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International Journal of Pharmaceutics 291 (2005) 197–209

international journal of pharmaceutics

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Detection of percolation phenomena in binary polar liquids by broadband dielectric spectroscopy

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Received 17 October 2003; received in revised form 28 May 2004; accepted 26 July 2004
Available online 4 January 2005

Abstract

In the previous papers [Stengele, A., Rey, St., Leuenberger, H., 2001. A novel approach to the characterization of polar liquids. Part 1: pure liquids. Int. J. Pharm. 225, 123–134; Stengele, A., Rey, St., Leuenberger, H., 2002. A novel approach to the characterization of polar liquids. Part 2: binary mixtures. Int. J. Pharm. 241, 231–240], it was shown that the Clausius–Mossotti–Debye equation for the quasi-static dielectric constant (ε) can be extended to liquids if the parameter E_i/E is introduced. E_i corresponds to the local mean field due to close molecule–molecule interactions after the application of an external electric field E. In the present paper it is demonstrated that the E_i/E parameter and the relaxation behavior of the dipole moment of the polar molecule in binary mixtures of water, respectively, methanol or benzylalcohol with 1,4-dioxane can be used for the detection of percolation phenomena. As 1,4-dioxane has no intrinsic dipole moment but can form hydrogen bonds and is completely miscible with water, respectively, methanol or benzylalcohol, percolation phenomena can be related to the relaxation behavior of the dipole moment of the polar co-solvent. The relaxation behavior of the binary mixtures can be modeled by applying the Debye equation, and the Cole–Davidson distribution function. Superpositions such as the Debye equation and the Cole–Davidson distribution function or a sum ($\sum_i$) of Debye equations are also considered.

Keywords: Broadband dielectric spectroscopy; Percolation phenomena; Modification of the Clausius–Mossotti–Debye equation; Binary polar solvent mixtures

1. Introduction

As it was shown in previous papers (Stengele et al., 2001, 2002), pure polar liquids can be characterized by the parameter E_i/E of the Clausius–Mossotti–Debye equation modified according to Leuenberger for the quasi-static dielectric constant (Stengele et al., 2001). In the present paper the emphasis was put on the analysis of binary mixtures of a polar liquid with 1,4-dioxane by applying broadband (0.2–20 GHz) dielectric spectroscopy (Kremer and Schönhals, 2003). 1,4-Dioxane was chosen as it has no dipole moment and is fully miscible with water, methanol and benzylalcohol due

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doi:10.1016/j.ijpharm.2004.07.057

to the formation of hydrogen bonds (The Merck Index, 1983). Interestingly, the relaxation behavior of the water dipole can be described in its state as a pure liquid with a single relaxation time τ, i.e. with the Debye equation for the complex permittivity (Smith et al., 1995). Thus, it is of interest to study first the relaxation behavior of the pure liquid and subsequently the change of its behavior as a result of the addition of 1,4-dioxane (V_{dx}/V). One can imagine that the volumetric addition of 1,4-dioxane to water may destroy totally or partially the water structure as a function of the volume percentage of 1,4-dioxane added. It can be speculated that the structure of water is fundamentally changed if 1,4-dioxane starts to percolate the water structure forming itself an infinite cluster. In case of water the question arises immediately whether a discrete number of additional relaxation times $\tau_1, \tau_2, \tau_3, \ldots$ show up after a partial destruction of the water structure or whether a continuity of relaxation times appear, which can only be described on the basis of a suitable distribution function such as the Cole–Davidson or the Havriliak–Negami equation (Kremer and Schönhals, 2003). In this paper superpositions such as the Debye and the Cole–Davidson distribution function or a sum ($\sum_i$) of Debye equations with different but discrete relaxation times τ_i were studied. The aim of this work is to detect percolation phenomena by analyzing the relaxation process and the E_{i}/E parameter for the binary mixtures of 1,4-dioxane with water, methanol and benzylalcohol.

1.1. *Broadband dielectric spectroscopy*

1.1.1. *General remarks*

The properties of polar solvents in the dipole relaxation region are usually described in terms of complex permittivity $\varepsilon^*(\omega)$:

$$\varepsilon^*(\omega) = \varepsilon'(\omega) - i\varepsilon''(\omega) \tag{1}$$

where $\varepsilon'(\omega)$ is the real part of the permittivity that is proportional to the energy stored reversibly in the system per period, and $\varepsilon''(\omega)$ is imaginary part that its proportional to the energy which is dissipated per period.

In a simplest case, when the polarization drop is characterized by only one relaxation time τ, the frequency dependence of the real $\varepsilon'(\omega)$ and imaginary $\varepsilon''(\omega)$ components of complex permittivity $\varepsilon^*(\omega)$ are expressed by the Debye equation (Eq. (4)) which is the most simplest equation but not all the systems show a Debye response. Usually the measured dielectric functions are much broader than predicted by the Debye function. It is, therefore, useful to consider the developments to the original Debye theory that have been proposed over subsequent years like the Cole–Davidson or the Havriliak–Negami relaxation behavior (Kremer and Schönhals, 2003). As already mentioned, we will also analyze the superposition of two Debye equations and the superposition of Debye equation with the Cole–Davidson distribution function. In this context it has to be kept in mind that the models may yield satisfying mean corrected coefficient R^2 which do not differ from each other very much. Thus, it becomes difficult to make a choice of the best model.

