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Research paper

The characterization of aprotic polar liquids and percolation phenomena in DMSO/water mixtures

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Abstract

In the previous papers of our research group it was shown, that the Clausius-Mossotti-Debye equation for the quasi-static dielectric constant (ε_r) can be extended to liquids if the parameter E_i/E is introduced. Thus, it is possible to characterize polar liquids with the easily accessible parameter E_i/E. This property is also reflected by the fact that the parameter E_i/E can be directly related to the empirical $E_T(30)$ and the normalized E_T^N parameter to describe the polarity of liquids proposed by Reichardt (Chem. Rev. 94, 2319-2358)

E_i corresponds to the local mean field due to close molecule-molecule interactions after the application of an external electric field E. In a recent work of our research group it was also demonstrated that the modified Clausius-Mossotti-Debye equation and the study of the relaxation time can be related to percolation phenomena in binary solvent mixtures leading to a valuable insight of the structure of polar liquids and to a better understanding of binary systems. In the present paper it is demonstrated that percolation phenomena for binary DMSO/water mixtures, become visible due to changes of parameters describing the dielectric spectrums.

The interpretation of the percolation effects leads to the following conclusion: DMSO/water mixtures seem to have in the whole range of miscibility the same microscopic structure like water with a coordination number $z\approx$ between 4 and 6 which could be the reason for the high permeability of DMSO through biological membranes.

$$E_T^N = \frac{E_T(\text{solvent}) - E_T(\text{TMS})}{E_T(\text{water}) - E_T(\text{TMS})} = \frac{E_T(\text{solvent}) - 30.7}{32.4} \tag{1}$$

Keywords: Modification of the Clausius-Mossotti-Debye-Equation; Percolation phenomena; Binary polar solvent mixtures; Empirical solvent polarity parameter E_T and E_T^N (minamalized); Dielectric spectroscopy

1. Introduction

Dimethyl sulphoxide (DMSO) [$(CH_3)_2SO$)] is a widely used solvent with pharmacological action including anti-inflammatory and bacteriostatic activity, analgesia, nerve blockade, diuresis, cholinesterase inhibitor, vasodilatation, and muscle relaxation [1]. DMSO also has the unique capability of penetrating living tissues without causing significant damage [2]. It has been used as a carrier to enhance the bladder absorption of chemotherapeutics such as Paclitaxel [2], Cisplatin, Pirarubicin, and Doxorubicin [3,4]. One of the most interesting and significant properties of DMSO is its ability to act as a carrier for transferring other drugs through the cell membrane [5]. By this we mean that liquid DMSO can be applied on the sole of the foot and within a very few seconds you will be able to taste the DMSO in your mouth. It has a very distinctive taste, something like kerosene or garlic. As a second step, if you mix any of many other different substances with DMSO, and again apply this mixture (liquid) to the sole of your foot you will get a different taste in your mouth, in the same few seconds. The difference in the taste will depend on the other substance, which was added to DMSO and then carried very quickly through the body to the tongue to be tasted. Due to that fact, DMSO with a relatively low intrinsic toxicity of 14.5 g/kg Oral-Rat measured by LD_{50} is an interesting absorption enhancer, but on the other hand, DMSO as a component in a formulation is problematic as it

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can facilitate other substances to cross the cell barrier including the blood-brain barrier, which can lead to undesired interactions with other drugs. Therefore, many drugs have an enhanced physiological effect when they are mixed with DMSO, which means that the dose can be reduced, which can lead to a reduction of possible side effects due to drug toxicity. DMSO plays also an important role as a cryoprotector to prevent denaturalization of proteins. This cryoprotective action appears to stem from its ability to prevent water crystal formation within the cells. DMSO is at the same time a commonly used solvent in the industry. It is often used to test new drugs in an early preclinical study because DMSO can typically dissolve lipophilic drugs and hydrophilic drugs [6]. In this context it has to be kept in mind that DMSO is completely miscible with water and that water is the key solvent for the existence of life.

As we can see many properties are closely related to its properties in water solutions. Therefore, it is important to study its ability to affect the intermolecular structure of water. Binary DMSO/water mixtures are also of great interest due to the fact that both solvents have a dipole moment and that hydrogen bonds can be formed between water and DMSO molecules. However, DMSO is an aprotic solvent, i.e. no hydrogen bonding between pure DMSO molecules exists. Hence, the hydrogen bonding involving DMSO leads to a decrease in the number of hydrogen bonds among water molecules. Therefore, DMSO/water mixtures represent one of the more complicated binary solvent systems, namely an associating component (water) plus a second component (DMSO) acting only as a hydrogen-bond acceptor (HBA) [7].

There have been many attempts to reveal the intermolecular structure of the DMSO/water mixture in order to understand the non-linear behavior of this solvent system as a function of its composition. Extreme deviations from additivity are observed for a wide range of properties, such as density and viscosity. The maximum deviations occur at X (DMSO) = 30–40% (Φ (DMSO) = 63–72%) corresponding to X (water) = 60–70% (Φ (water) = 28–37%) and suggest the probable existence of a stable DMSO hydrate or at least a strong hydrogen-bonded association between the two kind of molecules [8]. The aim of this paper is to interpret that behavior in the framework of the percolation theory by using parameters derived from low frequency dielectric spectroscopy such as the E_i/E parameter, g-values obtained from the Kirkwood-Fröhlich, and relative permittivity, and the relaxation time derived from high frequency dielectric spectroscopy.

2. Theoretical background

2.1. The Clausius-Mossotti-Debye equation modified according to Leuenberger for the quasi-static relative permittivity [9]

The original Clausius-Mossotti-Debye equation is only valid for molecules in the ideal gas phase, i.e. in the case, where the molecules are located far from each other and do not show any interaction:

$$\frac{\varepsilon_r - 1}{\varepsilon_r + 2}\frac{M_r}{\rho} = \frac{N_A}{3\varepsilon_0}\left(\alpha + \frac{\mu_g^2}{3kT}\right) \quad (2)$$

With ε_r, quasi-static relative permittivity; M_r, relative molecular mass; ρ, density (g.cm^{-3}); N_A, Avogadro constant number (6.023×10^{23} mol^{-1}); ε_0 = permittivity of the vacuum, 8.854×10^{-12} (C^2 J^{-1} m^{-1}); α, electric polarizability of the molecule (C.m^2.V^{-1}); μ_g, dipole moment in the state of an ideal gas (C.m); k, Boltzmann's constant (1.38×10^{-23} J K^{-1}); T, thermodynamic temperature (K).

The essential point of the original derivation of the Clausius-Mossotti-Debye equation consisted in the fact that the local mean field E_i being the result of short-range van der Waals interactions and of hydrogen bonding of neighboring molecules was neglected. The introduction of the term E_i/E with E_i, internal electric field, caused by interactions with other induced neighboring dipoles; E, external electric field, produced by the applied voltage, leads to the following modification:

$$\frac{\varepsilon_r - 1}{3\frac{E_i}{E} + (\varepsilon_r + 2)}\frac{M_r}{\rho} = \frac{N_A}{3\varepsilon_0}\left(\alpha + \frac{\mu_g^2}{3kT}\right) \quad (3)$$

The Clausius-Mossotti-Debye equation modified according to Leuenberger for the quasi-static relative permittivity [9] [Eq. (3)] can be used to characterize polar liquids. In case of a highly polar liquid such as water the value of E_i/E is -21.0 at room temperature.

2.2. g-values obtained form the Kirkwood-Fröhlich Equation [9]

Short-range interactions between dipoles are considered by the Kirkwood-Fröhlich Equation [Eq. (4)], which was introduced by Kirkwood [10] and further developed by Fröhlich [11].

$$\frac{(\varepsilon_r - \varepsilon_{r,\infty})(2\varepsilon_r + \varepsilon_{r,\infty})}{\varepsilon_r(\varepsilon_{r,\infty} + 2)^2} = \frac{N_A}{9\varepsilon_0 kT}\frac{\rho}{M_r}\mu_g^2 g \quad (4)$$

In Eq. (4), ε_r, respectively $\varepsilon_{r,\infty}$ corresponds to the relative permittivity characteristic for induced polarization, measured at a frequency low enough that both atomic and electronic polarization are the same as in the static field, respectively high enough ($\varepsilon_{r\infty}$) so that the permanent dipoles can no longer follow the field; g = correlation factor; the other quantities are the same as in Eq. (2).

