogen bonding

1. Introduction

Hydrogen bonding is a non-covalent interaction with an energy of several to a dozen times greater than k_BT at room temperature. This makes it highly important for numerous processes, particularly those essential for life. Understanding the hydrogen-bonded equilibria plays a key role in describing structural and dynamic properties of condensed matter. Despite more than 100 years of investigation, hydrogen bonding still attracts considerable interest in physical chemistry, materials science, and life sciences [1–9].

Both the infrared (IR) spectroscopy and the dielectric methods use electromagnetic radiation to investigate the properties of matter, but they apply different frequency ranges. Dielectric methods use the frequencies from 10^{-3} Hz to 0.3 THz, while infrared works in the 0.3–430 THz range (10–14,340 cm^{-1}). Besides, there is an important difference in the mechanism of response of molecules to electromagnetic radiation. In the case of IR spectroscopy, it is a resonance between normal vibrations and the incident radiation. As a result, each active vibration is visible in the absorption spectra and gives a response at characteristic frequency. In contrast to IR

spectra, the dielectric absorption originates from a relaxation of dipolar, or quadrupolar species under the influence of an electric field. Therefore, the process assigned to characteristic relaxation frequency is active not only at the given frequency but at frequencies lower and higher up to 1 decade than the relaxation frequency. This fundamental difference results in dissimilarity in the description of the influence of electromagnetic radiation on the matter and makes IR spectroscopy more comprehensive than the dielectric methods.

Here, we present three examples of joint use of IR spectroscopy and dielectric methods for studies of the hydrogen-bonded systems. We demonstrate that combined use of dielectric methods and IR spectroscopy improves interpretation of the experimental results and makes the conclusions more reliable. To make the paper easier to follow, the next section briefly introduces the principles of both methods.

2. Methods

2.1. IR Spectroscopy

Vibrational spectroscopy is based on interaction of IR radiation with matter. IR radiation covers a spectral range from 30 to 12,500 cm^{-1} and is divided into few smaller ranges: far-infrared (FIR)—30–400 cm^{-1}, mid-infrared (MIR)—400–4000 cm^{-1} and near-infrared (NIR)—4000–12,500 cm^{-1}. Each spectral range provides unique information on molecular vibrations and requires a specific instrumentation. Vibrational spectroscopy allows for fast and reliable examination of all kinds of samples, mostly in a non-invasive manner.

The theory of vibrational spectroscopy is based on the classical harmonic oscillator (HO) model. The potential energy of this oscillator is described by a parabola symmetric with respect of the equilibrium distance. The energy levels of the harmonic oscillator are given by:

$$E_{\text{harm}} = h\nu(n + 1/2) \tag{1}$$

where n is a vibrational quantum number (n = 0, 1, 2, 3, ...), h—Planck constant [$6.62607 \cdot 10^{-34}$ J·s], ν—vibrational frequency of the oscillator. The vibrational frequency for a diatomic molecule of m_1 and m_2 mass is given by:

$$\nu = \frac{1}{2\pi}\sqrt{\frac{f}{m_r}} \tag{2}$$

where f is the force constant and m_r is the reduced mass:

$$m_r = \frac{m_1 m_2}{m_1 + m_2} \tag{3}$$

As can be seen, the vibrational frequency depends on the force constants and the masses of both atoms. The force constant is related to the strength of the bonding between the oscillating atoms and provides chemically important information. Since this value is proportional to the bond order, IR spectroscopy allows for easy distinction of the single, double or triple bonds. The bands due to oscillations of heavy atoms are located at low wavenumber region, while the bands originating from vibrations of light atoms appear in the high wavenumber region of the spectrum. The inter- or intramolecular interactions modify the force constants and contribute to characteristic spectral changes in MIR and NIR spectra.

In the HO model the difference between the successive energy levels is constant:

$$\Delta E_{\text{harm}} = E_{n+1} - E_n = h\nu \tag{4}$$

This model allows only for transition between the successive energy levels ($\Delta n = \pm 1$). In practice, at room temperature the most populated is the lowest energy level (n = 0), hence in IR spectra are seen mainly $0 \rightarrow 1$ transitions (fundamentals). The HO model is an ideal approximation of molecular vibrations. More realistic model introduces the anharmonicity, which takes into consideration the fact that the change in the dipole moment is not linear function of the nuclear displacements. The potential energy of anharmonic oscillator (AO) is approximated by Morse function. By solving the Schrödinger equation with this potential one can obtain the energy levels of AO:

$$E_{\text{anharm}} = h\nu_0(n + 1/2) + h\nu_0\chi(n + 1/2)^2 \tag{5}$$

where ν_0 is the vibration frequency of HO and χ is the anharmonicity constant. In AO model the difference between the successive energy levels is not constant but depends both on χ and n as follows:

$$\Delta E_{\text{anharm}} = h\nu_0\big(1 - 2\chi(n + 1)\big) \tag{6}$$

From Equation (6) is seen that this difference becomes smaller with an increase in χ and n. Another important consequence of anharmonicity is extension of the vibrational selection rule. In the AO model are allowed the

transitions for $\Delta n = \pm 1, \pm 2, \pm 3, \ldots$ The transition for $\Delta n = \pm 2$ corresponds to the first overtone, for $\Delta n = \pm 3$ to the second overtone and so on. Since the overtones are forbidden in the HO model, they have much smaller intensities (10–100 times) than the fundamental transitions. The higher degree of the overtone, the weaker intensity of the corresponding band. The overtones of the high frequency oscillators (O-H, C-H, N-H) appear in NIR region, while the overtones of low frequency fundamentals ($\nu_0 < 2000$ cm^{-1}) are observed in MIR range. The model of the AO allows for the presence of the combination bands ($\nu_i \pm \nu_j$), which may occur both in MIR and NIR spectra. The intensities of the combination bands are much smaller than those of the fundamentals but due to a large number of possible combinations their contribution to MIR and NIR spectra is meaningful.