1.1.2. *The Clausius–Mossotti–Debye equation modified according to Leuenberger for the quasi-static dielectric constant (Stengele et al., 2001)*

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:

$$\frac{\varepsilon - 1}{\varepsilon + 2}\frac{M_{\mathrm{r}}}{\rho} = \frac{N_{\mathrm{A}}}{3\varepsilon_0}\left(\alpha + \frac{\mu_{\mathrm{g}}^2}{3kT}\right) \tag{2}$$

where ε is quasi-static relative dielectric constant; M_{r} is molecular weight; ρ is density; N_{A} is Avogadro number, 6.023×10^{23} (mol^{-1}); ε_0 is electric field constant in the vacuum, 8.854×10^{-12} ($\mathrm{C}^2\,\mathrm{J}^{-1}\,\mathrm{m}^{-1}$); α is polarizability of the molecule $\mathrm{C\,m^2\,V^{-1}}$; μ_{g} is dipole moment in the state of an ideal gas (C m); K is Boltzmann's constant, 1.38×10^{-23} ($\mathrm{J\,K^{-1}}$); T is 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} is internal electric field, caused by interactions with other induced neighboring dipoles; E is external electric field, produced by the applied voltage leads to the following modification:

$$\frac{\varepsilon - 1}{3(E_\mathrm{i}/E) + (\varepsilon + 2)} \frac{M_\mathrm{r}}{\rho} = \frac{N_\mathrm{A}}{3\varepsilon_0}\left(\alpha + \frac{\mu_\mathrm{g}^2}{3kT}\right) \tag{3}$$

The classical Clausius–Mossotti–Debye equation (Eq. (2)) is not valid for polar liquids but can be used to estimate quite accurately the dipole moment μ_g of water in a highly diluted solution of water in 1,4-dioxane simulating an ideal gas state condition (Hedestrand, 1929).

The Clausius–Mossotti–Debye equation modified according to Leuenberger for the quasi-static dielectric constant (Stengele et al., 2001) (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.

The aim of the present work is to detect percolation phenomena in liquid binary mixtures by analyzing the E_i/E parameter from the Clausius–Mossotti–Debye equation modified according to Leuenberger.

1.1.3. 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 $\varepsilon^* = \varepsilon', \varepsilon''$:

$$\varepsilon^*(\omega) = \varepsilon_\infty + \frac{\varepsilon - \varepsilon_\infty}{1 + i\omega\tau} \tag{4}$$

where ε^* is complex permittivity, ε is quasi-static dielectric permittivity (dielectric constant at ca. zero frequency) and ε_∞ is dielectric permittivity for induced polarization, measured at a frequency low enough that both atomic and electronic polarization are the same as in the static field and high enough so that the permanent dipoles can no longer follow the field ($\omega \to \infty$),τ is characteristic relaxation time (s^{-1}). ω is angular frequency (s^{-1}) and i is imaginary unit $= (-1)^{1/2}$.

Eq. (4) can be split for the real (ε') and imaginary part (ε'') of the complex permittivity:

$$\varepsilon'(\omega) = \varepsilon_\infty + (\varepsilon - \varepsilon_\infty)\frac{1}{1 + \omega^2\tau^2}, \tag{5}$$

and

$$\varepsilon''(\omega) = (\varepsilon - \varepsilon_\infty)\frac{\omega\tau}{1 + \omega^2\tau^2}. \tag{6}$$

Eqs. (5) and (6) can be interpreted as follows: If we consider the behavior of a sample containing mobile dipole which is 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 no ordering will be present. At low frequencies the dipole moment of the polar 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

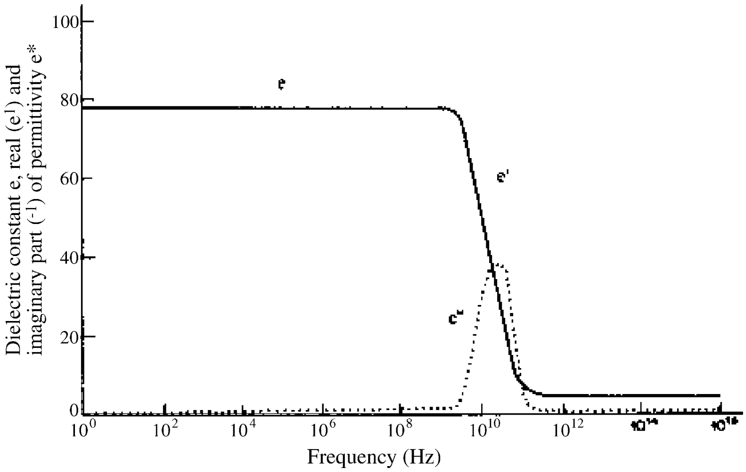

Fig. 1. Dielectric permittivity of a polar substance as a function of frequency (Decareau and Mudgett, 1985).

total polarization of the system falls. Thus, ε' and ε'' assume rather low values (see 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.

In practice, the Debye relaxation is seldom seen, as systems usually contain more than one relaxation time. In an organized system all dipoles relax "in phase", i.e. in a cooperative way, highly synchronized. Materials assumed to be composed of clusters would belong to that group of systems where a long-range force must exist to achieve a high order of its dynamical behavior. The relaxation bahavior of these clusters will affect the overall shape of the response, as well as the absolute values at any particular frequency. In a less organized system more than one relaxation time exists. The dipoles of water in its pure state can be described with a single relaxation time. Therefore, it may be assumed that the addition of a certain volume percentage of 1,4-dioxane to water may only slightly modify the water structure leading to more than one single relaxation time.

Thus, the case for two relaxation times τ_1, τ_2 the real and imaginary part of the Eq. (5), respectively, Eq. (6) can be modeled as follows:

The real part being

$$\varepsilon'(\omega) = \varepsilon_\infty + (\varepsilon - \varepsilon_\infty)\left\{\frac{l_1}{1+\omega^2\tau_1^2} + \frac{l_2}{1+\omega^2\tau_2^2}\right\} \tag{7}$$

and the imaginary part

$$\varepsilon''(\omega) = (\varepsilon - \varepsilon_\infty)\left\{\frac{l_1\omega\tau_1}{1+\omega^2\tau_1^2} + \frac{l_2\omega\tau_2}{1+\omega^2\tau_2^2}\right\} \tag{8}$$

where l_1 is weight factor of the relaxation time τ_1 and l_2 is weight factor of the relaxation time τ_2 being $l_1 + l_2 = 1$.