The correlation factor g is a measure of intermolecular correlations, considering one dipole surrounded by its z next neighbors (z = coordination number >1):

$$g = 1 + z\langle\cos\phi_{ij}\rangle \quad (5)$$

$\langle\cos\phi_{ij}\rangle$ is the average of the cosine of the angle between the two neighboring molecules i and j.

So we find for a parallel alignment of dipolar molecules, i.e. $\langle\cos\phi_{ij}\rangle = 1$, $g > 1$, and for an antiparallel alignment, i.e. $\langle\cos\phi_{ij}\rangle = -1$, $g < 1$.

The Kirkwood-Fröhlich Equation [Eq. (4)] is only valid for polar molecules. The value of g is ambiguous, as $g = 1$ stands either for disorder or equal amounts of parallel and antiparallel aligned molecules outweighing each other.

2.3. The Debye equation for the complex dielectric permittivity ε^*

The Debye equation describes the behavior of the frequency (ω) dependence of the complex dielectric permittivity $\varepsilon^* = \varepsilon'$, ε'',

$$\varepsilon^*(\omega) = \varepsilon_{r,\infty} + \frac{\varepsilon_r - \varepsilon_{r,\infty}}{1 + i\omega\tau} \tag{6}$$

with ε^*, complex permittivity; ε_r, quasi-static relative permittivity at ca. zero frequency and $\varepsilon_{r,\infty}$, relative permittivity for large frequencies ($\omega \to \infty$); τ, characteristic relaxation time (s^{-1}); ω, angular frequency (s^{-1}), and i, imaginary unit $= (-1)^{1/2}$. Eq. (6) can be split for the real (ε') and imaginary part (ε'') of the complex permittivity:

$$\varepsilon'(\omega) = \varepsilon_{r,\infty} + (\varepsilon_r - \varepsilon_{r,\infty}) \frac{1}{1 + \omega^2\tau^2}, \tag{7}$$

and

$$\varepsilon''(\omega) = (\varepsilon_r - \varepsilon_{r,\infty}) \frac{\omega\tau}{1 + \omega^2\tau^2}. \tag{8}$$

Eqs. (7) and (8) can be interpreted as follows: If we consider the behavior of a sample containing mobile dipoles which are being subjected to an oscillating electric field of increasing frequency, in the absence of the field, the dipoles will experience random motion due to thermal energy in the system and the 'microscopic' order depends on the result of the superposition of the thermal motion and the dipole-dipole interaction leading to the Kirkwood g-values which can appreciably be larger than unity. At low frequencies the dipole moment of the dipolar molecules, i.e. the entire molecule, orients in the applied electric field. Thus, the real part (ε') is approximately constant and the imaginary part (ε'') is close to zero. At higher frequencies the dipole can no longer follow the directions of the external applied field. The dipoles are unable to reorientate with that field and the total polarization of the system falls. Thus, ε' and ε'' assume rather low values (Fig. 1). However, at a specific frequency called resonance frequency (ω_{res}) located between these two extremes, the efficiency of the reorientation process is at maximum, as the rate of change in direction of the applied field matches the relaxation time of dipoles. Those dipoles will therefore undergo maximum reorientation, but the random oscillations superimposed on that system would be at minimum. At the resonance frequency (ω_{res}) the imaginary part (ε'') assumes a maximum value, which corresponds to the frequency of maximum energy absorption.

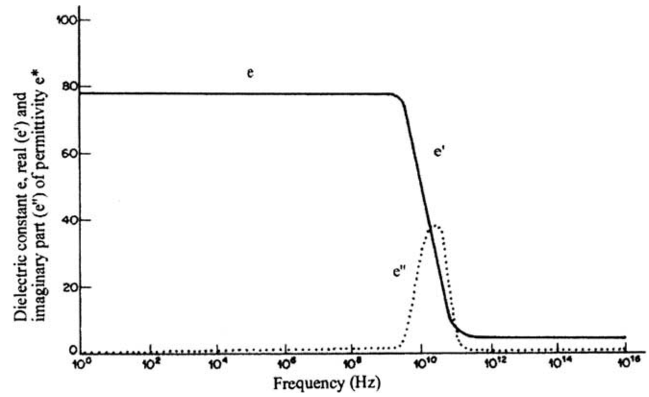

Fig. 1. Relative permittivity, ε_r, of a polar substance as a function of frequency (after Decareau and Mudget [12]).

2.4. Application of percolation theory

Peyrelasse et al. [13] studied the conductivity and permittivity of various water/AOT/oil systems (AOT = surfactant active agent = sodium bis(2-ethylhexyl) sulfosuccinate) being able to interpret the results according to the phenomenon of percolation. In a second step they studied the viscosity of those systems and they concluded that the shape of viscosity curves could also be interpreted, at least qualitatively, in the framework of percolation theory. They also suggested that the phenomenon of percolation must be involved in other physical properties.

The aim of this work is to study the phenomenon of percolation in binary solvent mixtures parameters by analyzing parameters derived from dielectric spectroscopy trying to find a connection between different physical properties.

We chose the DMSO/water system for our study because the mixtures exhibit higher viscosities than either of the two pure components, with a large viscosity maximum near X (DMSO) = 35%, (Φ (DMSO) = 68%), respectively Φ (water) = 32%) [14]. Moreover, there have been many attempts to revel the structure of the DMSO/water mixture in order to understand the maximum deviations detected at X (DMSO) = 30–40% (Φ (DMSO) = 63–72%) corresponding to X (water) = 60–70% (Φ (water) = 28–37%) observed for a wide range of properties, such as freezing point [15], density, and viscosity [8]. Kaatze et al. [16] found a typically minimum around X (DMSO) = 30% (Φ (water) = 37%) for the adiabatic compressibility suggesting the existence of homogeneous hydrogen-bonded networks rather than the presence of stoichiometrically well-defined DMSO: $2H_2O$ complexes.

Soper and Luzar [8] could moreover demonstrate through a neutron diffraction study of DMSO/water mixtures that although there is clearly some disordering of the water structure, the broadly tetrahedral coordination of water molecules remains intact: part of the hydrogen bonding has simply been transferred from the water/water complex to water/DMSO complex, and the proportion of this transfer increases with increasing concentration of DMSO (Fig. 2).

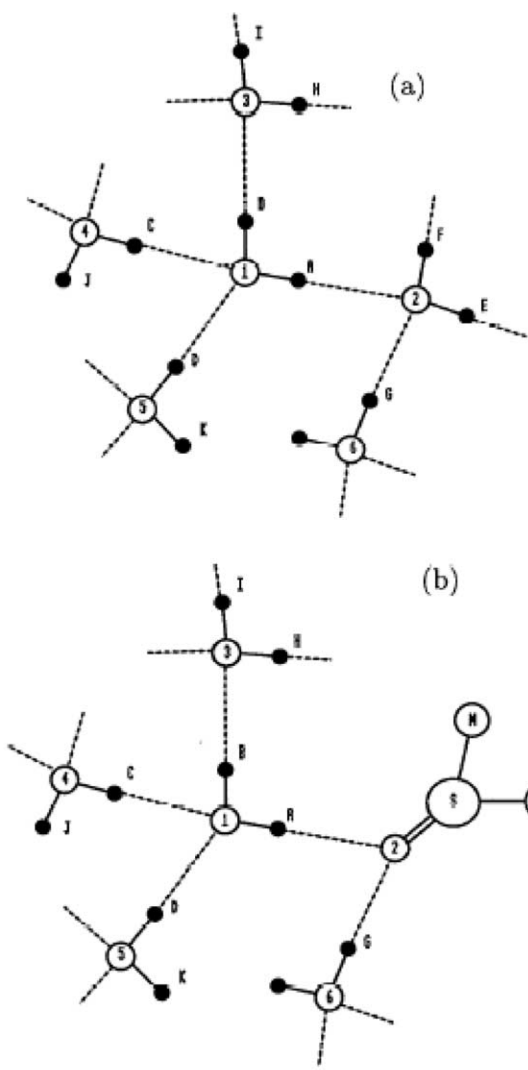

Fig. 2. Schematic view of hydrogen bonding in pure water (a) and DMSO/water (b). Solid lines represent intramolecular bonds, dashed lines represent hydrogen bonds. In (a) water molecule 1 is coordinated by five other molecules, 2, 3, 4, 5, and 6, with the first four at roughly tetrahedral positions the hydrogen A at the origin it sees one hydrogen (B) at 155 pm, four hydrogens (C, D, E, F) at $\approx$230 pm, one hydrogen (G) at $\approx$300 pm, and four hydrogens (H, I, J, K) at $\approx$380 pm, with a broad range of additional positions available due to the disorder. In (b) water molecule 2 has been replaced by a DMSO molecule, which is roughly 50% larger than the water molecule it replaces and adds two or three lone pair electrons, but no hydrogens, to form hydrogen bonds. Now, hydrogens E and F have disappeared, so substantially reducing the height of the peaks at 230 pm and 380 pm, and, if DMSO contributes three lone pairs, emphasizing the peak at $\approx$300 pm. If DMSO were to form much stronger hydrogen bonds with water than water does to itself, this reduction in peak height should become marked at high concentration (after Soper and Luzar [8]).