The band are IR active if the given normal vibration leads to changes in the dipole moment (μ). The intensities of the vibrational bands (I) are proportional to:

$$I \approx \left(\frac{\partial \mu}{\partial q}\right)^2 \tag{7}$$

This means that the most intense bands in IR spectra originate from vibrations of polar groups like O-H, N-H, C-Cl, C=O or SO_2. Usually, the asymmetric vibrations give rise to stronger bands than the corresponding symmetric vibrations. An opposite situation takes place in Raman spectroscopy. Hence, the IR/Raman band intensities give information on the chemical bonds.

A creation of the hydrogen bonding leads to evident changes in IR spectra [10–12]. First of all, the position of the band due to the stretching vibration of the hydrogen-bonded group (X-H) reveals red-shift (sometimes blue-shift) proportional to the strength of the hydrogen bonding. This shift may vary from a dozen or so for weak bonds to more than 1000 cm^{-1} for very strong bonds and is often used as a measure of the strength of hydrogen bonding. The next important effects, due to the hydrogen bonding formation, are the intensity increase and the broadening of the bands. A simultaneous observation of these effects in the vibrational spectra is the most sensitive proof of the presence of hydrogen bonding. In the spectra of hydrogen-bonded system may appear one, two or more bands originating from the free X-H groups and different kinds of associates. Therefore, it is evident that vibrational spectroscopy is a powerful tool for studies of hydrogen-bonded systems.

2.2. Dielectric Methods

The quantity measured in the dielectric experiments is the electric permittivity, conveniently presented as a complex parameter:

$$\varepsilon = \varepsilon' - j\varepsilon'' \tag{8}$$

where ε' is the real part, related to the electric polarization, ε'' is the negative imaginary part, related to energy dissipation, $j = \sqrt{-1}$. An example of the frequency dependence of the electric permittivity is presented in Figure 1:

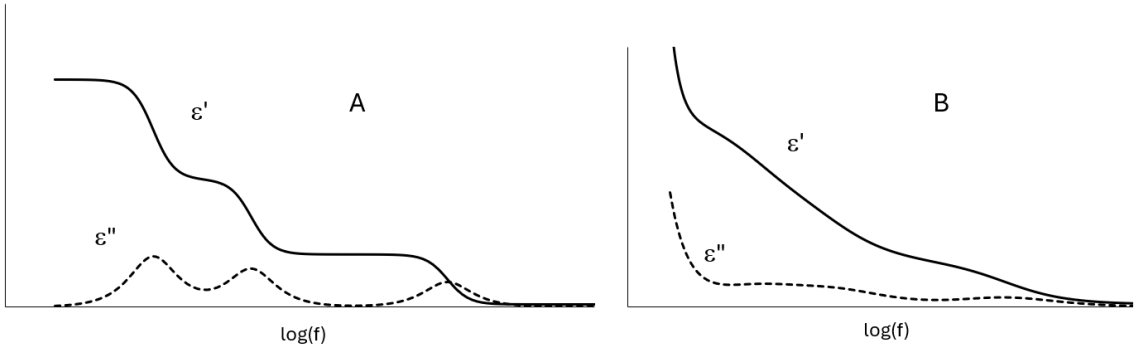

Figure 1. Example of the dependence of the real (ε') and negative imaginary (ε'') components of the permittivity for three well-separated processes (**A**), and for a continuous distribution of relaxation times (**B**).

In the case of "A" scheme, the three Debye-like processes are visible. Dispersion curve, ε'(f) demonstrate three stepwise decreases, absorption curve, ε''(f) three clear maxima at the relaxation frequencies. The scheme B presents a situation of many overlapping processes or continuous distribution of relaxation times, and for low frequencies the electrode polarization responsible for low-frequency increase of ε', and DC conductivity responsible for low-frequency increase of ε''. Interpretation of dielectric relaxation experiments requires the fitting

of relaxation function. The obtained relaxation times and the distribution parameters allow one to conclude on the mechanism and kinetics of the response of matter to the external electric field. Measurements of the temperature dependence of the relaxation time permits to calculate the activation energy of the relaxation process. In measurements at high frequencies (GHz range), the dielectric response is mainly related to molecular motions, including overall molecular rotation and vibration of molecules or dipolar fragments. In the radio-frequency range, collective motions involving large numbers of molecules, as well as the translational motion of ionic species, become apparent. At low frequencies the dielectric response is dominated by translational motion, electrode polarization, and macroscopic processes activated by the applied electric field.

If one tries to compare IR and dielectric experiments, ε'' is related to the absorption coefficient, and ε' is equal to the second power of the refractive index. However, the response in dielectric experiment is an effect of relaxation, and the response in IR spectroscopy results from resonance between internal degrees of freedom and the electric field component of infrared light.

The fundamental role in description of the influence of electric field on the matter plays the electric polarization. Polarization is the macroscopic dipole moment of unit volume, created under the influence of the external electric field,

$$P = \frac{N \langle m \rangle_E}{V} \tag{9}$$

where N—is the number of molecules in a volume V, $\langle m \rangle_E$ is the mean value of the projection of the global dipole moment m on the direction of the electric field E. Global dipole moment is a sum of permanent dipole moment and induced dipole moment. There are three main sources of polarization: dipolar, atomic, and electron polarization. Dipolar polarization is generated by permanent dipole moments of molecules due to the rotational movement of molecules in the direction of an external field. Atomic polarization is a result of the deformation of molecules, while electron polarization is linked with the movement of electron density under the influence of an external electric field. Sum of atomic and electron polarization is called an induced polarization.

