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A novel approach to the characterization of polar liquids. Part 2: binary mixtures

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Abstract

Theoretical descriptions of solvent and solubility properties, important for a rational development of liquid dosage forms, have so far not proved completely satisfying. In this work, the modified Debye equation according to Leuenberger, which was introduced earlier for the description of polar and nonpolar pure liquids, is extended to liquid binary mixtures. Between 290.7 and 343.2 K, several binary aqueous systems were investigated. The values of (E_i/E) (E_i = internal electric field, E = external electric field), calculated by means of the modified Debye equation, were compared to the correlation factor g of the Kirkwood-Fröhlich equation, which describes the molecules' preference for either parallel or nonparallel alignment. The previously found correlation between $|m|$ of $(E_i/E) = m(1/T) + b$ (T = temperature) and the Hildebrand solubility parameter δ for pure liquids was investigated for binary mixtures. Furthermore, the applicability of percolation theory to the description of binary liquid mixtures was examined. This new approach allows the description of irregular solutions and provides a useful tool for a more rational design of liquid dosage forms.

Keywords: Dielectric permittivity; Modification of Clausius-Mossotti/Debye equation; Percolation theory; Regular solutions; Solubility parameter

1. Introduction

The description of the properties of solvents and solvent mixtures are a fundamental basis for the rational development of robust liquid drug formulations. Most solvent theories so far are based on the description of cohesive and adhesive forces between molecules: the Hildebrand parameter δ, the Hildebrand-Scatchard equation (Hildebrand and Scott, 1950) and the Hansen parameters (Hansen, 1967).

These approaches did not prove satisfactory, especially for systems containing water with its high dielectric constant ($\varepsilon = 78.4$ at 298.2 K (Riddick and Bunger, 1970)). In addition, it has to be kept in mind that the solubility parameter δ is temperature dependent, not easily accessible through experiment for nonvolatile compounds, and that the partial solubility parameters were determined empirically (Hansen and Beerbower, 1971).

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The extension of the Debye equation according to Leuenberger, which was introduced earlier for pure liquids (Stengele et al., 2001), is based on a different approach. It describes both polar and nonpolar molecules in the gaseous and liquid state.

The aim of this work is the application of the extended Debye equation to binary mixtures. The results are compared to the corresponding values of the Kirkwood-Fröhlich factor g, a measure for molecular pair correlations in polar liquids. Values for the Hildebrand parameter δ determined via the extended Debye equation are compared to those calculated according to the assumption of volume-wise contribution of the pure liquids (Barton, 1991).

Furthermore, the applicability of the percolation theory for the description of liquid binary mixtures is examined.

1.1. Theoretical background

An excellent survey of the theoretical background was given by Böttcher (1973) a detailed description of the different models, especially of the newly introduced extension of the Debye equation, can be found in the preceding publication (Stengele et al., 2001).

Pure pharmaceutical solvents, for example water and ethanol, are dielectrics, i.e. insulating materials. According to X-ray and neutron scattering experiments (Tabor, 1991) liquids can be considered as 'ordered systems' (Göpel and Wiemhöfer, 2000). A perfectly ordered system is represented by an ideal crystal with its defined lattice structure. The other extreme is an ideal gas with the complete absence of molecular interactions. In a real gas and definitely in a liquid, glass, and amorphous solid there are interactions in between the molecules, which can promote a 'local order'.

When brought into an external electric field E, permanent dipoles are orientated and a small displacement of the electrons relative to the nuclei occurs; the electric field E polarizes the dielectric and is thus weakened; a similar phenomenon occurs when a crystal is exposed to an electric field.

1.2. The modified Debye equation according to Leuenberger

The derivation of the modified Debye equation according to Leuenberger (Eq. (1)) is described in detail elsewhere (Stengele et al., 2001).