Table 1
Values of the bond and site percolation thresholds for various two and three dimensional lattices. Also given is the coordination number defined as the number of bonds meeting at an interior lattice site [17]

Lattice	Site	Bond	Coordination number z
Honeycomb	0.696	0.653	3
Square	0.593	0.500	4
Triangular	0.500	0.347	6
Diamond	0.430	0.388	4
Simple cubic	0.312	0.249	6
BCC	0.246	0.180	8
FCC	0.198	0.119	12
Bethe	$1/(z-1)$	$1/(z-1)$	z

Percolation thresholds of an ideal system occupied by isometric particles depends on the lattice type, the type of percolation (bond or site), and on the euclidean dimension of the lattice (see Table 1). In the following work only the case of site percolation is discussed. In an ideal system the lattice size is extremely large, i.e. infinite compared to the size of a unit lattice cell. Unfortunately, for most of the lattices the percolation thresholds (p_c) cannot be calculated in a straightforward way, but have to be estimated experimentally by computer simulation of such a lattice and its random occupation.

2.5. Structural differences between a solid, liquid, and a gas

The case of an ideal gas is very clear: the atoms or molecules do not interact due to the large distances in between. The difference between a liquid and a gas becomes difficult in case that the distances between the atoms and molecules are reduced. E.g. in case of CO_2 above the critical point it is difficult to decide, whether it behaves like a gas or a liquid. Officially this phase is called a supercritical gas.

On the other hand, an ideal crystalline solid has a perfect structure (see Fig. 3). A liquid can be considered as a modified solid. The information obtained by diffraction experiments is often presented graphically by means of the 'radial distribution function'. The radial distribution function is a measure of the average density as a function of distance from some arbitrary origin. In Fig. 3 we see that liquid Hg resembles more the solid than the gaseous state, suggesting the existence of short-range order in liquids and the legitimate description of liquid as a modified solid. It is therefore evident that a liquid is somehow structured but the structure is not perfect. It should be possible however to give an estimate concerning e.g. the coordination number of the structure of the liquid. In case of water it can be assumed that the coordination number is in the vicinity of 4. This reasoning is supported by the fact that water is present in the form of H_2O clusters, which disintegrate and/or formed again. The half-life of these structures is considered to be around 10^{-10} to 10^{-11} s ('flickering clusters', 'formation and dissolution of Nano-Icebergs'). Solidified water (ice) has a coordination number $z=4$ having a diamond structure [19]. It has to be

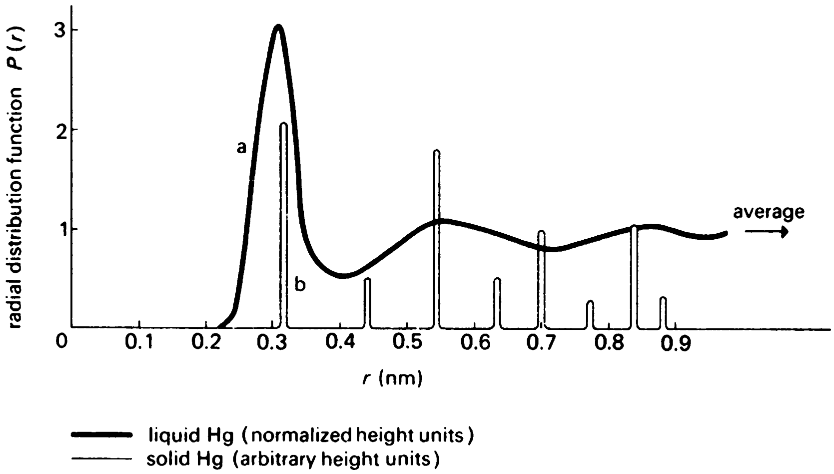

Fig. 3. Radial distribution function in liquid and solid mercury. The radius is measured from an arbitrary atom chosen as origin [18].

kept in mind that the density of liquid water is higher than in case of ice. Thus a closer mean packing of liquid water can be expected with z between 4 and 6.

3. Materials and methods

3.1. Solvents

The binary mixtures of DMSO/water, α,α-diglycerol/ water, and 1,4-dioxane/water were examined at 298.2 K. Bidistilled water was freshly prepared by means of a Fontavapor 285 (Büchi AG CH-Flawil). Dimethyl sulfoxide of high purity (≥99.5%) was acquired commercially from Fluka Chemie GmbH CH (art. No. 41644). DMSO/water solutions were stored tightly covered since DMSO is strongly hygroscopic. 1,4-Dioxane of high purity was acquired commercially from Fluka Chemie GmbH CH-Buchs (art. No. 42512). α,α-diglycerol was supplied by Solvay GmbH D-Rheinberd (art.No. 71021328).

3.2. Experimental set-up and data analysis

3.2.1. Measurement of the static permittivity and conductivity: The use of the E_i/E parameter in the characterization of aprotic liquids at room temperature: Data analysis

The measurement of the static permittivity and conductivity as well as the calculation of the E_i/E parameter for binary liquid mixtures is described in detail in a recent work of our research group [20].

For the determination of the relative permittivity, the precision LCR meter at 100 KHZ, Agilent Technologies Inc. USA-Palo Alto, CA was used. The sample was kept at 298.2 K (±0.1 K) with a thermostat (Thermomix UB and Frigomix U-1, B. Braun Biotech International GmbH D-Melsungen).

E_i/E for binary mixtures was calculated according to the following equation [21]:

$$\frac{E_i}{E} = \frac{M_{\mathrm{r,m}}}{3\rho_{\mathrm{m}}} \frac{\varepsilon_{\mathrm{r,m}} - 1}{\frac{N_{\mathrm{A}}}{3\varepsilon_0}\left[\Phi_1\left(\alpha_1 + \frac{\mu_{\mathrm{g},1}^2}{3kT}\right) + \Phi_2\left(\alpha_2 + \frac{\mu_{\mathrm{g},2}^2}{3kT}\right)\right]} - \frac{\varepsilon_{\mathrm{r,m}} + 2}{3} \tag{9}$$

where ρ_{m}, density of mixture; $M_{\mathrm{r,m}}$, relative molecular mass of the mixture; $\varepsilon_{\mathrm{r,m}}$, quasi-static relative permittivity for the mixture; Φ_1, volume fraction of liquid 1; Φ_2, volume fraction of liquid 2.

The volume fraction of water was calculated according to the following equation:

$$\Phi_1 = \frac{X_{1,\mathrm{m}} V_{1,\mathrm{m}}}{X_{1,\mathrm{m}} V_{1,\mathrm{m}} + X_{2,\mathrm{m}} V_{2,\mathrm{m}}} \quad \text{with } \Phi_1 + \Phi_2 = 1 \tag{10}$$

Where $X_{1,\mathrm{m}}$ is the mol fraction of water in the mixture; $X_{2,\mathrm{m}}$ is the mol fraction of DMSO in the mixture; $V_{1,\mathrm{m}}$ is the partial molar volume of water in the mixture and $V_{2,\mathrm{m}}$ is the partial molar volume of DMSO in the mixture.

The dipole moments μ_{g} used for calculations are literature values for the gas phase [22].

The polarizability was determined via the Lorentz-Lorenz equation, which gave excellent results compared with literature data [23] both for polar and nonpolar compounds (see Eq. (11)).

$$\frac{n^2 - 1}{n^2 + 2} \frac{M_{\mathrm{r}}}{\rho} = \frac{N_{\mathrm{A}}}{3\varepsilon_0}\alpha \tag{11}$$

The measurements of the density ρ were made using a vibrating-tube densimeter (Density Meter Anton Paar AG A-8054 Graz DMA 58;8), refractive indices n_{D} were measured with an Abbé refractometer (A. Krüss Optronic GmbH, D-22297 Hamburg AR8; 30098).