1.1.4. *The Cole–Davidson relaxation behavior and its superposition with the Debye equation*

$$\varepsilon^*(\omega) = \varepsilon_\infty + \frac{\varepsilon - \varepsilon_\infty}{(1+i\omega\tau_0)^\beta} \tag{9}$$

The Cole–Davidson relaxation behavior (Eq. (9)) can be described as follows, taking into account the real and imaginary part:

$$\varepsilon'(\omega) = \varepsilon_\infty + (\varepsilon - \varepsilon_\infty)(\cos\phi)^\beta \cos\beta\phi, \tag{10}$$

$$\varepsilon''(\omega) = (\varepsilon - \varepsilon_\infty)(\cos\phi)^\beta \sin\beta\phi, \tag{11}$$

$$\text{with}\ \ \phi = \arctan(\omega\tau_0). \tag{12}$$

where τ_0 is Cole–Davidson relaxation time (s^{-1}), β ($0 < \beta \le 1$) describes an asymmetric broadening of relaxation function. In case of $\beta = 1$ the Cole–Davidson equation is identical with the Debye equation (Eq. (4)).

It is evident to check first whether the application of the Debye equation may be sufficient in order to avoid a distribution with the additional parameter β. Thus, before using a more complex distribution, which is just "descriptive" we analyze first the relaxation behavior with the superposition of two Debye equations (Eqs. (7) and (8)) second the relaxation behavior with the Cole–Davidson distribution function and third whether a superposition of the Debye equation with the Cole–Davidson distribution function (Eqs. (13) and (14)) describes satisfactory the relaxation behavior of the binary mixtures:

$$\varepsilon'(\omega) = \varepsilon_\infty + (\varepsilon - \varepsilon_\infty) \times \left[l_1\left(\frac{1}{1+\omega^2\tau_1^2}\right) + l_2((\cos\phi)^\beta \cos\beta\phi)\right] \tag{13}$$

$$\varepsilon''(\omega) = (\varepsilon - \varepsilon_\infty)\left[l_1\left(\frac{\omega\tau_1}{1+\omega^2\tau_1^2}\right) + l_2((\cos\phi)^\beta \sin\beta\phi)\right] \tag{14}$$

with $\phi = \arctan(\omega\tau_0)$, and $l_1 + l_2 = 1$

1.2. *Application of percolation theory*

Percolation theory (Stauffer and Aharony, 1998) is a mathematical concept that can be applied in many different fields. The starting point is the definition of a *lattice* (see Fig. 2A). In the present case the lattice is formed by substance A (e.g. water, methanol or benzylalcohol). We will increase the amount of substance B (e.g. 1,4-dioxane) in the system formed by substance A and at the same time, different dielectric spectroscopy parameters for each concentration will be measured.

If we start adding substance B we pass from Fig. 2A to B. At that point clusters of substance B will appear. A *cluste*r is a group of occupied nearest neighbor lattice sites. In Fig. 2B we find two clusters formed by two B-molecules and a cluster of three B-molecules. Those clusters are inserted into the structure of substance A.

If we increase the B concentration it arrives a point represented by Fig. 2C where we observe the existence of a cluster that connects the top with the bottom, and the left with the right site of the lattice. In Fig. 2C it is possible to see the infinite cluster for B-molecules in dotted line and the infinite cluster for A-molecules in solid line. We passed from a disconnected state to a connected one. At that concentration we have a *percolation cluster*. B starts to dominate the system. That transition suggests an important transformation of the system and should be therefore detected when we measure different dielectric spectroscopy parameters. That critical concentration is called the *lower percolation threshold* (p_c). Finally and if we add volumetrically more and more B it arrives a critical concentration where the binary system is completely dominated by B and we find the *upper percolation threshold* (p_c) as the component A is no longer percolating and starts to form isolated clusters. That transition also suggests an important transformation of the system and should also be detected when we measure different dielectric spectroscopy parameters. According to the explanation above we have to bear in mind that in three dimensions the lower p_c should be detected in the range of 5–45% (V_{dx}/V) and the upper p_c at ca. 55–95% (V_{dx}/V) depending on the "microscopic" lattice structure. In Section 2 it will be explained how to detect the lower and upper percolation thresholds by subdivision of curves into segments by means of nonlinear regression analysis.

Table 1
Physical properties of the solvents studied at room temperature

	Dipole moment (D)	MW (g mol^{-1})
Methanol	1.70	32.04
Benzylalcohol	1.71	108.14
Water	1.85	18.02
1,4-Dioxane	0.00	88.11

Source: CRC Handbook of Chemistry and Physics (1997). The dipole moment is given in Debye units (D). The conversion factor to SI units is 1 D = 3.33564 × 10^{-30} C m.

2. Materials and methods

2.1. Solvents

The binary mixtures of water/1,4-dioxane, methanol/1,4-dioxane, and benzylalcohol/1,4-dioxane were examined at 298.2 K. Bidistilled water was freshly prepared by means of a Fontavapor 285 (Büchi AG CH-Flawil). The organic solvents of high purity were acquired commercially from Fluka Chemie GmbH CH-Buchs [benzylalcohol (art. no. 13160), 1,4-dioxane (art. no. 42512) and methanol (art. no. 65550)] (see Table 1).

The samples were prepared by weighing the necessary amounts of solvents/solutes into glass flasks. The samples were then shaken vigorously for 15 s and then stirred for 1 min using a Vortex mixer.

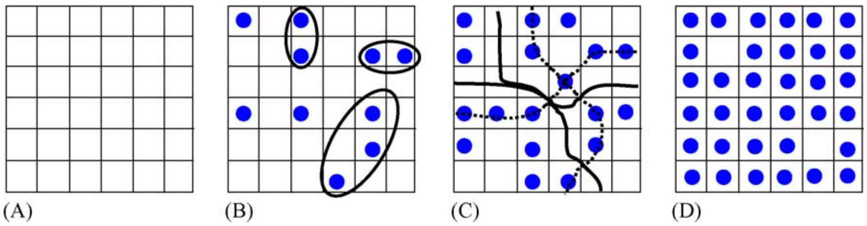

Fig. 2. (A–D) Percolation on a square lattice.

2.2. Experimental setup and data analysis

2.2.1. Measurement of the static permittivity and conductivity

The static permittivity and conductivity in this work were measured via the impedance and conductance, respectively, by means of a LCR (inductance L, capacitance C, and resistance R) Meter at a low ac frequency, so the measured permittivity corresponds to the dielectric constant measured in direct current (dc).