The Debye equation, which describes well polar molecules in the gas phase or diluted in a nonpolar liquid, is extended to the description of polar molecules in the liquid state. For this purpose, the internal electric field E_i, which was assumed to be zero by Debye, is reintroduced, leading to the following equation:

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

ε, relative permittivity, dielectric constant; E_i, internal electric field, caused by interactions with other induced neighbouring dipoles; E, external electric field, produced by the applied voltage; M_r, molecular weight; ρ, density; N_A, Avogadro's number, 6.023×10^{23} (mol^{-1}); ε_0, electric field constant in vacuum, 8.854×10^{-12} ($C^2\,J^{-1}\,m^{-1}$); α, polarizability $cm^2\,V^{-1}$; μ_g, dipole moment in the gas phase cm; k, Boltzmann's constant, 1.38×10^{-23} ($J\,K^{-1}$); T, temperature (K).

The term (E_i/E) was successfully used for the description of molecular interactions in pure solvents (Stengele et al., 2001). It will now be applied to binary mixtures and compared to the corresponding values of the Kirkwood-Fröhlich factor g (see chapter 1.3).

1.3. The Kirkwood-Fröhlich equation

Short range interactions between dipoles are considered by the Kirkwood-Fröhlich Eq. (2), which was introduced by Kirkwood (1939) and further developed by Fröhlich (1958).

$$\frac{(\varepsilon-\varepsilon_\infty)(2\varepsilon+\varepsilon_\infty)}{\varepsilon(\varepsilon_\infty+2)^2}=\frac{N_A}{9\varepsilon_0kT}\frac{\rho}{M_r}\mu_g^2 g \quad (2)$$

ε_∞, dielectric constant characteristic 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; g, correlation factor.

Values for ε_∞ are not easily obtained experimentally with high frequency electric fields. Thus, ε_∞ is in general replaced by the square of the refractive index n, making use of the Maxwell relation (Maxwell, 1892).

The Kirkwood-Fröhlich Eq. (2) 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. For associating compounds the usage of n^2_D instead of ε_∞ is problematic, as e.g. for water at 293 K: $n^2_D = 1.7$ and $\varepsilon_\infty \approx 4.5$ (Craig, 1995).

1.4. Binary mixtures and percolation theory

Percolation theory was introduced by Flory (1941) and Stockmayer (1943) to characterize gelation processes. It can be applied in very different areas such as fire propagation in forests, oil prospection, glass transition processes, supercooled water, or pharmaceutical powder technology. An excellent introduction to the percolation theory was given by Stauffer and Aharony (1998) a survey of applications can be found in the book of Sahimi (1994) and—for pharmaceutical powder technology—in the review paper of Leuenberger (1999).

Site percolation deals with the random occupation of a chosen n-dimensional lattice by items, such as trees, molecules, particles, etc. A typical percolation model takes into account a three-dimensional lattice, where the sites are either occupied with the probability p or remain empty with the probability $(1-p)$. At a defined probability p_c, which is called the percolation threshold, a cluster is formed that spans the entire lattice. Therefore, above this threshold p_c this percolating cluster dominates the overall properties of the system. If binary mixtures are investigated, sites are either occupied by component A (p) or by B ($p-1$).

In bond percolation, all sites are occupied and the probability of bonds between the items is investigated.

It has to be kept in mind that in a three-dimensional system two percolation thresholds exist. Thus, three sections can be found. When the concentration of component A is much larger than that of component B ($p_{(A)} \gg p_{(B)}$, $p_{(A)} \gg p_{c(A)}$), the properties of the system are determined by those of A, as B is embedded as isolated, finite clusters in A (Section 1). If $p_{(B)} \gg p_{(A)}$, $p_{(B)} \gg p_{c(B)}$, the properties of the system are determined by those of B (Section 3). The intermediate Section 2, where $p_{(B)} \approx p_{(A)}$, is determined by both A and B, as both components form infinite clusters, coherent networks permeating the system (e.g. Luginbühl and Leuenberger, 1994; Stauffer and Aharony, 1998).

The analysis of a binary mixture between a polar (A) and a nonpolar (B) liquid is of special interest in view of the possible application of percolation theory to liquid binary mixtures. The system of 1,4-dioxan and water can be used for this investigation, as it is fully miscible, despite the very different properties of the components. 1,4-dioxane is a cyclic diether possessing through its symmetry no overall dipole moment. It is fully miscible with water due to hydrogen bonding to the exposed oxygen atoms. The water molecule possesses a high dipole moment ($\mu_g = 6.17 \times 10^{-30}$ cm). It forms up to four hydrogen-bonds per molecule, thereby building a three-dimensional network.