Dipole polarization is related to the permanent dipole moment of molecules. The dipole moment is a vector quantity and provides information on the structure, conformation, and interactions between molecules. The theory of dipolar polarization was originally elaborated by P. Debye [13]. This theory allows to calculate the mean value of the projection of the permanent dipole moment in the direction of the external electric field, the quantity responsible for dipolar polarization:

$$\langle \mu \rangle_E = \mu_s \left[coth(y) - \frac{1}{y} \right] \cong \mu_s \left[\frac{y}{3} - \frac{y^3}{45} + \frac{y^5}{945} + \cdots \right] \tag{10}$$

where μ_S is the permanent dipole moment of a molecule, $y = \mu_S \cdot F/k_BT$. The quantity y is a ratio between the energy of interaction of dipole moment with the internal electric field $(\mu_S \cdot F)$ and the energy of thermal movement (k_BT), k_B—Boltzmann constant, and T is the temperature. The internal electric field F is usually different from the external field (E). Relationships between F and E was discussed in local field theories [14]. In liquids, usually an Onsager local field is used. Dielectric experiments provide an electric permittivity in function of frequency, temperature and in the case of mixtures in function of concentration. Experiments are usually supplemented by density and refractive index measurements. The main quantity available from these measurements is the dipole moment of molecules. The dipole moment of polar molecules measured in the gas phase or in a diluted solution in nonpolar solvents is characteristic for the molecule and allows to conclude on molecular structure. Dipole moment measurements provide also information on electron delocalization and impact of resonance effects on the measured dipole moments [15]. Dielectric measurements are very useful in the investigation of hydrogen-bonded systems [16–18]. The dipole moment is sensitive to intermolecular interactions, hence the measurements in function of concentration supply information on the structure of complexes. Formation of hydrogen-bonded complexes may either increase or decrease the dipole moment. In the case of parallel arrangement, the mean dipole moment increases, while it decreases in the opposite instance. Classical example represents the carboxylic acids dissolved in non-polar solvent. At very low concentrations of acid, the dipole moment approaches the value for the isolated acid molecules but further increase in concentrations leads to significant decrease of the experimental mean dipole moment. This is an effect of the formation of acid dimers with antiparallel configuration of dipole moments. Measurements of dipole moments of alcohols allows to conclude on molecular structure of hydrogen-bonded complexes.

Very useful are the dielectric measurements performed in strong electric field of an intensity of a dozen megavolts per meter, called the NDE effect. In these measurements a special instrumentation is necessary [19]. The usefulness of the NDE technique in studies of associating liquids results from the influence of strong electric

field on association equilibria. In the presence of the strong electric field, the associates with large dipole moments are favoured energetically, and the association constants are shifted toward highly polar forms.

To describe an alcohol-hydrocarbon mixture it is often assumed that the mixture is classified as an ideally associated. This means that the mixture consists of a few different associates treated as independent components and that the mixing is ideal. Activities of all associates, or mole fractions when the system is assumed to be ideal, are interrelated by a set of appropriate equilibrium constants:

$$nA_1 \rightleftharpoons A_n; \qquad K_n = a_n \cdot a_1^{-n} \tag{11}$$

where K_n is an equilibrium constant of formation of associates composed of n alcohol molecules, a_1 is the activity of monomers, and a_n is the activity of the associate composed of n alcohol molecules. The equilibrium constant is related to the free enthalpy of formation of A_n associate:

$$K_n = \exp\left[-\frac{\Delta G_n^0}{RT}\right] \tag{12}$$

where ΔG^0_n—standard free enthalpy of formation of the associate composed of n alcohol molecules. Additionally, it is often supposed that:

$$\Delta G_n^0 = (n-1) \cdot \Delta G_2^0 \tag{13}$$

for open associates, and

$$\Delta G_n^0 = n \cdot \Delta G_2^0 \tag{14}$$

for cyclic associates. The only parameters required to describe association equilibria are the mole fraction of monomers and the free enthalpy of formation of open dimers (ΔG^0_2). As for ΔG^0_2 could be obtained from the enthalpy of formation of a single hydrogen bond, the concentration of monomers must be fitted to experimental data. However, each experimental data set needs additional parameters to link the concentration of associates with the observables. In the case of IR spectroscopy, the additional parameters are the molar absorptions of individual associates, as regards the dielectric experiments these parameters are the dipole moments of associates. In general, these data are not known, and additional assumptions have to be made, or the fitting of additional parameters is necessary.

The electric permittivity measurements offer two independent parameters describing the associative equilibria. The first one is the electric permittivity measured in the function of concentration supplemented by density and refractive index measurements. The second one is the NDE effect describing the influence of a strong electric field on the system. The model that allows calculating the concentration of individual associates using measured data was elaborated by J. Malecki [20] and tested in many systems [21–25]. Starting point of the model is the information on dipole moments of associates and the assumption that the associates are rigid. It means that the external field does not change the conformation or dipole moment of associates. However, the field can change the population of associates toward forms with large dipole moments. If different conformers of a given associate are treated as individual species, the doubtful assumption of rigidity of associates could be overcome. The dipole moment one can calculate using quantum-mechanical methods or predict from the geometry of associates [26]. Assuming the Onsager local field, the following equation allows to calculate the mean square and mean forth power of dipole moment of alcohol molecules [20]:

$$\langle \mu^2 \rangle = \frac{9\epsilon_0 k_B T V_{\text{mol}}}{N_A} \frac{(\varepsilon_0' - n_D^2)(2\varepsilon_0' + n_D^2)}{\varepsilon_0'(n_D^2+2)^2} \frac{1}{x_{\text{mol}}} \tag{15}$$

$$\langle \mu^4 \rangle = -\frac{45\epsilon_0 k_B^3 T^3 V_{\text{mol}}}{N_A} \frac{\left(2\varepsilon_0'^2 + n_D^4\right)(2\varepsilon_0' + n_D^2)^2}{\varepsilon_0'^4 (n_D^2+2)^4} \left(\frac{\Delta\varepsilon}{E^2}\right) \frac{1}{x_{\text{mol}}} \tag{16}$$

where ϵ_0 is the electric permittivity of vacuum, k_B is the Boltzmann constant, N_A is the Avogadro number, V_{mol} is the molar volume of the mixture, ε_0' is the static value of a real part of electric permittivity (the value measured at the frequency as low as all dipoles can follow external field change), n_D is the refractive index at sodium D line, x_{mol} is the mole fraction of alcohol in the mixture; $\Delta\varepsilon/E^2$ is the NDE effect. An exemplary relationship of $\langle\mu^2\rangle$ and $\langle\mu^4\rangle$ in function of concentration is presented in Figure 2.