For calculating the respective contributions of the liquids, their volume contributions are considered. For the description of binary mixtures by means of percolation theory, the volume fractions are used, as they are more meaningful for the characterization of geometric three-dimensional networks than molar fractions [21].

The correlation factor g was calculated following the Kirkwood-Fröhlich equation for binary mixtures, using the volume fractions for calculations instead of molar fractions, so that the results are comparable to the values for E_i/E [21].

$$\frac{(\varepsilon_{r,m}-\varepsilon_{r,\infty,m})(2\varepsilon_{r,m}+\varepsilon_{r,\infty,m})}{\varepsilon_{r,m}(\varepsilon_{r,\infty,m}+2)^2} = \frac{N_A}{9\varepsilon_0 kT}\frac{\rho_m}{M_{r,m}}(\Phi_1\mu_{g,1}^2+\Phi_2\mu_{g,2}^2)g \quad (12)$$

For $\varepsilon_{r,\infty,m}$, the square of the refractive index of the mixture at $\lambda=589.3$ nm was used.

The molar volume of a pure liquid is defined as:

$$V_m = \frac{M_r}{\rho}\ [\mathrm{cm^3\ mol^{-1}}] \quad (13)$$

where M_r, relative molecular mass (g mol^{-1}) and ρ, density (g cm^{-3}).

In order to get a parameter, which defines the density of the squared dipole moment per molar volume ($D_{\mu\mu}$), the following variables were defined [24]:

$$D_{\mu\mu} = \frac{\mu^2}{V_m}\ [D^2\ \mathrm{mol\ cm^{-3}}] \quad (14)$$

The dipole moment μ is given in debye units (D). The conversion factor to SI units is 1 $D=3.33564\times10^{-30}$ C m.

The squared value of the Hansen parameters ($\delta_d^2, \delta_p^2, \delta_h^2$ i.e. partial solubility parameters) was taken according to the Hansen equation (see Eq. (15)).

$$\delta_t^2 = \delta_d^2+\delta_p^2+\delta_h^2 \quad (15)$$

For the study of the correlation between the parameter E_i/E and the squared value of the total respectively of the partial solubility parameters as well as for the correlation between E_i/E parameter and $D_{\mu\mu}$ respectively E_i/E and the $E_T(30)$ parameter [25] or the normalized E_T^Nvalues [25] the data compiled in Table 2 were analyzed.

3.2.2. Some comments concerning the standard error of E_i/E

The value of E_i/E of the polar liquids can be calculated on the basis of well established literature values of the parameters in equation [3] such as molecular weight M_r dipole moment μ, polarizability α, density δ and the static dielectric constant ε_1. For the discussion of the correlation between E_i/E it is however essential to keep in mind that the solubility parameters have intrinsically an important standard error. Thus due to the error propagation rule of Gauss a subsequent standard error of E_i/E can be estimated as follows; i.e. the standard error is low and can be neglected in a first approximation.

In case of the linear relationship between E_i/E and $(\delta_i)^2$, i.e. $E_i/E=a+b\ (\delta_i)^2$ with i=t (total), d (dispersive), p (polar), h (hydrogen bonding) partial solubility parameters the rules of the Gaussian error propagation lead to the following equation:

$$\Delta\left(\frac{E_i}{E}\right) \approx \pm\sqrt{(\Delta a)^2+(\delta_i^2)^2(\Delta b)^2+b^2(\Delta\delta_i^2)^2} \quad (16)$$

Table 2
Physical properties of pure solvents

Substance	E_i/E-value	δ_t^2 (MPa)[a]	δ_p^2 (MPa)[a]	δ_h^2 (MPa)[a]	δ_d^2 (MPa)[a]
DMSO	−13.26	712.89	268.96	104.04	338.56
Acetonitrile	−10.97	595.36	324.00	37.21	234.09
Dimethylformamide	−10.08	615.04	187.69	127.69	302.76
Dimethylacetamide	−9.78	515.29	132.25	104.04	282.24
Methylpyrrolidone	−8.79	524.41	151.29	51.84	324.00
Acetone	−5.37	400.00	108.16	49.00	240.25
Methyl ethyl ketona	−3.92	361.00	81.00	26.01	256.00
Tetrahydrofuran	−1.04	376.36	32.49	64.00	282.24
Ethyl acetate	−0.79	327.61	28.09	51.84	249.64
1,4-Dioxane	0.02	420.25	3.24	54.76	361.00

Substance	$(\delta_p^2+\delta_h^2)^{1/2}$	$D_{\mu\mu}$ (D^2 mol cm^{-3})	$E_T(30)$ (Kcal mol^{-1})[b]	E_T^N [b]
DMSO	19.31	0.220	45.10	0.44
Acetonitrile	19.01	0.294	45.60	0.46
Dimethylformamide	17.76	0.199	43.20	0.39
Dimethylacetamide	15.37	0.148	42.90	0.38
Methylpyrrolidone	14.25	0.175	–	–
Acetone	12.54	0.113	42.20	0.36
Methyl ethyl ketona	10.34	0.086	41.30	0.33
Tetrahydrofuran	9.82	0.038	37.40	0.21
Ethyl acetate	8.94	0.032	38.10	0.23
1,4-Dioxane	7.62	0.000	36.00	0.16

[a] Source: Barton [26].
[b] Source: Reichardt [25].

with Δa, standard error of the intercept a; Δb, standard error of the slope b.

Due to the empirical determination that it is extremely difficult to find in the existing literature (see e.g. [26] a reliable value for the standard error of the individual solubility parameter. To be on the save side a rough and conservative value of the standard error of the total and partial solubility was adopted:

$$\Delta\delta_t \approx \pm 0.5\ (MPa)^{1/2} \quad \text{respectively} \quad \Delta\delta_t^2 \approx \pm 0.25\ (MPa)$$

It is evident that the resulting standard error of E_i/E is much larger than in reality but the result gives an additional information about the significance of the linear correlations plotted taking into account the uncertainty of the values of the solubility parameters.

In case of the correlation between E_i/E with $D_{\mu\mu}$ and the other parameters, the same procedure was used for the estimation of $\Delta E_i/E$ using the following estimates for $\Delta D_{\mu\mu} \approx 0.002$; $\Delta E_t^N \approx 0.01$.

3.2.3. Measurement of the complex permittivity: Calculation of the relaxation time (τ)

The measurement of the complex permittivity as well as the calculation of the relaxation time (τ) for binary liquid mixtures is described in detail in a recent work of our research group [20].

For the determination of the real (ε') and imaginary (ε'') permittivity the HP 8720D Vector Network Analyzer, Agilent Technologies Inc. USA-Palo Alto, CA was used. The sample was kept at 298.2 K ($\pm$0.1 K) with a thermostat (Thermomix UB and Frigomix U-1, B. Braun Biotech International GmbH D-Melsungen). Measurements were made between 0.2 and 20 GHz at 401 frequencies. The Auto Sweep Time Mode was selected. This mode maintains the fastest sweep speed possible for the current measurement settings. A sweep time = 13.052 s was obtained for measurements between 0.2 and 20 GHz at 401 frequencies.

The following softwares were used for data analysis: *Excel* Microsoft corp. USA-Redmond WA 98052-6399 Version 97 SR-2 and *SYSTAT for Windows* SPSS Inc.

USA-Chicago IL 60606-6307 Version 7.0, where the inclusion of both real and imaginary parts for fitting can be made as the term ($\varepsilon_r - \varepsilon_{r,\infty}$) occurs in both parts (see Eqs. (7) and (8)). Data were fitted in these equations by using nonlinear regression (Gauss-Newton with Least Squares estimation).

3.2.4. Subdivision of curves into segments by means of nonlinear regression for the detection of percolation thresholds

The subdivision of curves into segments by means of nonlinear regression in order to detect percolation thresholds is described in a recent work of our research group [20].

From theory, we assume that the properties of a binary mixture should behave like the volume-wise addition of the properties if the pure liquids. If deviations from this theoretical assumption occur, the splitting up of the curve into small number of segments leads to the distinction of percolation thresholds, critical volume fractions, and to a better description of properties of the system. The subdivision of data into a number of segments may be appropriate if the number of segments is small, the mathematical model describing the segments simple, viz straight lines, and if there are sharp transitions between the segments [27,28].