For the measurement of the static permittivity and conductivity the following apparatus were used: *Precision LCR Meter* (Agilent Technologies Inc. HP 4284A; 2940J01533), and *Test Fixture* (Agilent Technologies Inc. USA-Palo Alto CA 94304-1185 HP 16047C).

To the test fixture it was connected a *Cylinder Condensator* (by courtesy of Ramsden and the Mechanische Werkstatt Biozentrum, Universität Basel). The inner electrode has a diameter 12.92 mm, and height 9.85 mm, and the outer electrode has a diameter 18.74 mm.

To the cylinder condensator it was connected a *Thermostat* (B. Braun Biotech International GmbH D-34209 Melsungen: Thermomix UB; 852042/9; 9012498/Frigomix U-1; 852042/0; 8836 004), allowing temperature control of ±0.1 K. The temperature was checked by means of a *Digital Thermometer* (Haake GmbH D-76227 Karlsruhe DT 10, Pt. 100 platinum resistance thermometer (±0.1 K)).

For the measurement setup used in this work the capacitance C and the conductance G were measured in a parallel circuit mode (Lehnert, 1992). As test frequency 100 kHz was chosen, giving stable results and being 10^3–10^5 lower than the relaxation frequencies of the dipoles of the liquids measured in this work.

The measurements were made by means of a personal computer connected to the LCR Meter, using the software HP VEE 5.01 (Agilent Technologies Inc. USA-Palo Alto CA 94304-1185).

The cylinder condensator was brought to the measuring temperature (298.2 K) and filled with the sample. 5 min after the required temperature was reached, the sample was measured 5 times, waiting for 1 min after each measurement.

2.2.1.1. Data analysis: calculation of the E_i/E parameter for binary polar liquid mixtures.

For a Capacitor C_{MUT} filled with the material under test (MUT) The static permittivity ε – for $\omega \ll \omega_{\mathrm{res}}$ – equals the real part of the permittivity.

$$\varepsilon' = \frac{C_{\mathrm{MUT}}}{C_{\mathrm{vacuum}}}. \tag{15}$$

where ε' is real part of permittivity ε^*; C_{MUT} is capacitance of material under test (F); C_{vacuum} is capacitance of vacuum (F).

In the present work, the measured C_{air} is substituted for C_{vacuum}, the calculated values for ε are corrected via a calibration curve (Eq. (16)).

$$\varepsilon_{\mathrm{lit}} = 2.7394\varepsilon_{\mathrm{exp}} - 1.8031 \quad r^2 = 1.000. \tag{16}$$

E_i/E for binary mixtures was calculated according to the following equation (Stengele et al., 2002):

$$\frac{E_{\mathrm{i}}}{E} = \frac{M_{\mathrm{r,m}}}{3\rho_{\mathrm{m}}} \frac{\varepsilon_{\mathrm{m}} - 1}{(N_{\mathrm{A}}/3\varepsilon_0)\{V_1[\alpha_1 + (\mu_{\mathrm{g},1}^2/3kT)] + V_2[\alpha_2 + (\mu_{\mathrm{g},2}^2/3kT)]\}} - \frac{\varepsilon_{\mathrm{m}} + 2}{3} \tag{17}$$

where ρ_{m} is density of mixture; $M_{\mathrm{r,m}}$ is molecular weight of the mixture; ε_{m} is quasi-static relative dielectric constant for the mixture; V_1 is volume fraction of liquid 1; V_2 is volume fraction of liquid 2.

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 three-dimensional networks than molar fractions (Stengele et al., 2002).

2.2.2. Measurement of the complex permittivity

The measuring system consists of a dielectric probe connected to a network analyzer by means of a semi-rigid coaxial cable. An electromagnetic signal is generated by the network analyzer and transmitted into the material under test (MUT) via cable and probe. The signal is reflected by the MUT its phase and amplitude are compared by the network analyzer to those of the incident electromagnetic wave.

For the measurement of the complex permittivity the following apparatus was used: *Network Analyzer* Agilent Technologies Inc. USA-Palo Alto CA 94304-1185 HP 8720D; US38111202.

To the Network Analyzer it was connected a *High-Temperature Dielectric Probe Kit* Agilent Technologies Inc. USA-Palo Alto CA 94304-1185 HP 85070B OPT 002.

The sample was kept at the required temperature through immersion in a *Thermostat* (B. Braun Biotech International GmbH D-34209 Melsungen: Thermomix UB; 852 042/9; 9012 498/Frigomix U-1; 852 042/0; 8836 004), allowing temperature control of ±0.1 K.

The temperature was checked by means of a *Digital Thermometer* (Haake GmbH D-76227 Karlsruhe DT 10; Pt. 100 platinum resistance thermometer (±0.1 K).

The measurements were made by means of a personal computer connected to the Network Analyzer, using *software HP 85070B Probe Software Program* (Agilent Technologies Inc. USA-Palo Alto CA 94304-1185).

The 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 dielectric probe was calibrated at the measurement temperature ($T_{\mathrm{meas}} = 298.2\,\mathrm{K}$) by air, a metal block, and bidistilled water. The computer software requires a fast performance of these calibration steps, which does not allow for an exact temperature adjustment. Therefore, this operation was followed by a calibration refresh procedure, using bidistilled water at $T_{\mathrm{meas}} \pm 0.1\,\mathrm{K}$. Calibration and refresh calibration were made before starting measurements at T_{meas} and after every fifth sample.

For measurement, the probe was immersed in the sample, which was brought to T_{meas} by means of a water bath/refrigerator. Special attention has to be paid to avoid air bubbles in the probe and the stability of the coaxial cable. Using the thermostat as a water bath, the sample was stabilized at $T_{\mathrm{meas}} \pm 0.1\,\mathrm{K}$ before starting the measurement.

2.2.2.1. Data analysis: calculation of the relaxation time τ. 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.

In order to find the values for the dielectric spectroscopy parameters such as the relaxation time τ or distribution parameter β, the raw data $\varepsilon'(\omega)$, $\varepsilon''(\omega)$ obtained directly from the dielectric relaxation measurements must be fitted to an equation describing the process.