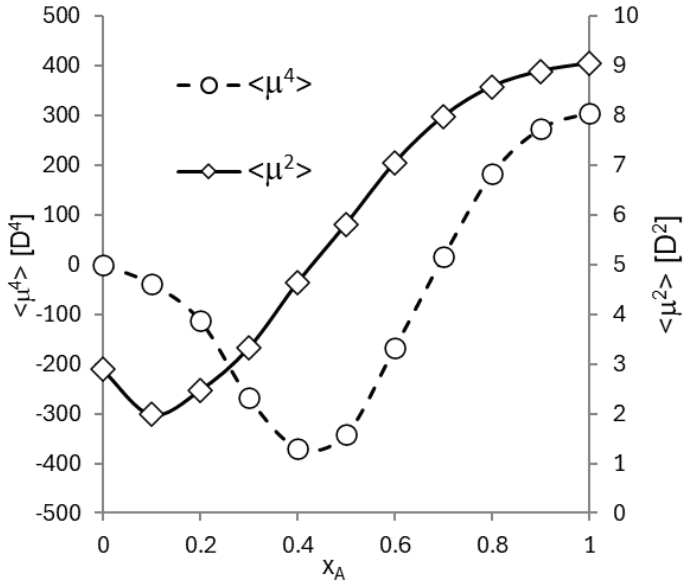

Figure 2. The concentration dependence of $<\mu^2>$ and $<\mu^4>$ for mixture of 1-hexanol in *n*-hexane.

The negative values of $<\mu^4>$ means that the electric field shifts the equilibrium toward associates with larger dipole moments, for example, from cyclic to open associates. The dielectric measurements offer two independent experimental quantities ($<\mu^2>$ and $<\mu^4>$) measured as a function of concentration. This means that not only the concentration of monomers but also other quantities, such as free enthalpy of formation of open/cyclic associates, dipole moments, or conformation of associates could be fitted. On the other hand, too many adjustable parameters fitted to experimental data decrease the reliability of the obtained results. A weak point of this method is the necessity to know or to fit dipole moments of all associates. Besides, if the mixture could not be treated as an ideal one, the activity coefficients of all components should be known [27]. Additional data obtained by other methods may improve the reliability of the model predictions. In this context very promising is combination of dielectric methods with NIR spectroscopy, which can easily record NIR spectra of the mixture in the whole concentration range. From the intensity of "free" O-H band, it is possible to determine the concentration of monomers and terminal O-H groups in the open associates. The same values one can obtain from dielectric measurements using Małecki's model [20]. The comparison of the same values obtained by two independent methods allows for mutual control of the results.

3. Proof of Concept

Creation of hydrogen bonding has a significant effect on various microscopic and macroscopic properties of the systems. To understand the molecular mechanism of these changes it is necessary to use appropriate research tools. One of the most powerful tools for studies of hydrogen bonding is vibrational spectroscopy, which provides detailed information on the structure and interactions at a molecular level [2,4–6]. The formation of hydrogen bonding leads to numerous variations in vibrational spectra. The most evident changes result from the band shift, intensity increase and the band broadening. Often, in the spectra of hydrogen-bonded system appears new bands due to various hydrogen-bonded species. Therefore, an analysis of the vibrational spectra is a valuable source of information on the hydrogen bonding.

Dielectric methods also are very useful for investigation of the hydrogen bonding. Formation of the hydrogen bonds leads to a change of the dipole moment of molecules and complexes that has a considerable effect on dielectric properties. In the previous paragraph this effect was described in detail. However, each of the methods has limitations that make it difficult to draw final conclusions. In the case of dielectric methods, for the description of hydrogen-bonded systems, the most important are measurements at low frequencies. Unfortunately, these measurements are difficult because of the conductivity and the electrode polarization effect. In the case of vibrational spectroscopy, band overlapping and uncertainty in the assignment of individual bands could be a serious problem. In this context, the collaborative use of different but complementary methods gives a chance for more reliable interpretation of experimental results.

3.1. Strong Acid-Base Interactions

Strong hydrogen bonding between the carboxylic groups and tertiary amines leads to formation of complexes with a possibility of proton transfer and the possible presence of individual anions. The mixture of propionic acid-triethylamine is an example of pseudo-protic ionic liquid [28,29]. The structure of this mixture was a subject of thorough examinations [30]. We measured dielectric permittivity, conductivity, density, refractive index, viscosity, and heat of mixing as a function of concentration. The experimental data demonstrated that the mixture of a molar ratio of 2:1 or 3:1 acid:amine reveals maxima of electric permittivity, conductivity, and viscosity (Figure 3).

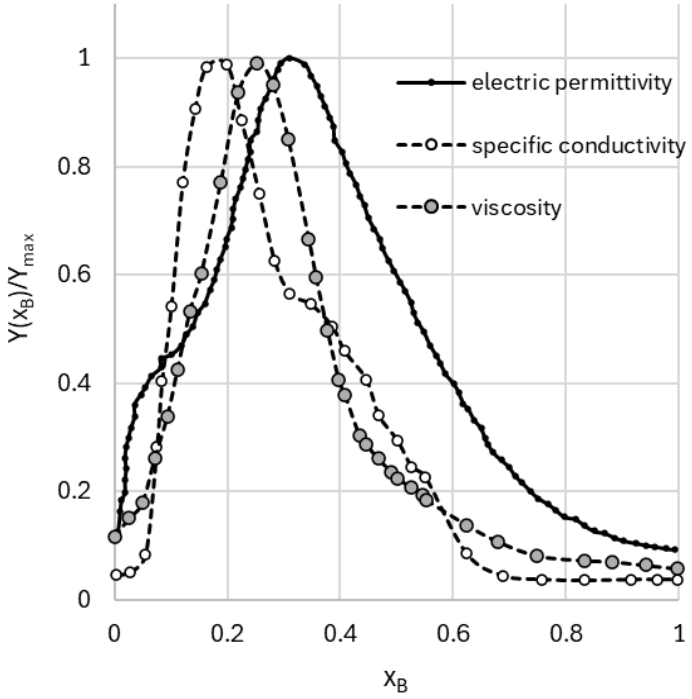

Figure 3. The dependence of electric permittivity, specific conductivity, and viscosity as a function of mole fraction of triethylamine (x_B) in propionic acid.