In case of $E_i \neq 0$ being the result of clusters formed by water molecules connected by hydrogen bonds, E_i should be close to zero for a low concentration of water molecules in 1,4-dioxane ($p_{(water)} \ll p_{c(water)}$). If large water clusters can be formed-at least for a sufficient time period-the value of the internal electric field E_i should become $\neq 0$ for concentrations $p_{(water)} \gg p_{c(water)}$. Thus, the hypothesis can be put forward that (E_i/E) will increase for water concentrations $p_{(water)} \gg p_{c(water)}$ and will have its maximum value for $p_{(water)} = 1$. This would mean that for a 1,4-dioxane/water system two segments should be observed with $|E_i/E| \approx 0$ for $p_{(water)} \ll p_{c(water)}$ and $|E_i/E| > 0$ for $p_{(water)} \gg p_{c(water)}$. As the direction of E_i is not clear, the absolute values are taken. A cooperative behaviour of the water molecules forming an infinitive cluster can be anticipated.

In case of a binary mixture of two polar solvents, which both can build networks through hydrogen bonds, it would be expected that for (E_i/E) three regions can be distinguished.

A comparison between the values of (E_i/E) and the g-values of the Kirkwood-Fröhlich equation is of interest, as these approaches are based on different assumptions concerning the structure of the dielectric. For mixtures of two polar liquids, which both can build networks through hydrogen bonds, it is expected that three regions can be distinguished for g, as the change from isolated clusters to infinite clusters can be expected to lead also to changes of molecular alignment. No calculations will be made for the systems 1,4-dioxane/water, as the Kirkwood-Fröhlich equation is only valid for polar molecules.

The investigated binary mixtures are examined with regard to the hypotheses outlined above.

2. Materials and methods

2.1. Solvents

The binary mixtures of glycerol/water and 1,2-propanediol/water were examined at 298.2 K. The binary mixtures of 1,4-dioxane/water, ethanol/water, and 1-propanol/water were investigated in the temperature range of 290.7–343.2 K.

The physical properties and quality of the solvents studied can be found in the preceding publication (Stengele et al., 2001).

2.2. Experimental setup

The experimental setup was described in details elsewhere (Stengele et al., 2001).

The dielectric constant ε was measured by means of a LCR meter at 100 kHz. The temperature was kept at the required value (± 0.1 K) with a thermostat.

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

The dipole moments μ_g used for calculations are literature values for the gas phase (CRC Handbook of Chemistry and Physics, 1997).

2.3. Calculations

2.3.1. Calculation of (E_i/E) of the modified Debye equation according to Leuenberger

(E_i/E) for binary mixtures was calculated according to the following equation (cf. Eq. (1)):

$$\frac{E_i}{E} = \frac{M_{r,m}}{3\rho_m} \frac{\varepsilon_m - 1}{\frac{N_A}{3\varepsilon_0}\left[V_1\left(\alpha_1 + \frac{\mu_{g,1}^2}{3kT}\right) + V_2\left(\alpha_2 + \frac{\mu_{g,2}^2}{3kT}\right)\right]} - \frac{\varepsilon_m + 2}{3} \quad (3)$$

ρ_m, density of mixture; V_1, volume fraction of liquid 1.

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.

The values for the polarizability α were calculated using the Lorentz-Lorenz equation (Eq. (4)), (Lorentz, 1880; Lorenz, 1880) which gave excellent results compared to literature data (Riddick and Bunger, 1970) both for polar and nonpolar compounds.

$$\frac{n^2 - 1}{n^2 + 2}\frac{M_r}{\rho} = \frac{N_A}{3\varepsilon_0}\alpha \quad (4)$$

2.3.2. Calculation of correlation factor g of the Kirkwood-Fröhlich equation

The correlation factor g was calculated following the Kirkwood-Fröhlich equation for binary mixtures (Hasted, 1973), using the volume fractions for calculations instead of molar fractions, so that the results are comparable to the values for (E_i/E) (Section 2.3.1):

$$\frac{(\varepsilon_m - \varepsilon_{\infty,m})(2\varepsilon_m + \varepsilon_{\infty,m})}{\varepsilon_m(\varepsilon_{\infty,m} + 2)^2} = \frac{N_A}{9\varepsilon_0 kT}\frac{\rho_m}{M_{r,m}}(V_1\mu_{g,1}^2 + V_2\mu_{g,2}^2)g \quad (5)$$