Close attention must be paid to choose an adequate equation and fitting procedure, and the number of fitting parameters. Usually a compromise has to be found between a large number of free parameters, offering a most adequate fit of the data, and a small number, providing robust and meaningful results, especially when data of, e.g. various water concentrations are to be compared.

It has to be kept in mind that the resulting relaxation time τ depends on the mathematical model applied. The choice of best equation describing the process was based on literature and on the comparison of the mean corrected coefficient R^2 obtained after fitting the raw data $\varepsilon'(\omega)$, $\varepsilon''(\omega)$ for every concentration into different equations. If the mean corrected coefficient R^2 coefficient does not differ significantly between the different mathematical models, it is not possible to make an unambiguous choice of a model. The choice of the best equation describing the process was also based on the overall look of the obtained curves.

As the Havriliak–Negami equation did not lead to a significantly better mean corrected coefficient R^2 values but includes an additional free parameter α (symmetric distribution parameter) and in order facilitate the understanding these results are not included in this paper.

The fitting software used for evaluation was *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 $(\varepsilon - \varepsilon_\infty)$ occurs in both parts. This allows reformulation of equations as following: Considering the real and imaginary part of the Debye equation (Eqs. (5) and (6)):

$$\varepsilon'(\omega) = \varepsilon_\infty + (\varepsilon - \varepsilon_\infty)\frac{1}{1+\omega^2\tau^2} = \varepsilon_\infty + (\varepsilon - \varepsilon_\infty)A \tag{18}$$

$$\varepsilon''(\omega) = (\varepsilon - \varepsilon_\infty)\frac{\omega\tau}{1+\omega^2\tau^2} = (\varepsilon - \varepsilon_\infty)B \tag{19}$$

$$(\varepsilon - \varepsilon_\infty) = \frac{\varepsilon'(\omega) - \varepsilon_\infty}{A} = \frac{\varepsilon''(\omega)}{B} \tag{20}$$

Therefore,

$$\varepsilon''(\omega) = (\varepsilon - \varepsilon_\infty)\frac{\omega\tau}{1+\omega^2\tau^2} = (\varepsilon'(\omega) - \varepsilon_\infty)\frac{B}{A} \qquad (21)$$

$$\begin{aligned}\varepsilon'(\omega) &= \varepsilon_\infty + (\varepsilon - \varepsilon_\infty)\frac{1}{1+\omega^2\tau^2} \\ &= \varepsilon_\infty + (\varepsilon - \varepsilon_\infty)A = \varepsilon_\infty + \varepsilon''(\omega)\frac{A}{B} \qquad (22)\end{aligned}$$

The data, i.e. the mean based on three separate measurements, are fitted to the chosen equation (e.g. Eq. (21) or (22)) by using nonlinear regression (Gauss–Newton with Least Squares estimation).

2.2.2.2. Subdivision of curves into segments by means of nonlinear regression: detection of percolation thresholds. 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 onto 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 (Bellmann and Roth, 1969; Seber and Wild, 1989).

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

The data were inspected in order to decide about a suitable number of sub-segments and potential critical concentrations. For the following example (see Table 2), three sub-segments seem appropriate with critical values for volume fraction $(V_x/V)_{\text{crit}} \approx 4$–6 and 8–10.

The data were arbitrary split into three straight sub-segments around these possible $(V_x/V)_{\text{crit}}$, 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:

$$y = A(m_1x + b_1) + B(m_2x + b_2) + C(m_3x + b_3) \qquad (23)$$

Table 2
Subdivision of curves into segments: example

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

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 volume fractions: $(V_x/V)_{\text{crit1}} = 3.85$ and $(V_x/V)_{\text{crit2}} = 9.24$. Those intersections points correspond to the lower and upper percolation thresholds.

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 three-dimensional networks than molar fractions.

2.2.3. Other measurements

The measurements of the density ρ were made using a *vibrating-tube densimeter*, refractive indices n_D were measured by means of an *Abbé refractometer*.

Physical properties which were necessary for calculations, such as the dipole moment in the gas phase μ_g (CRC Handbook of Chemistry and Physics, 1997) and the polarizability α of the investigated compounds were obtained as follows: The values of the dipole moment in the gas phase μ_g were taken from the literature. The polarizability was determined via the Lorentz–Lorenz equation, which gave excellent results compared with literature data (Riddick and Bunger, 1970) both for po-

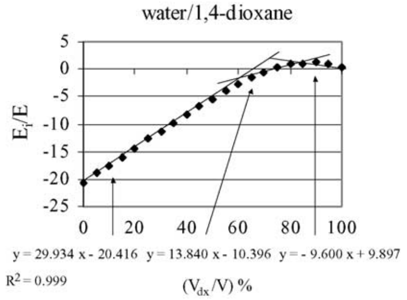

Fig. 3. E_i/E values as a function of the percent volume fraction of 1,4-dioxane (V_{dx}/V) for water/1,4-dioxane binary mixtures at 298.2 K. The critical points are located at ca. 62 and 86% (V_{dx}/V).

lar and nonpolar compounds (see Eq. (24)).

$$\frac{n^2-1}{n^2+2}\frac{M_r}{\rho}=\frac{N_A}{3\varepsilon_0}\alpha \tag{24}$$

3. Results and discussion

3.1. Percolation phenomena observed in binary mixtures based in the results of the modified Clausius–Mossotti–Debye equation (Eq. (17))

The E_i/E values for the investigated binary mixtures at 298.2 K are represented in Figs. 3–5. For the water/1,4-dioxane and methanol/1,4-dioxane binary mixtures data can be clearly divided in two segments (Figs. 3 and 4): a convex curve of slightly positive values, and a linear relationship between E_i/E and the percent of the volume fraction of 1,4-dioxane (V_{dx}/V). The E_i/E values of water/1,4-dioxane, methanol/1,4-dioxane and benzylalcohol/1,4-dioxane can be subdivided in three linear segments that will be explained according to percolation theory.