The presence of maximum of electric conductivity proves the existence of ions capable of moving in an electric field. This property is characteristic for electrolytes as well as for ionic liquids. The maximum of the electric constant shows the presence of dipoles able to reorient in an external electric field. This behavior is typical rather for dipolar liquids than for ionic liquids. It is evident that the mixture of a 2:1 or 3:1 acid:amine ratio has properties of both the ionic liquids and the dipolar molecules with a high dipole moment. However, the conductivity is lower than that in the typical ionic liquids, and the dipole moment is not as large as for the hydrogen-bonded complexes with proton transfer. Analyzing the dielectric data, we assumed the existence of a complex equilibrium between acid dimers, hydrogen-bonded acid-amine complexes, complexes with proton transfer, and free ions (Figure 4).

$$
\begin{array}{ccccc}
 & & HA & & \\
 & & -HA \uparrow\downarrow +HA & & \\
 & & \overset{+B}{\underset{-B}{\rightleftarrows}} & & \\
HA\cdots HA & & HA\cdots HA\cdots B & \rightleftarrows & A^{\ominus}\cdots HA\cdots HB^{\oplus} \rightleftarrows A^{\ominus} + (HAHB)^{\oplus} \\
-HA \uparrow\downarrow +HA & & & & -HA \uparrow\downarrow +HA \\
 & & \overset{+B}{\underset{-B}{\rightleftarrows}} & & \\
HA\cdots HA\cdots HA & & HA\cdots HA\cdots HA\cdots B & \rightleftarrows & A^{\ominus}\cdots HA\cdots HA\cdots HB^{\oplus} \rightleftarrows A^{\ominus} + (HAHAHB)^{\oplus}
\end{array}
$$

Figure 4. The proposed equilibria scheme in the propionic acid (*HA*)-triethylamine (*B*) mixture.

To verify the correctness of above equilibrium we needed additional information. In the next step, we recorded NIR spectra of acid-amine mixture in function of concentration. We applied NIR spectroscopy because the acid-amine mixtures exhibit extremely strong absorption in MIR range, resulting in substantial experimental difficulties. In contrast to the fundamental region, NIR spectra one can record in the full concentration range using easy-to-handle quartz cells with very convenient optical path lengths (1–10 mm). The important band, which provides information on the proposed acid-amine equilibria is located near 7830 cm^{-1}. This band arises from coupling between the second overtone of the C–H stretching vibration and the C–N stretching vibration [31] and is visible in non-associated amines only. Formation of the N···H-O hydrogen-bonded complex leads to disappearance of this band. In the studied mixture this band disappears with the increase of acid content indicating the formation of strong hydrogen bonding. The additional proof of the presence of the proposed equilibria provides an analysis of the absorption below 6000 cm^{-1}. In this frequency range are located the key bands used for characterization of hydrogen-bonded complexes [32]. With the increase in amine mole fraction (x_B) up to 0.3, the band intensities are almost constant. The intensity decrease was observed for x_B higher than 0.3. This observation proves that at low amine concentrations, the number of hydrogen-bonded complexes per unit volume is almost constant. The decrease of number of O-H···O bonds, due to disruption of acid-acid associates, is compensated by formation of OH···N bonds in acid-amine complexes. When x_B is larger than 0.3 the absorption in this spectral range starts to decrease, evidencing the reduction of number of hydrogen-bonded complexes per unit volume.

Concluding, an application of both dielectric methods and NIR spectroscopy for examination of acid-base mixture allows to describe the structure and interaction of a system with strong hydrogen bonding in a more comprehensive way.

3.2. Hydrogen Bonding of Alcohols in the Pure Liquid Phase

Hydrogen bonding may lead to formation of many kinds of associates, both linear and cyclic. In pure alcohols, as well as in the concentrated solutions with non-polar solvents the most abundant species are long linear associates. On the other hand, in diluted solutions dominates short associates (open and cyclic) and monomers [32]. A molecular mechanism of transformation of large associates into monomers is still a subject of debate [33–38]. There are proposed two main mechanisms for this process. The first one assumes that the terminal alcohol molecules dissociate at first, since the terminal hydrogen bonding is weaker than the interior ones. The second mechanism assumes that large associates break up into smaller ones, then to dimers and finally to monomers. To bring more light into this problem we performed MIR/NIR and dielectric measurements of neat octanols [39]. For analysis of complex NIR spectra we applied two-dimensional (2D) correlation spectroscopy [40,41]. This technique assumes that two correlated signals vary with the same waveforms. When the spectral responses follow different functions, the results of 2D analysis should be analyzed with a great caution [42,43].

NIR or MIR spectra provide information on the bands originating from vibrations of the free and hydrogen-bonded O–H groups. These bands can be readily distinguished in the conventional vibrational spectra, whereas the absorption from the free O–H in the monomeric species and the terminal OH groups in the open associates is heavily overlapped. In Figure 5 the temperature-dependent NIR spectra of 3-octanol are displayed.