The data were inspected in order to decide about a suitable number of sub-segments and potential critical intersection points. The procedure is demonstrated with the following example using x, y-values as a model (see Table 3), three sub-segments seem appropriate with critical intersection points at $x_{crit} \approx 4$–6 and 8–10.

In a second step they were arbitrary split into three straight subsegments around these possible critical intersection values x_{crit} e.g. the first four points to subsegment A, the next four to subsegment B, the last four to subsegment C. Using nonlinear regression, the data were fitted to the following equation:

$$y = A(m_1x + b_1) + B(m_2x + b_2) + C(m_3x + b_3) \tag{17}$$

The final decision to which segment the data are to be assigned is made considering the mean corrected coefficient R^2 for the overall fit. For this example, the best fit ($R^2 = 0.999$) was received for a distribution 4/4/4 (A: $y = -0.26x + 13.00$; B: $-1.65x + 18.35$; C: $0.53x - 1.79$).

The critical values correspond with the intersection points of the segments. In the example they are located at the following critical values $x_{crit1} = 3.85$ and $x_{crit2} = 9.24$. Those two intersections points divide the range into three sections.

Thus, this method can be used to give an estimate for the location of percolation thresholds in a binary mixture. It has to be kept in mind that the lower percolation threshold in a three dimensional system is in the Φ range 0–50% and the

Table 3
Subdivision of curves into segments (after Hernandez-Perni et al. [20])

x	y	Data belong to segment		
		A	B	C
1.0	12.7	1	0	0
2.0	12.6	1	0	0
3.0	12.1	1	0	0
4.0	12.0	1	0	0
5.0	10.0	0	1	0
6.0	8.5	0	1	0
7.0	7.0	0	1	0
8.0	5.0	0	1	0
9.0	3.0	0	0	1
10.0	3.5	0	0	1
11.0	4.0	0	0	1
12.0	4.6	0	0	1

upper one in the range Φ of >50%–100%. It is possible that only one percolation threshold is visible depending on the method of detection. On the other hand additional critical concentration can give evidence of a structural change of the ‘lattice’ i.e. of the local ‘order’ of the binary liquid.

The software used was: *Systat for Windows* SPSS Inc. USA-Chicago IL 60606-6307 Version 7.0.

For the description of binary mixtures by means of percolation theory, the volume fractions are used, as they are more meaningful for the detection of the percolation thresholds, described by Stauffer and Aharony [29] (Introduction to Percolation Theory) as ‘geometrical phase transitions’.

4. Results and discussion

4.1. The use of the E_i/E parameter in the characterization of aprotic liquids at room temperature

It was possible to show in a previous paper [24] that there is a correlation between E_i/E and the total and the partial solubility parameters. It became evident that the squared correlation coefficient could be still improved if E_i/E is correlated to the squared value of the total and partial solubility parameters. Thus, for the following analysis the E_i/E-values were correlated as a first choice with the squared value of the total and partial solubility parameters. A close inspection of the data in Table 2 leads to the following results. A satisfactory correlation between the E_i/E parameter and the squared value of the total Hildebrand solubility parameter was obtained (see Fig. 4, Eq. (18)).

$$E_i/E = -0.03\,\delta_t^2 + 10.17 \quad r^2 = 0.83; \tag{18}$$

This result is not as good as in the case of polar substances able to form hydrogen bonds ($E_i/E = f(\delta_t^2)$: $r^2 = 0.99$), where we also found an excellent respectively good correlation between the E_i/E parameter and the squared of the partial Hildebrand solubility parameters δ_h

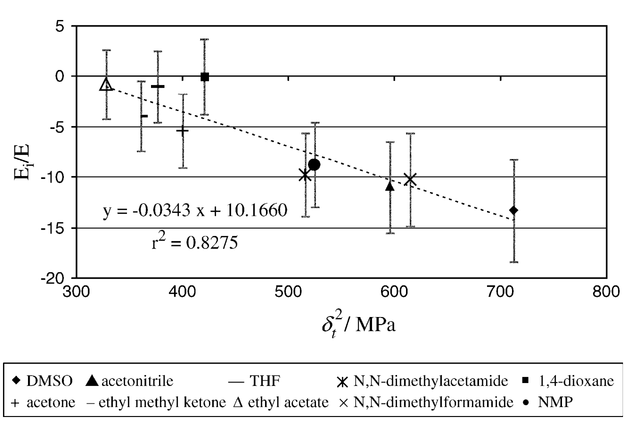

Fig. 4. E_i/E values as a function of the squared total Hildebrand solubility parameter for aprotic substances (according to Barton [26]) at 298.2 K.

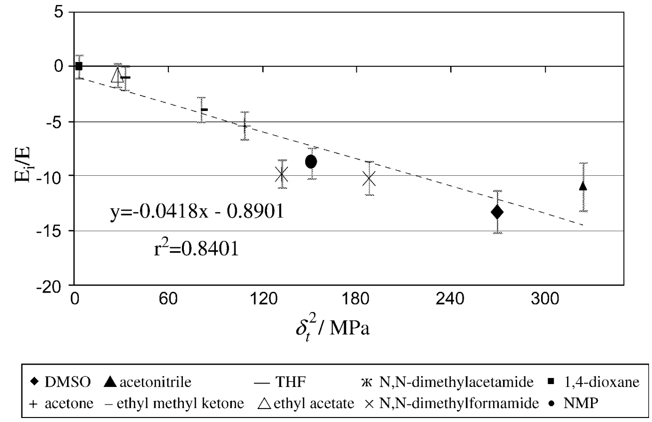

Fig. 5. E_i/E values as a function of the squared partial Hansen solubility parameter δ_p for aprotic substances (according to Barton [26]) at 298.2 K.

and δ_p ($E_i/E = f(\delta_h^2)$: $r^2 = 0.98$ respectively $E_i/E = f(\delta_p^2)$: $r^2 = 0.92$). For aprotic substances a satisfying correlation can be established with the polar component of the Hansen equation (see Fig. 5, Eq. (19)). However no correlation exists between the E_i/E parameter and the hydrogen-bonding component of the Hansen equation (see Fig. 6, Eq. (20)), which is not surprise due to the fact that no hydrogen bonding between pure aprotic molecules exists.

$$E_i/E = -0.04\delta_p^2 - 0.89 \quad r^2 = 0.84 \tag{19}$$

$$E_i/E = -0.07\delta_h^2 - 1.47 \quad r^2 = 0.26 \tag{20}$$

However, it is of interest that E_i/E can also be correlated with the combined partial solubility parameter $\delta_{hp} = (\delta_h^2 + \delta_p^2)^{1/2}$, which leads to an improved correlation coefficient of $r^2 = 0.95$.

As expected, no correlation can be observed with the dispersive partial solubility parameter δ_d^2, i.e. ($r^2 < 0.01$).

It is important to keep in mind that the squared values of the solubility parameters were taken for two reasons:

(a) For polar substances the relation $E_i/E = f\,(D_{OH})$ was analyzed [24] (D_{OH} defines the density of OH-groups

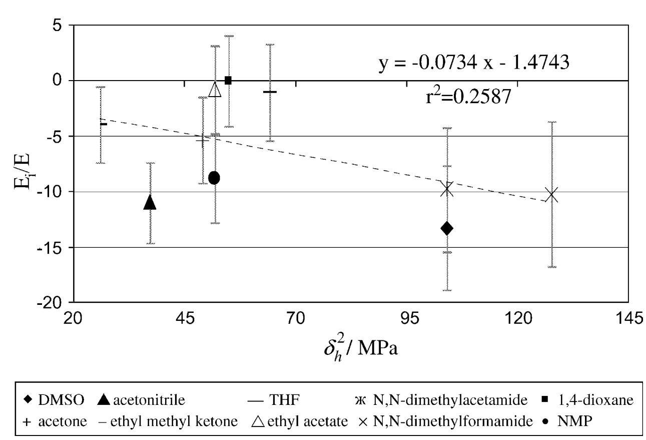

Fig. 6. E_i/E values as a function of the squared partial Hansen solubility parameter δ_h for aprotic substances (according to Barton [26]) at 298.2 K.

per volume). We were therefore looking at the system per volume. The close molecular-molecular interactions per volume are correlated with the density of hydroxy groups per molar volume (D_{OH}). When the relation $E_i/E=f$ (solubility parameter) was investigated, the squared value of the solubility parameters is taken due to the fact that the squared solubility parameter corresponds to the endoergic process of separating the solvent molecules to provide a suitably sized enclosure for the solute and measures the work required to produce a cavity of unit volume in the solvent. This term is related to the tightness or structuredness of solvents as caused by intermolecular solvent/solvent interactions [26]. Therefore, the squared solubility parameter gives us the amount of van der Waals interactive energies that held the molecules of the liquid together per molar volume.

$$\delta = \left[\frac{\Delta H - RT}{V_m}\right]^{1/2} \quad \text{or} \quad \delta^2 = \frac{\Delta H - RT}{V_m} \tag{21}$$

For aprotic substances the squared value of the solubility parameters was taken for the same reason. We need a relation per molar volume.