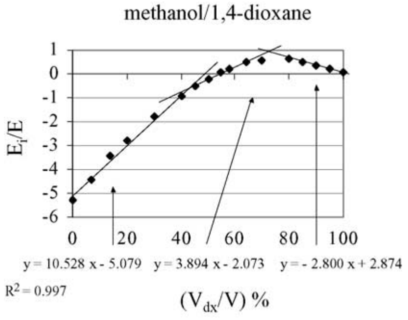

Fig. 4. E_i/E values as a function of the percent volume fraction of 1,4-dioxane (V_{dx}/V) for methanol/1,4-dioxane binary mixtures at 298.2 K. The critical points are located at ca. 45 and 74% (V_{dx}/V).

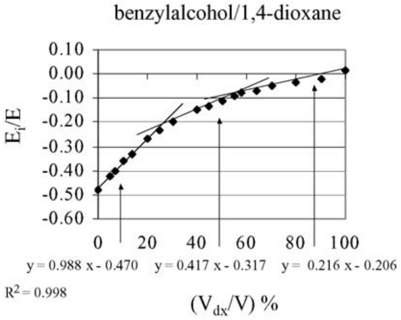

Fig. 5. E_i/E values as a function of the percent volume fraction of 1,4-dioxane (V_{dx}/V) for benzylalcohol/1,4-dioxane binary mixtures at 298.2 K. The critical points are located at ca. 27 and 55% (V_{dx}/V).

3.1.1. Water/1,4-dioxane binary mixtures

The data for the E_i/E values of the water/1,4-dioxane binary mixtures as a function of the percent of the volume fraction of 1,4-dioxane (V_{dx}/V) were inspected in order to decide about a suitable number of subsegments and potential critical concentrations which could correspond with the lower and upper percolation thresholds (see Fig. 3). By means of nonlinear regression the curve for water/1,4-dioxane mixtures could be split into three sections whose intersections are located at 62% (V_{dx}/V) and 86% (V_{dx}/V) (see Fig. 3).

It can be assumed that water forms isolated clusters and is definitely no longer percolating the system for (V_{dx}/V) percentages above 86%. That intersection point corresponds with the upper p_c. Thus, water may start to percolate at a volume fraction of $100-86\% = 14\%$ (V_{wa}/V). However, the detailed analysis indicates that only above 38% (V_{wa}/V), i.e. below 62% (V_{dx}/V), water may assume its normal structure leading to the value of $E_i/E = -20.4$ for the pure liquid (see linear part of the curve). It is evident that 38% (V_{wa}/V) represents a critical concentration corresponding to a structural change with a lower coordination number but it cannot be excluded that it could also be a percolation threshold.

It is important to realize that between 0% (V_{dx}/V) and 62% (V_{dx}/V) (linear part of the curve), the lower p_c could not be detected by analyzing the E_i/E parameter. One has to assume that 1,4-dioxane fits well into the water structure and the lower p_c of 1,4-dioxane cannot be detected for this reason.

3.1.2. Methanol/1,4-dioxane binary mixtures

For 1,4-dioxane/methanol mixtures, the dependence of the E_i/E values as a function of percent of the volume fraction of 1,4-dioxane (V_{dx}/V) can be divided into three segments whose intersections are located at 45% (V_{dx}/V) and 74% (V_{dx}/V) (see Fig. 4). It can be assumed that methanol forms isolated clusters above 74% (V_{dx}/V), i.e. that methanol percolates the system, above 26% (V_{metOH}/V). The final structure of methanol seems to be achieved at a higher concentration of methanol, i.e. above 55% (V_{metOH}/V), i.e. below 45% (V_{dx}/V). It seems that 1,4-dioxane starts to percolate the system above 45% (V_{dx}/V). Thus, above 45% (V_{dx}/V) and below 74% (V_{dx}/V) both 1,4-dioxane and methanol percolate the system. The critical concentration at ca. 45% (V_{dx}/V) could correspond with a structural change in the lattice. It is a rather high value for a lower p_c. Nevertheless, we cannot exclude that possibility. It is convenient to see Section 3.2.2 in order to compare the critical concentrations obtained with the E_i/E values with those obtained after analyzing the relaxation time.

3.1.3. Benzylalcohol/1,4-dioxane binary mixtures

In Fig. 5 the dependence of E_i/E as a function of percent of the volume fraction of 1,4-dioxane (V_{dx}/V) added to benzylalcohol can be subdivided into three segments with the intersections located at 27% (V_{dx}/V) and 55% (V_{dx}/V). The first intersection at ca. 27% (V_{dx}/V) can be interpreted as the lower p_c of 1,4-dioxane. The second one at 55% (V_{dx}/V) can be assumed as the upper p_c, where benzylalcohol starts to form isolated clusters. One has to keep in mind, that the determination of the upper p_c is not very precise as the slopes of the line of the middle and upper segments are not very different.

3.2. Percolation phenomena observed in binary mixtures based in the results of broadband dielectric spectroscopy of binary mixtures at 298.2 K

3.2.1. Water/1,4-dioxane binary mixtures

The binary system water 1,4-dioxane was analyzed as follows: first with the approximation of the relaxation behavior with a single Debye function and second with the superposition of a Debye function and Cole–Davidson distribution function, as a function of the percent of the volume fraction of 1,4-dioxane (V_{dx}/V) added.

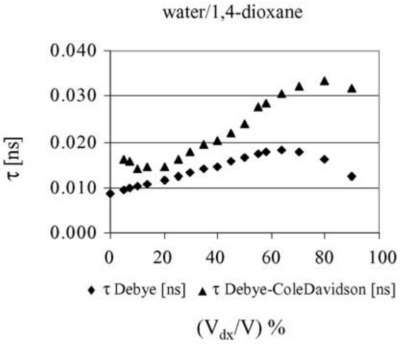

Fig. 6. Two different models for the description of the relaxation behavior of the water dipole in water/1,4-dioxane mixtures at 298.2 K as a function of the percent volume fraction of dioxane (V_{dx}/V).