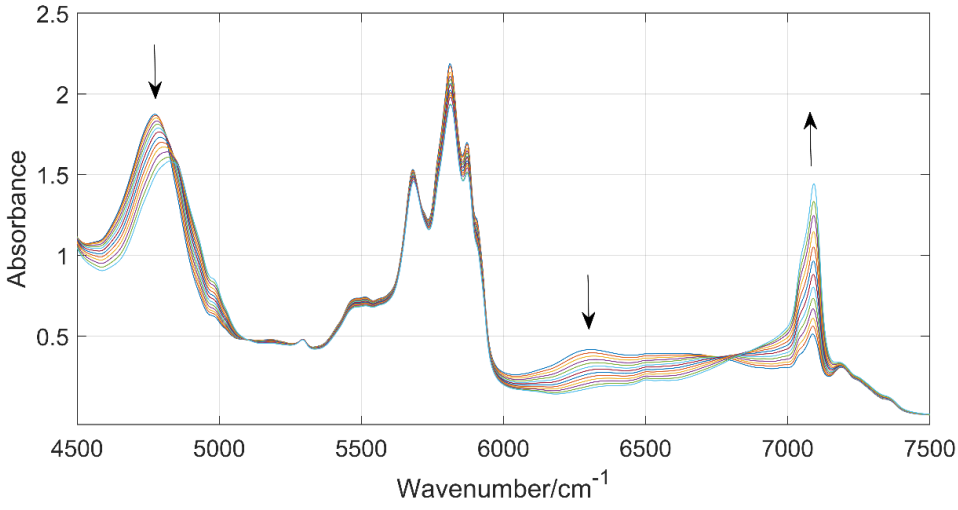

Figure 5. Temperature-dependent NIR spectra of 3-octanol from 20 to 80 °C with a temperature step of 5 °C. The arrows indicate direction of spectral changes with an increase in temperature.

As can be seen, upon the temperature rise, some bands decrease in intensity, while the other bands increase in intensity. The strong band near 7100 cm^{-1} is due to absorption from the free O-H groups, and it includes the contributions from the monomers and free terminal O-H groups in the linear associates. In the NIR spectra (Figure 5) these two bands are heavily overlapped. To separate these two peaks we applied 2D correlation analysis, which allows for the resolution enhancement [40,41]. Indeed, the asynchronous spectrum (Figure 6) develops two peaks at 7033 and 7093 cm^{-1} which can be assigned to the free terminal O-H groups and O-H groups in the monomers, respectively.

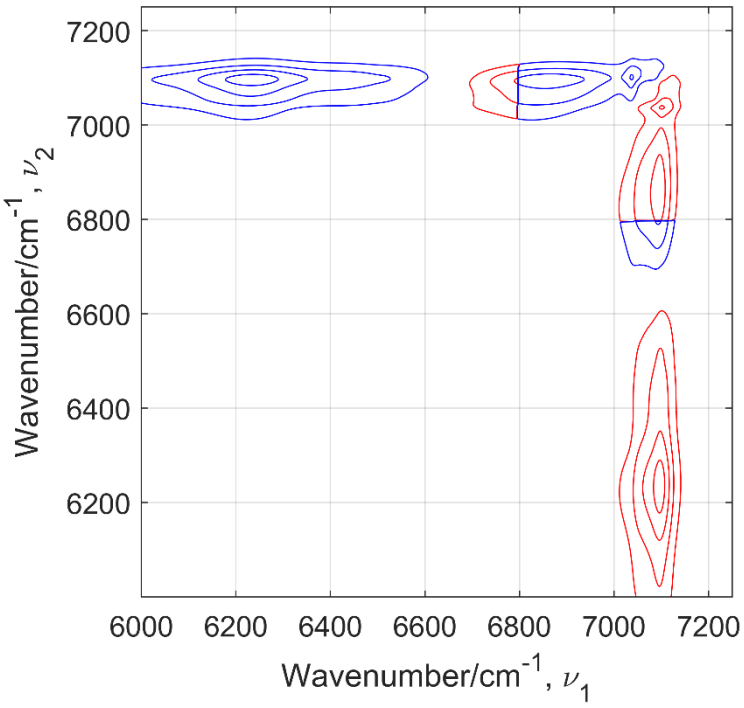

Figure 6. Asynchronous spectrum obtained from temperature-dependent [20:5:80 °C] NIR spectra of 3-octanol. In red the positive peaks are shown, while in blue negative peaks.

From the sign of the peaks in the asynchronous spectra, one can conclude that the population of the monomers increases faster than that of the terminal O-H in the linear associates. On this basis, it can be concluded that multimer dissociation occurs primarily through the detachment of terminal alcohol molecules, resulting in the formation of monomers and shorter associates.

As a next step, we determined the dielectric properties of neat 1-octanol and 3-octanol as well as solutions of both alcohols in CCl_4. The measurements were carried out at low frequencies assigned to static electric permittivity. This condition allowed us to analyze the results in the frame of the mean dipole moment of the alcohol dissolved in non-polar solvent. The data obtained reveal that at low concentrations, 1-octanol and 3-octanol exist preferably in the monomeric forms. An increase of alcohol concentration results in formation of the cyclic associates. This tendency is stronger for 3-octanol than that for 1-octanol. Dielectric experiments prove the existence of large population of monomers in 1-octanol confirming the dissociation mechanism proposed from NIR data. Besides, based on these results we corrected an assignment of the 3350 cm^{-1} band. Originally this band was assigned to the cyclic associates, while dielectric measurements at different concentrations reveal that the band at 3350 cm^{-1} is contributed by small cyclic and linear associates.