(b) The squared values of the total and partial solubility parameters have the advantage that the dimension is equal to energy per volume having a clear meaning. Nevertheless, It is important to point out that the squared values were slightly better for δ_h i.e. $E_i/E=f(\delta_h^2)$; in the same order for δ_t i.e. $E_i/E=f(\delta_t^2)$ and slightly worse for δ_p i.e. $E_i/E=f(\delta_p^2)$. It is of interest, that a very good correlation is found for combined solubility parameters δ_{ph} and δ_{ph}^2 $E_i/E=f((\delta_h^2+\delta_p^2))$ and $E_i/E=f((\delta_h^2+\delta_p^2)^{1/2})$ (see Table 4).

For similar polar substances being able to form hydrogen bonds, only a good estimation for the total (δ_t) and the squared value of the partial solubility parameter (δ_p) can be obtained by determining the corresponding E_i/E values.

According to Eq. (22), a linear dependence between E_i/E and $D_{\mu\mu}$ also exists for aprotic liquids (see Fig. 7).

$$E_i/E = -47.82 D_{\mu\mu} - 0.16 \quad r^2 = 0.87 \tag{22}$$

Finally, it was also possible to find a good correlation between the E_i/E parameter and the empirical solvent polarity parameter $E_T(30)$ at room temperature. Automatically, it is also found a good correlation between the E_i/E parameter and the normalized $ET(30)-\text{values}=E_T^N$

Table 4
Correlation coefficient obtained for different correlations between the E_i/E parameter and the total and partial solubility parameters for aprotic liquids

Aprotic substances			
	r^2		r^2
$E_i/E=f(\delta_t^2)$	0.828	$E_i/E=f(\delta_t)$	0.832
$E_i/E=f(\delta_p^2)$	0.840	$E_i/E=f(\delta_p)$	0.901
$E_i/E=f(\delta_h^2)$	0.259	$E_i/E=f(\delta_h)$	0.226
$E_i/E=f(\delta_d^2)$	0.005	$E_i/E=f(\delta_d)$	0.005
$E_i/E=f(\delta_h^2+\delta_p^2)$	0.915	$E_i/E=f((\delta_h^2+\delta_p^2)^{1/2})$	0.949

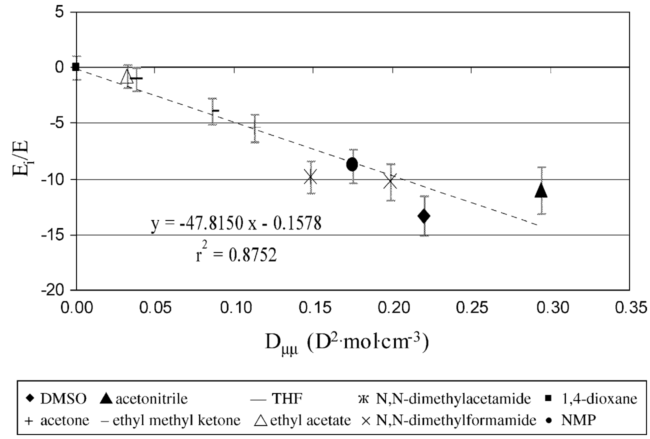

Fig. 7. E_i/E values as a function of $D_{\mu\mu}$ for aprotic substances at 298.2 K.

parameter (see Fig. 8, Eq. (23)). That confirms the important role of the E_i/E parameter in the characterization of not only polar liquids able to form hydrogen bonds but also aprotic liquids.

$$E_i/E = -45.14 E_T^N + 8.65 \quad r^2 = 0.90 \tag{23}$$

4.2. Percolation phenomena observed in binary DMSO/water mixtures based in the results of the modified Clausius-Mossotti-Debye equation

The E_i/E-values for the investigated binary DMSO/water mixtures at 298.2 K are represented in Fig. 9a and b. The E_i/E-values can be subdivided in three linear segments. The intersections are located at ca. Φ (water) = 32% and Φ (water) = 74%. The lower intersection at ca. Φ (water) = 32% can be interpreted as the percolation threshold of water. The second one at ca. Φ (water) = 74% can be assumed as the upper percolation threshold, where DMSO starts to form isolated clusters and is no longer percolating the system.

DMSO/water mixtures represent one of the more complicated binary systems, namely an associating

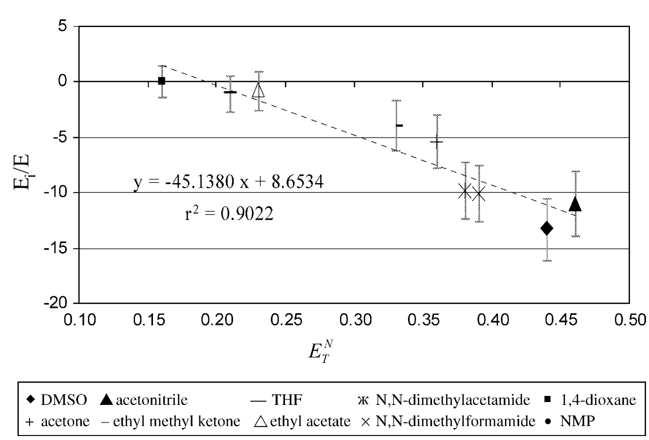

Fig. 8. E_i/E values as a function of E_T^N for aprotic substances (according to Reichardt [25]) at 298.2 K.

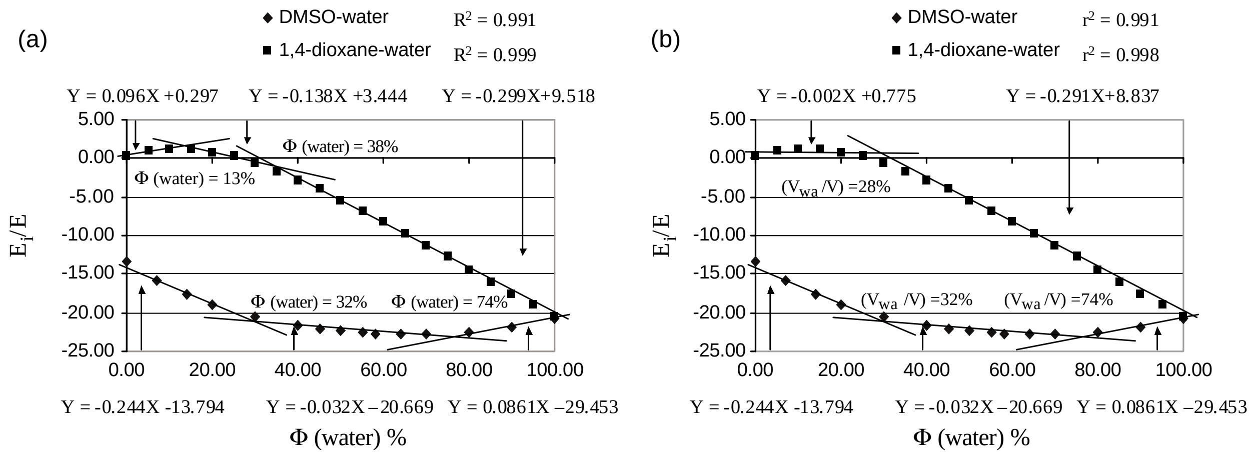

Fig. 9. (a/b) E_i/E values as a function of the Φ (water) for the binary DMSO/water mixtures with critical concentrations located at ca. Φ (water) ≅ 32% and Φ (water) ≅ 74% at 298.2 K, and E_i/E values as a function of the Φ (water) for the binary 1,4-dioxane/water mixtures at 298.2 K with three sections with critical concentrations at ca. Φ (water) ≅ 13% and Φ (water) ≅ 38% at 298.2 K.

component (water) plus a second component (DMSO) acting only as a hydrogen bond acceptor [7].