In Fig. 6 the relaxation behavior of the dipole moment of water at 298.2 K in 1,4-dioxane and water mixtures is modeled by one Debye function (see Section 2.2.2.1) and with the superposition of one Debye function with the Cole–Davidson distribution. With one Debye equation we only obtain a mean correlated coefficient R^2 between 0.99 and 0.98 for the range of 0–25% (V_{dx}/V). In the range above 25% (V_{dx}/V) R^2 starts decreasing adopting a minimum of $R^2 = 0.66$ for 90% (V_{dx}/V).

According to Fig. 6 the superposition of the Debye and Cole–Davidson equations yields a good fit with $R^2 = 0.99$–0.98 for the whole range. In the latter case (see Fig. 7) l_1 belonging to the Debye part of the superposition becomes zero at the presumed lower p_c of ca. 20% (V_{dx}/V). Thus, below the lower p_c, it is possible to describe the relaxation behavior just with one Debye function based on the excellent fitting of the data with R^2 values >0.99. Above the lower p_c the relaxation behavior is well described by the Cole–Davidson distribution function only ($l_2 = 1$, $l_1 = 0$, see Fig. 7). Compared to the dependence of E_i/E parameter (see Fig. 3) the lower p_c is clearly visible.

In Fig. 8 the β parameter (skewness) of the Cole–Davidson equation is plotted as a function of the percent of the volume fraction of 1,4-dioxane (V_{dx}/V) added. In this plot the lower p_c at ca. 24% (V_{dx}/V) and the upper one at ca. 62% (V_{dx}/V) are visible. These

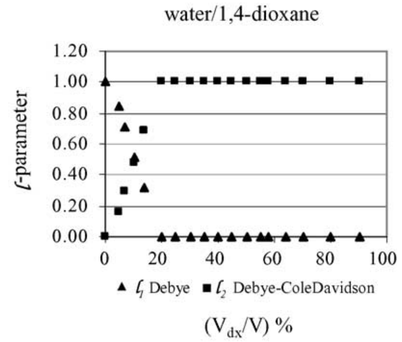

Fig. 7. Weight factor of relaxation time (l parameter: l_1, l_2) for water/1,4-dioxane binary mixtures at 298.2 K as a function of the percent volume fraction of dioxane (V_{dx}/V) calculated with the superposition of one Debye equation (l_1) with the Cole–Davidson distribution function (l_2).

findings are compatible with the findings of Fig. 6 (τ values) for the lower p_{c} but not with Fig. 3 (E_{i}/E values) for the upper p_{c}.

Summarizing, the lower p_{c} would be located at ca. 20% (V_{dx}/V) and the upper p_{c} at ca. 86% (V_{dx}/V). The critical point obtained at ca. 62% (V_{dx}/V) would be interpreted as a structural change in the lattice. Nevertheless, it cannot be excluded that the critical point obtained at ca. 62% (V_{dx}/V) could also be a p_{c}.

3.2.2. Methanol/1,4-dioxane binary mixtures

In case of the binary mixtures methanol/1,4-dioxane the best fits were obtained with the Debye and Cole–Davidson distribution function (Fig. 9). The values can be subdivided into three segments with the intersections located at 20% (V_{dx}/V) and 48% (V_{dx}/V). Below 20% (V_{dx}/V) it is possible to describe the relaxation behavior of methanol with one Debye function. However, the R^2 values being in the range of 0.96–0.99 are not as high as in the case of water with R^2 values >0.99

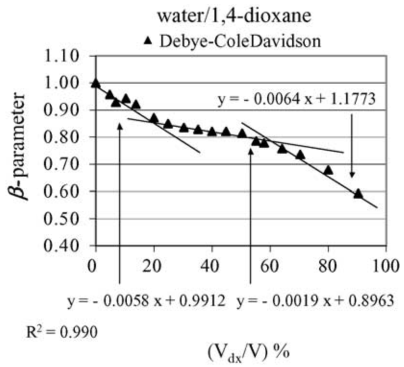

Fig. 8. Skewness of the distribution of relaxation times (β parameter) for water/1,4-dioxane binary mixtures at 298.2 K as a function of the percent volume fraction of dioxane (V_{dx}/V) calculated with the superposition of Debye and Cole–Davidson equations. The critical points are located at ca. 24 and 62% (V_{dx}/V).

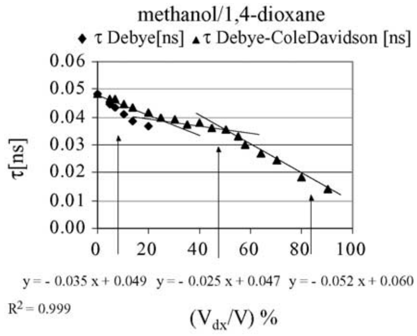

Fig. 9. Relaxation behavior of the dipole of methanol in 1,4-dioxane mixtures calculated on the basis of one Debye function (range 0–20% (V_{dx}/V)) and on the basis of the superposition of one Debye equation with the Cole–Davidson distribution function at 298.2 K as a function of the percent volume fraction of dioxane (V_{dx}/V). The critical points are located at ca. 20 and 48% (V_{dx}/V).

The data of Fig. 9 allow only a rough estimate of the two percolation thresholds and the three ranges: range I (0–20% (V_{dx}/V)) with a decrease of the main relaxation time τ, range II (20–48% (V_{dx}/V)), i.e. where both components percolate and range III (48–1% (V_{dx}/V) 1,4-dioxane) with a significant decrease of the main relaxation time.

The relaxation behavior of the dipole of methanol can be best described by one Debye function in the range of 0% (V_{dx}/V) to ca. 20% (V_{dx}/V). For higher percentages of 1,4-dioxane the behavior can be best approximated by a superposition of one Debye with a Cole–Davidson distribution function (see Fig. 9). However the plot of the β parameter does not reveal clearly percolation thresholds.

The comparison of these results with the findings of the critical concentrations of the E_{i}/E values indicates that it is difficult to decide whether the critical concentration describes a percolation threshold or a structural change of the lattice.

The critical concentrations obtained with the E_{i}/E values are located at ca. 45% (V_{dx}/V) and 74%(V_{dx}/V).