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

2.3.3. Calculation of the Hildebrand solubility parameter δ for mixtures

For binary mixtures, the Hildebrand solubility parameter δ was calculated according to Barton (1991) as following:

$$\delta_{\text{mixture}} = V_1\delta_1 + V_2\delta_2. \quad (6)$$

It has been previously found that for pure polar and nonpolar solvents, a linear relationship between the absolute value of the slope $|m|$ of $(E_i/E) = m(1/T) + b$ and the corresponding values of the Hildebrand solubility parameter δ $((\text{J m}^{-3})^{0.5})$ at 298.2 K can be established (Stengele et al., 2001)

$$\delta = 2.4|m| + 20348;\ R^2 = 0.971. \quad (7)$$

Every investigated binary liquid mixture of the systems 1,4-dioxane/water, ethanol/water, and 1-propanol/water was measured at 8 temperatures between 290.7 and 343.2 K. A linear regression between (E_i/E) and $1/T$ was calculated, and via $|m|$ the values for δ were determined.

3. Results

3.1. Calculation of (E_i/E)-values according to the modified Debye equation

The (E_i/E)-values for the investigated binary mixtures at 298.2 K are presented in Fig. 1.

For the mixture of 1,4-dioxane and water the data can be clearly divided into two segments: $V_{\text{water}} \approx 0.0 - 0.3$: a convex curve of slightly positive values, $V_{\text{water}} \approx 0.3 - 1.0$: a linear relationship between (E_i/E) and V_{water} $((E_i/E) = -28.06 \times V_{\text{water}} + 8.29,\ R^2 = 0.997)$.

The (E_i/E)-values of the aqueous mixtures of both ethanol and 1-propanol depend linearly on V_{water} ($R^2 = 0.999$ and 0.998, respectively).

For glycerol/water and 1,2-propanediol/water we find a concave curve over the whole concentration range, these curves can be subdivided into three linear segments (Bellman and Roth, 1969; Leu, 1993), the intersections for glycerol/water are located at $V_{\text{water}} = 0.21$ and 0.62 (over-all $R^2 = 0.999$), and for 1,2-propanediol at $V_{\text{water}} = 0.20$ and 0.63 (over-all $R^2 = 0.999$).

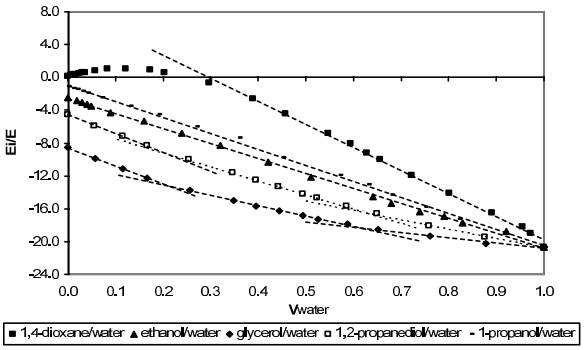

Fig. 1. (E_i/E)-values of the investigated aqueous binary solutions at 298.2 K. Ethanol/water and 1-propanol/water show over the whole concentration range, 1,4-dioxane/water above $V_{\text{water}} \approx 0.3$ a linear dependence of (E_i/E) versus the volume fraction of water. The concave curves of glycerol/water and 1,2-propanediol/water can each be subdivided into three linear segments.

3.2. Calculation of g-values according to the Kirkwood-Fröhlich equation

The g-values for the binary mixtures of ethanol/water, glycerol/water, 1,2-propanediol/water, and 1-propanol/water at 298.2 K are presented in Fig. 2.