It is interesting to compare the behavior of 1,4-dioxane/water and DMSO/water mixtures (see Fig. 9a and b). In binary 1,4-dioxane/water mixtures an upper percolation threshold for Φ (water) > 50% is not visible. However the curve can be divided into three segments with critical concentrations at Φ (water) = 13% and Φ (water) = 38%. It is possible that water starts to percolate at ca. Φ (water) = 13%, or that a change of the 'lattice structure' of the 1,4-dioxane/water systems occurs. It can be shown that the water molecules form isolated islands in a continuous phase of 1,4-dioxane as it is possible to get a better estimate of the dipole moment of water using the classical Debye equation for decreasing water concentration below Φ (water) = 13%. A second critical concentration is-as mentioned-observed at Φ (water) = 38%, which would correspond in fact to a bond percolation threshold of lattices with a coordination number close to 4 (diamond lattice) (see Table 1)

In this context it has to be kept in mind that the structure of ice at normal pressure and close to 0 °C corresponds to a tetrahedral configuration with the coordination number 4. According to the model of water described by a dynamic equilibrium of 'nano-icebergs' which are formed and dissolved, a coordination number close to 4 can be adopted. The upper percolation threshold is-as mentioned-not visible, which indicates that 1,4-dioxane fits well into the water. It can be assumed that the volume of a single water cluster with five water units has a similar relative molecular mass [M_r = 90.10 gmol^{-1}], and a similar volume as one 1,4-dioxane molecule [M_r = 88.11 gmol^{-1}].

It has to be taken into account that the relationship of E_i/E in the 1, 4-dioxane-water mixture can also be divided only into two segments with a slightly smaller squared correlation coefficient (r^2 = 0.998 instead of 0.999). In this case it is evident that the critical concentration corresponds to the lower site percolation threshold of a lattice with a coordination number between $z \approx 4$ and 6 (Φ water ≈ 28%). Thus further studies are necessary to get conclusive results if one or two critical concentrations exist.

With binary DMSO/water mixtures both percolation threshold can be detected: The lower one at ca. Φ (water) = 32% and the upper one at ca. Φ (water) = 74%. If the E_i/E values of the pure solvents are not taken into account the following percolation thresholds are obtained for binary DMSO/water mixtures: the lower value at ca. Φ (water) = 34%, and the upper value at ca. Φ (water) = 66%. If we consider our binary mixture being somehow structured that it complies with the idea of having a critical concentration at ca. Φ (water) = 34% for the lower p_c respectively Φ (water) = 66% (Φ (DMSO) = 34%) for the upper p_c, which corresponds to the site percolation thresholds of a three-dimensional lattice with a coordination number of z between 4 and 6. Thus, it can be concluded that DMSO does not seem to induce a major disruption of the water structure. Between the two percolation thresholds both components percolate. Thus, more hydrophobic substances can be dissolved in the continuous phase of DMSO. Thus, the special physiological properties of the DMSO/water mixtures may be related to the fact, that the water structure is not heavily modified and that both components have a dipole. It seems to be the case that the tetrahedral coordination remains more or less in this dynamic equilibrium of the liquid intact [8] within the whole range of DMSO/water mixtures. On the other hand, the value of E_i/E decreases to a minimum at the upper percolation threshold indicating a higher local electric field E_i. This effect can be related to the high dipole moment of DMSO. This dipole moment is also responsible for the different behavior of DMSO/water mixtures compared to 1,4-dioxane/water mixtures of the E_i/E values (see Fig. 9a respectively 9b) with 1,4-dioxane lacking a dipole moment.

4.3. Percolation phenomena observed in DMSO/water mixtures based on the results of g-values according to the Kirkwood-Fröhlich equation

The g-values for the binary mixtures of DMSO/water at 298.2 K are presented in Fig. 10. The curve can be subdivided into three linear segments. The intersections of the linear segments are located at ca. Φ (water) = 35% and ca. Φ (water) = 77%. These findings are compatible with the findings of Fig. 9a and b (E_i/E-values of the DMSO/water mixtures) for the lower and upper p_c as it is well known that the location of the critical concentrations may be influenced by the sensitivity of the parameter to be chosen to detect the p_c.

Unlike polar liquids capable of forming hydrogen bonds [21] such as α,α-diglycerol in a mixture with water, the aprotic DMSO behaves differently with respect to the g-values (see Fig. 10). In the case of DMSO we find a region nearly constant with g-values close to $g \approx 1$ till ca. Φ (water) = 35%. Thus, this finding confirms that there is no structure breaking effect of the DMSO structure by adding water. Below Φ (water) = 35%, i.e. below the lower percolation threshold the water molecules fit well into the DMSO-structure of the liquid. Due to the value of $g \approx 1$ the water molecules are either randomly distributed in the solvent mixture or in an antiparallel alignment with the dipole moment of DMSO.

Above the critical concentration of Φ (water) = 35% the g-values are increasing i.e. the dipole moments of water and DMSO assume more and more a parallel alignment. A parallel alignment of the dipole moments is being formed due to the increase in the hydrogen-bond formation. From the point of view of percolation theory Φ (water) = 35% corresponds with the lower percolation threshold

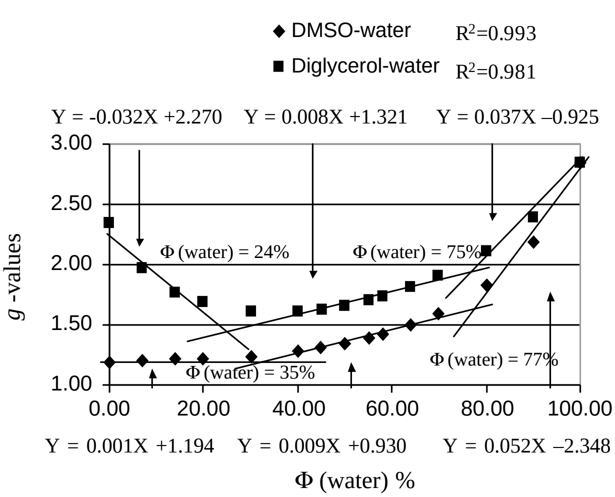

Fig. 10. The values of the correlation factor g of the Kirkwook-Fröhlich Eq. (Eq. (3)) as a function of the Φ (water) for the binary DMSO/water mixtures with intersections at ca. Φ (water) = 35% and Φ (water) = 77% at 298.2 K, and as a function of the Φ (water) for the binary α,α-diglycerol/water mixtures with intersections at ca. Φ (water) = 24% and Φ (water) = 75% at 298.2 K.

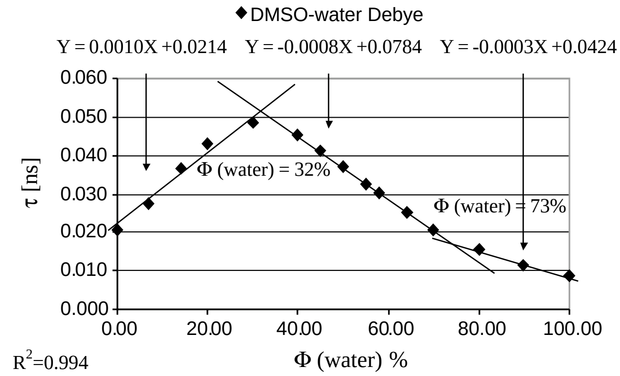

Fig. 11. Relaxation behavior of the dipole of DMSO in water mixtures as a function of the Φ (water) with intersections at ca. Φ (water) = 32% and Φ (water) = 73% at 298.2 K which can be described by the Debye equation.

(see section 4.2) where water starts to form infinite clusters, both water and the DMSO percolate the system up to ca. Φ (water) = 77% where the second percolation threshold is found. From that point DMSO starts to form isolated clusters and is no longer percolating the system.

4.4. Relaxation time according to the Debye equation for the complex dielectric permittivity ε*

The Debye equation is able to characterize the whole range of DMSO/water mixtures with $R^2 = 0.994$ showing with respect to the relaxation time (τ) a lower percolation threshold ca. Φ (water) = 32% and an upper percolation threshold ca. Φ (water) = 73% (Fig. 11). It is of interest to point out that as an example in the case of the methanol/water mixtures the behavior of the relaxation time can be only be described by a single Debye equation with a $R^2 \geq 0.997$ between Φ (water) = 58–100%. The fact that the Debye equation is able to describe the *whole* range of DMSO/water mixtures is another strong evidence that the lattice type seems to remain intact. It is worth to realize that the percolation thresholds remain more or less at the same positions (see Table 5) independent of the choice of the parameters for their detection. In addition to the example of methanol/water mixtures with two dipoles it is of interest to look at the behavior of 1,4dioxane/water mixtures as only the dipole of water is present. In case of the 1,4-dioxane/water mixture [20] the behavior of the relaxation time can only be described by a single Debye function with an adequate correlation coefficient R^2 between Φ (water) = 80–100%. Only the superposition of a Debye equation with the Cole-Davidson equation leads to a satisfactory R^2 values for the whole range.