3.3. Association of 1-hexanol in n-hexane Solutions

The next example of successful cooperation between NIR spectroscopy and dielectric methods comes from the study of binary mixture of 1-hexanol with n-hexane [27]. We used n-hexane as a solvent of 1-hexanol because both molecules have similar shape and size. Therefore, one can expect that the non-ideality related to the entropy is negligible, and the mixture could be classified as a regular. We performed measurements of electric permittivity at the frequencies assigned to the static permittivity, density, refractive index, and the NDE effect. All these data were measured in the whole concentration range, from pure solvent to pure alcohol. The obtained results were analyzed using the model developed by Malecki [20]. The measured data were transformed into concentration dependence of $<\mu>^2$ and $<\mu>^4$ (Figure 2). As mentioned before, these calculations require many initial parameters, such as dipole moments of associates, associating constants, and activity coefficients (if the system is not an ideal

one). The dipole moment of monomer of 1-hexanol is available from experiments in the gas phase or in diluted solutions in non-polar solvents [44]. Dipole moments of associates could be estimated from the geometry [15,26] or calculated by quantum-mechanical methods. The association constant one can approximate assuming additivity of free enthalpy (Equations (13) and (14)). During calculations we fitted concentration of monomers, free enthalpy of formation of OH···O bond in open and cyclic associates, dihedral angle between the dipole moments in open associates (necessary to calculate of the dipole moment of associates [15,26]) and the mean activity coefficient. Figure 7A,B presents the fraction of alcohol molecules involved in open and cyclic multimers consisting of "i" alcohol molecules, calculated for different alcohol concentrations.

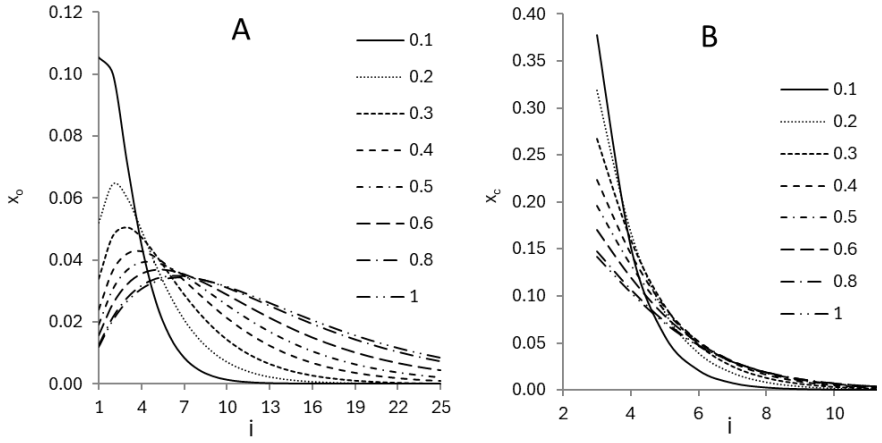

Figure 7. Fraction of alcohol molecules involved in open (**A**) and cyclic (**B**) multimers composed of **i** alcohol molecules. Different lines represent various fractions of alcohol.

It is of note that the relationship for each concentration of alcohol has the most probable number of alcohol molecules involved in the open associates. For example, the dimers are the most probable associates at the mole fraction of 1-hexanol equal to 0.2, and heptamers are the most probable species in the neat 1-hexanol. In the case of cyclic species, at all concentrations dominate small associates. The cyclic dimmers were not considered because the theoretical calculations suggested instability of this form. It is interesting that the most populated species are not tetramers, as was suggested in many previous papers [38,45,46], but cyclic trimers. As shown, four molecules per associate is an average number of alcohol molecules in the cyclic associates. Probably, for this reason the tetramers are frequently treated as the most abundant cyclic species in alcohols. It is also evident that the results of the spectral analysis strongly depend on the concentration of alcohol.

Along with the dielectric measurements, we recorded NIR spectra of the mixtures in the 4000–10,000 cm^{-1} range (Figure 8).

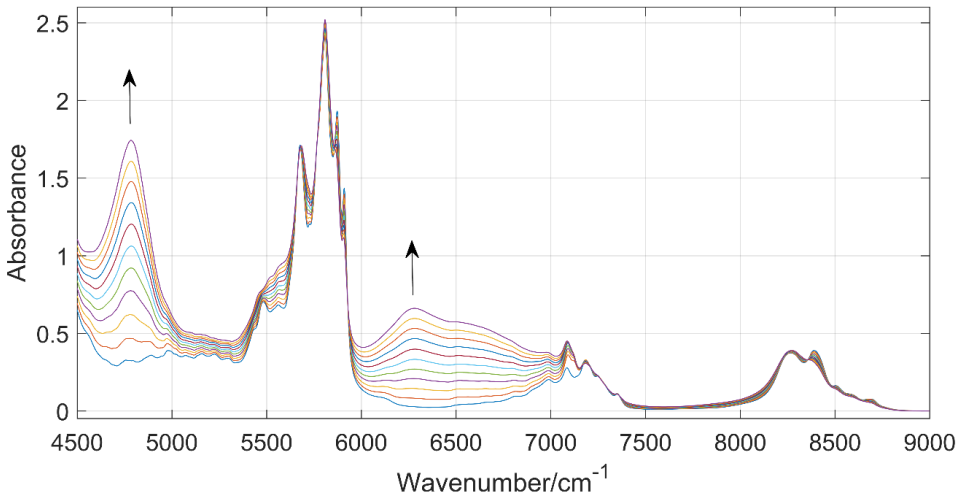

Figure 8. NIR spectra of 1-hexanol/hexane mixture in the whole range of mole fractions. The arrows indicate direction of spectral changes with an increase of 1-hexanol content.

The data were analyzed in the first overtone region of the "free" O–H stretching vibration 7100 cm^{-1}. Because this band was overlapped by the C–H combination bands {δ(CH) + 2ν(CH)}, extraction of its parameters required a detailed analysis of the band shape and application of a curve-fitting procedure. An exemplary result of this procedure is displayed in Figure 9.