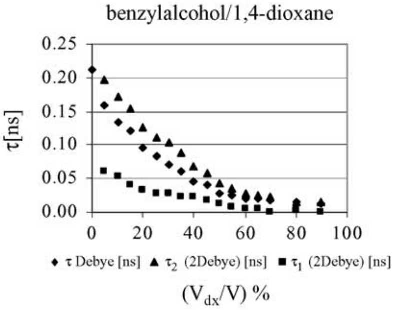

Fig. 10. Two different models to fit the relaxation time behavior for benzylalcohol/1,4-dioxane binary mixtures at 298.2 K as a function of the percent volume fraction of 1,4-dioxane (V_{dx}/V).

With the relaxation time we find the critical concentrations at ca. 20% (V_{dx}/V) and 48% (V_{dx}/V). We can conclude with a high probability that the lower p_c would be located at 20% (V_{dx}/V), the upper p_c at ca. 74% (V_{dx}/V) and the critical concentration founded with E_i/E and τ at ca. 45% (V_{dx}/V), respectively, 48% (V_{dx}/V) could be interpreted as a structural change without changing the subsequent upper p_c. However it cannot be excluded that this point could also reflect a p_c.

3.2.3. Benzylalcohol/1,4-dioxane binary mixtures

With benzylalcohol/1,4-dioxane binary mixtures the situation is as follows.

Fig. 10 shows two different models to fit the relaxation time behavior for benzylalcohol/1,4-dioxane binary mixtures at 298.2 K as a function of the percent volume fraction of 1,4-dioxane (V_{dx}/V). With one Debye equation we only obtain a mean corrected coefficient R^2 between 0.99 and 0.97 for the range of 0% to ca. 20% (V_{dx}/V). Thus, in the 1,4-dioxane poor region, i.e. till 1,4-dioxane starts to percolate the system (as ca. 20% (V_{dx}/V)), the behavior of the relaxation of the benzylalcohol dipole can be described by the simple Debye equation.

Interestingly the superposition of two Debye equations is able to characterize nearly the whole range of benzylalcohol/1,4-dioxane mixtures with $R^2 > 0.97$ for less than 70% (V_{dx}/V), i.e. below the upper p_c of ca. 58–63% (V_{dx}/V) (see Fig. 10). In fact it is possible to conclude that the addition of 1,4-dioxane leads to two distinct modes of relaxation, which can be described by two relaxation times τ_1, τ_2. The values of the relaxation times depend on the mixture ratio. A closer inspection of both relaxation times τ_1, τ_2 as a function of the amount of 1,4-dioxane added reveal percolation phenomena, as shown in Fig. 11A and B, showing a lower p_c at ca. 19–22% (V_{dx}/V) and an upper p_c at ca. 58–63% (V_{dx}/V).

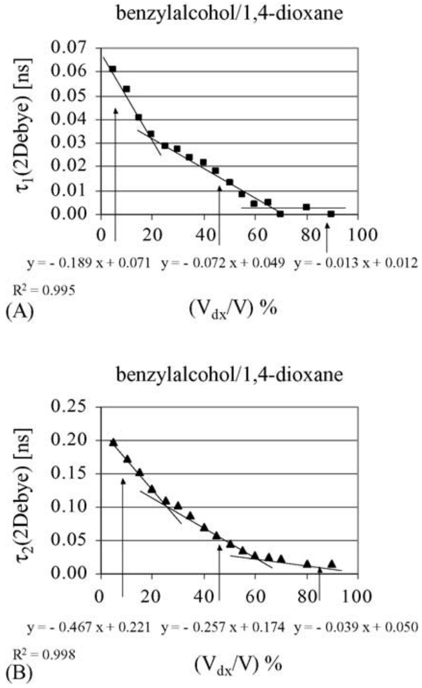

Fig. 11. Relaxation times obtained from the superposition of two Debye equations for benzylalcohol at 298.2 K as a function of the percent volume fraction of 1,4-dioxane (V_{dx}/V). (A) Relaxation time τ_1 with critical points located at ca. 19 and 63% (V_{dx}/V). (B) Relaxation time τ_2 with critical points located at ca. 22 and 58% (V_{dx}/V).

A closer inspection of the weights l_1 and l_2 of the superposition of the two Debye equations leads to a symmetric behavior of the relaxation times τ_1, τ_2 (see Fig. 12).

These findings are also compatible with the findings of Fig. 5 (E_i/E values) for the lower and upper p_c.

If we compare with water/1,4-dioxane and methanol/1,4-dioxane we observe that for benzylalcohol/1,4-dioxane mixtures the upper p_c is detected at lower concentration and no critical concentration are related to a structural change. We can conclude that the behavior between water/1,4-dioxane and methanol/1,4-dioxane is similar due to more similarities in the lattice structure.

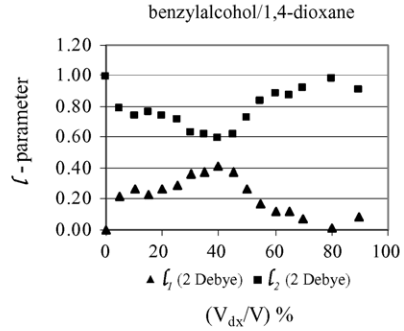

Fig. 12. Weight factor of relaxation time (l parameter: l_1, l_2) for benzylalcohol/1,4-dioxane binary mixtures at 298.2 K as a function of the percent volume fraction of 1,4-dioxane (V_{dx}/V) calculated with the superposition of two Debye equations.

4. Conclusions

It could be shown that the application of the broad-range dielectric spectroscopy together with the analysis of the quasi-static permittivity using the modified Clausius–Mossotti–Debye equation can be used to detect percolation phenomena in binary polar liquid mixtures. It leads to a valuable insight into the structure of polar liquids and to a better understanding of binary systems. However, it has to be kept in mind, that besides of percolation thresholds as critical concentrations it is also possible to detect a change of the coordination number as a function of the volume ratio of the components, which involves a change of the lattice type. It is sometimes difficult to discriminate between p_c or lattice change and more studies are needed in order to distinguish those processes.

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