4.5. Other physical properties explaining the phenomenon of percolation in binary DMSO/water mixtures.

It is evident that percolation thresholds can also be detected with other physical parameters. The corresponding

Table 5
Percolation thresholds found for E_i/E-parameter from the modified Clausius-Mossotti-Debye Eq., g-values obtained form the Kirkwood-Fröhlich Eq., relaxation time (τ), dielectric constant (ε), viscosity, density, refractive index, adiabatic compressibility and freezing point as a function of the % volume fraction of water in the investigated DMSO-water binary mixtures.

	Low percolation threshold (% (V_{wa}/V))	Upper percolation threshold (% (V_{wa}/V))
E_i/E-parameter	32	74
g-values	35	77
Relaxation time (τ)	32	73
Dielectric constant (ε)	32	64
Viscosity[a]	32	Not detectable
Density	34	Not detectable
Refractive index	28	Not detectable
Adiabatic compressibility[b]	37	Not detectable
Freezing point[c]	32	Not detectable

[a] Source: Marshall et al. [14].
[b] Source: Kaatze et al. [16].
[c] Source: Havemeyer [15]).

results are compiled in Table 5 (and ind Figs. 12–14) taking into account the literature data concerning the viscosity, adiabatic compressibility and freezing point of binary mixtures. With the relative permittivity we can detect not only the lower but also the upper percolation threshold. With refractive index and density it is only possible to detect the lower percolation threshold. Tommila and Pajunen [30] also measured the dielectric constant of several binary DMSO/water mixtures observing a maximum at X (water) = 72% (Φ (water) = 40%) but they did not give a clear interpretation. Cowie and Toporowski [31] also measured the viscosity, density and refractive index of several binary DMSO/water mixtures. They also observed a positive deviation from linearity in those properties but could not give a clear interpretation. They only suggested a greater degree of association in DMSO/water mixtures than in water alone i.e. they did not seem to realize the percolation phenomenon.

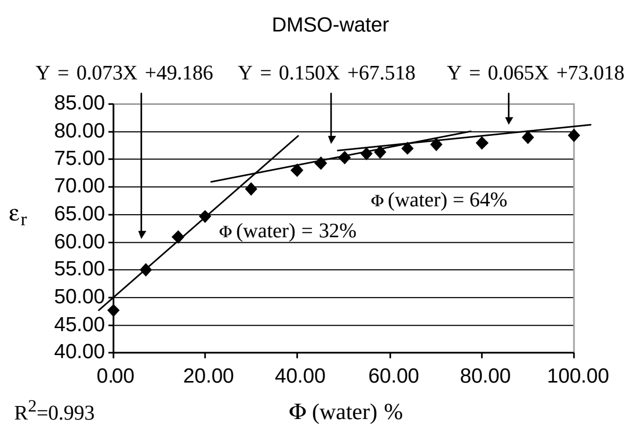

Fig. 12. Relative permittivity, ε_r, values as a function of the Φ (water) for the binary DMSO/water mixtures with intersections at ca. Φ (water) = 32% and Φ (water) = 64% at 298.2 K.

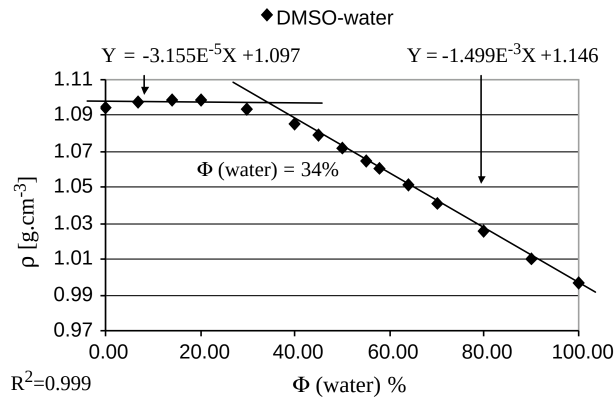

Fig. 13. Density values as a function of the Φ (water) for the binary DMSO/water mixtures with an intersection at ca. Φ (water) 34% at 298.2 K.

5. Conclusions

It is demonstrated the important role of the E_i/E parameter in the characterization of not only polar liquids able to form hydrogen bonds but also aprotic liquids being an easier measurable alternative parameter to describe the polarity of liquids.

The phenomenon of percolation could be well demonstrated in the case of DMSO/water liquid mixtures.

The value of E_i/E at room temperature in the binary mixtures can also be related to the viscosity changes, which was earlier shown by Peyrelasse et al. [13] to be a percolation phenomenon.

It was possible to clarify the maximum value of the viscosity detected at Φ (water) = 34% in the frame of percolation theory. This was possible by measuring the following parameters: E_i/E parameter obtained through the modified Clausius-Mossotti-Debye equation, g-values obtained from the Kirkwood-Fröhlich equation, relaxation time and dielectric constant data by using dielectric spectroscopy, and density and refractive index. The results are listed together with literature data concerning the viscosity, adiabatic compressibility, and freezing point of

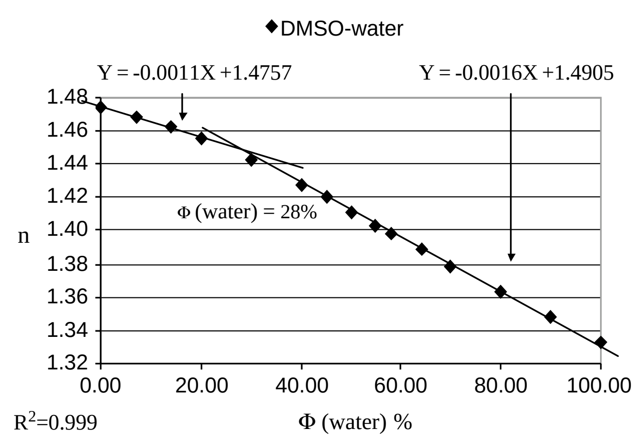

Fig. 14. Refractive index values as a function of the Φ (water) for the binary DMSO/water mixtures with an intersection at ca. Φ (water) 28% at 298.2 K.

binary solvent mixtures. The values of the lower and upper percolation thresholds are comparable and it is of interest, that as a function of the parameter studied, only one or two percolation thresholds can be detected.

In Hernandez-Perni et al. [20] it become evident that for binary 1,4-dioxane/water mixtures, the upper percolation threshold is not visible, which indicates that 1,4-dioxane fits well into the water. With binary DMSO/water mixtures both percolation thresholds can be detected. Nevertheless, it seems to be the case, that the tetrahedral coordination remains intact, which is supported by the specific location of the percolation thresholds and by the measurement of the g-values of (see below). For binary DMSO/water mixtures we also observe that the value of E_i/E decreases to a minimum at the upper percolation threshold indicating a higher local electric field E_i. This effect can be related to the high dipole moment of DMSO.

Unlike polar liquids capable of forming hydrogen bonds [21] such as α,α-diglycerol in a mixture with water, the aprotic DMSO behaves differently with respect to the g-values. Here we find a region nearly constant with g-values close to $g \approx 1$ till ca. Φ (water) = 35%. Thus, there seems to be no structure breaking effect of the DMSO structure by adding water. Below the lower percolation threshold the water molecules fit well into the DMSO/ structure of the liquid. Due to the value of $g \approx 1$ the water molecules are either randomly distributed in the solvent mixture or in an antiparallel alignment with the dipole moment of DMSO. It can be concluded that DMSO and water have as a liquid a similar lattice structure with a coordination number z between 4 and 6, which facilitates the complete miscibility and seem to be one of the reasons for the special physiological behavior of DMSO/water mixtures.

As a final conclusion it is demonstrated that the use of percolation theory revealing percolation thresholds give insight into the 'lattice structure' of DMSO/water mixtures and contribute to lift a bit the mystery of the behavior of DMSO/water mixtures.

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