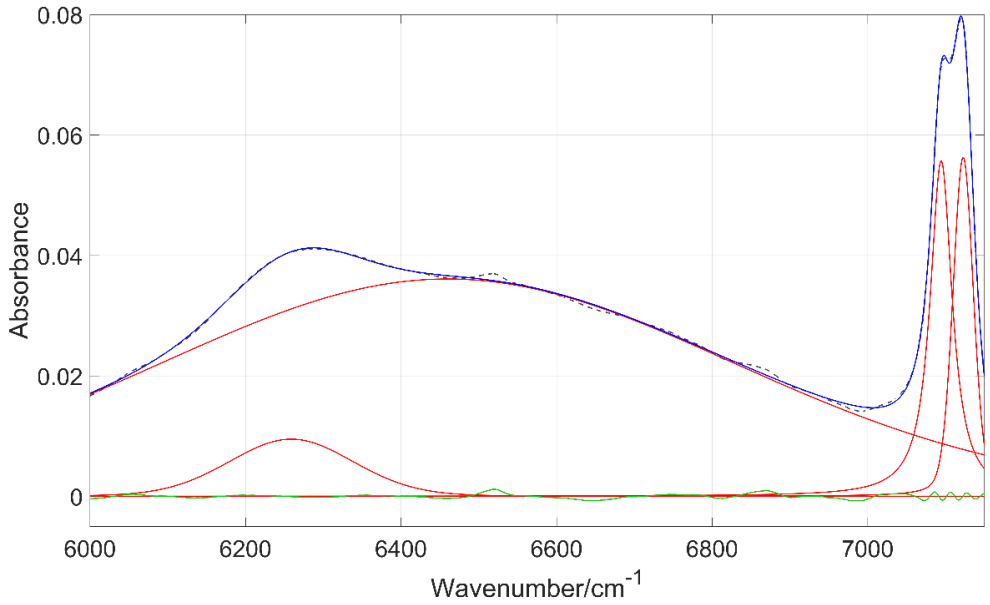

Figure 9. Curve fitting of NIR spectrum of 1-hexanol/n-hexane mixture at mole fraction of 1-hexanol 0.1. Black dotted line—experimental spectrum, blue line—reconstructed spectrum, red line—the spectra of resolved components, green line—the difference spectrum (experimental—reconstructed).

From these results we obtained the area of the band due to the free O-H groups. Using the molar absorption coefficient of this band (107.0 ± 1.0 in [$dm^3 \cdot mol^{-1} \cdot cm^{-2}$]) determined for long-chain n-alcohols [39], it was possible to calculate the fraction of the free O-H groups for different concentrations of 1-hexanol in n-hexane. One has to mention that the concentration of these groups obtained from NIR spectra includes the contribution from monomeric species and the terminal free O-H in the open associates. The comparison of the results obtained from dielectric and spectroscopic measurements reveals that the concentration of the "free" O–H groups obtained from NIR spectra is only slightly higher than the concentration of the monomers derived from the dielectric measurements. It is significantly lower than sum of contributions from the monomers and terminal O-H groups. This suggests that the "free" O–H band observed by NIR spectroscopy is associated predominantly with the monomeric species, while the contribution from the terminal O-H groups in the linear associates is negligible. This assumption contradicts commonly accepted interpretation of IR spectra of alcohols and therefore requires additional verification by independent experiments and/or theoretical calculations. This important conclusion could be an inspiration for further studies.

4. Conclusions

Both dielectric methods and vibrational spectroscopy provide information at a molecular level, but this information has a different physical origin and therefore supplies an independent insight from different sides. To study such complex phenomenon as hydrogen bonding in a comprehensive way, it is necessary to use few different experimental techniques. Such joint application of various approaches may deliver new information not accessible from each of these methods used separately. Here we present three examples of simultaneous use of dielectric measurements and vibrational spectroscopy for examination of hydrogen-bonded systems. The first example is devoted to composition dependent studies of the binary mixture of propionic acid-triethylamine [30]. Our results have shown the presence of the hydrogen bonded acid-base complexes, charge-transfer complexes and dissociated ionic species. Several mixture parameters have extreme at the specific mixture compositions, evidencing the presence of well-defined complexes and complicated equilibrium in the mixture. NIR spectroscopy confirmed the presence of particular species and processes elucidated from the dielectric measurements. The next example was taken from our paper on association of 1-octanol and 3-octanol [39]. Both methods reveal that at diluted solutions of alcohols in CCl_4 dominates the cyclic (non-polar) species. Increasing alcohol concentration shifts the equilibrium towards the linear (polar) associates and this process is more evident for 1-octanol, while 3-octanol

prefers formation of the cyclic species. It has been evidenced that the dissociation of the associates of alcohols into monomers does not appear directly but proceeds through intermediate species. At first, dissociate the terminal molecules of alcohol since this bonding is weaker than the internal bonds. The last example presents our results on studies of 1-hexanol in n-hexane [27]. The mixture was examined in the whole range of mole fractions using dielectric methods and NIR spectra. Dielectric results suggest that at low content of 1-hexanol dominates the cyclic associates, while increase in alcohol concentration shifts the equilibrium to the linear species. Similar picture was obtained from analysis of NIR spectra. However, we observed significant discrepancies in the population of the free and associated O-H groups obtained from both methods.

Alcohols are a particularly interesting class of compounds since they may form various kinds of hydrogen-bonded associates. Dielectric methods and NIR spectroscopy provides, to some extent, complementary information on the molecular origin of changes due to formation of the hydrogen bonding. For example, the dielectric methods can easily distinct between the linear and cyclic associates, while this information is obscured in the vibrational spectra. The bands due to various hydrogen-bonded species are often heavily overlapped, and the separation of individual contributions requires the use of advanced computational methods like curve-fitting or 2D correlation spectroscopy. However, the curve-fitting of complex spectral envelopes is sensitive to the input parameters and may provide unreliable results. Therefore, these results should be confirmed by an independent method. The agreement between results obtained from spectroscopic and dielectric methods is highly desired. On the other hand, the possible discrepancy may appear even more inspiring, since it allows to overcome the routine interpretation and gain a new and deeper insight into the phenomena studied.

In this short review, we have presented the benefits of the collaborative use of two different but complementary methods to examination of hydrogen-bonded complexes. We believe that the simultaneous application of several research methods during realization of a single project represents the most effective approach to extend our knowledge. Here, we have reported our experience in combined use of NIR spectroscopy and dielectric methods. While each of these techniques independently provides valuable information on studied phenomena, their integration leads to more comprehensive understanding. Research projects conducted by interdisciplinary teams offer the most promising way to a deeper understanding of Nature.

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