For the examined mixtures, the addition of water to the pure alcohols and polyols leads in all cases to a decrease of g, even for 1,2-propanediol and glycerol, where the value of g for the pure polyol is smaller than that of water. For all four

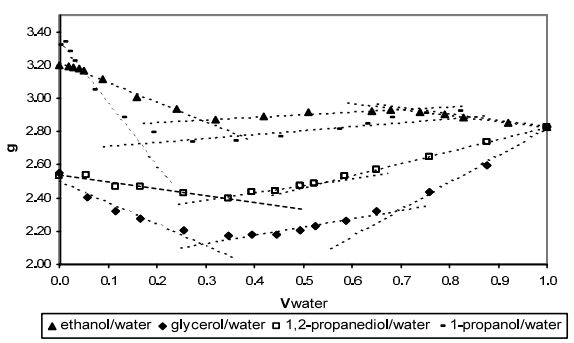

Fig. 2. The values of the correlation factor g of the Kirkwood-Fröhlich Eq. (2) for the binary mixtures of ethanol/water, glycerol/water, 1,2-propanediol/water, and 1-propanol/water at 298.2 K. As a first approximation, all curves can be subdivided into three linear segments.

binary mixtures, a minimum is reached at a water volume fraction $V_{water} \approx 0.3$.

As a first approximation, the curves can be subdivided into three linear segments. The intersections of the linear segments are for ethanol/water at $V_{water} = 0.29$ and $V_{water} = 0.69$ (over-all $R^2 = 0.997$), for glycerol/water at $V_{water} = 0.29$ and $V_{water} = 0.70$ (over-all $R^2 = 0.985$), for 1,2-propanediol/water at $V_{water} = 0.33$ and $V_{water} = 0.54$ (over-all $R^2 = 0.993$), and for 1-propanol/water at $V_{water} = 0.21$ and $V_{water} = 0.80$ (over-all $R^2 = 0.981$).

3.3. Comparison of results: modified Debye model and Kirkwood-Fröhlich approach

It has previously been shown (Stengele et al., 2001) that no algebraic connection can be made between the modified Debye equation and the Kirkwood-Fröhlich approach, as these equations are based on different assumptions concerning the examined microstructure of the liquid. No empirical connection can be made, either: $(E_i/E)f(V_{water})$ for ethanol for example is a linear function, $gf(V_{water})$ on the other hand can be clearly divided into three segments.

3.4. Modified Debye model and Hildebrand solubility parameter δ

The binary mixtures series 1,4-dioxane/water, ethanol/water, and 1-propanol/water were investigated in the temperature range of 290.7–343.2 K (8 temperatures with intervals of 7.5 K). The values for the solubility parameter δ, which are based on (E_i/E)-values (Eq. (7)), have been compared to those calculated according to Barton (1991) (see chapter 2.3.3). The results are presented in Figs. 3–5.

4. Discussion

4.1. Calculation of (E_i/E)-values according to the modified Debye equation

For the mixture of 1,4-dioxane/water, we receive in the 1,4-dioxane rich part ($V_{water} \approx 0.0 -$ 0.3) slightly positive (E_i/E)-values, these were independently reproduced by two co-workers. A possible explanation could lie in the structure of 1,4-dioxan, which leads to its in many ways exceptional properties: a cyclic flexible diether, through its symmetry possessing no overall dipole moment, but fully miscible with water due to hydrogen bonding to the exposed oxygen atoms.

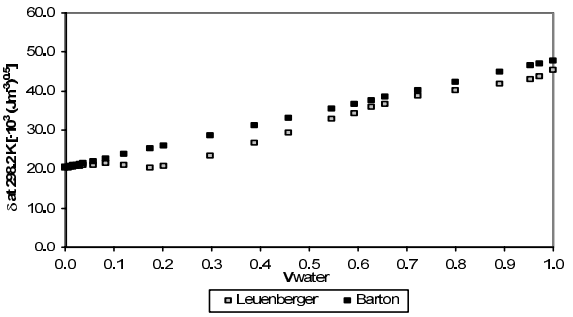

Fig. 3. The Hildebrand solubility parameter δ calculated according to Barton and via $(E_i/E)f(1/T)$ (Leuenberger) for the binary mixture of 1,4-dioxane/water.

(E_i/E) in aqueous solutions is clearly dominated by water, as it depends in the binary aqueous solutions of ethanol and propanol (over the whole concentration range) and in 1,4-dioxane/water (above $V_{water} \approx 0.3$) linearly on its volume fraction. In 1,2-propanediol and glycerol solutions three linear segments are found. These can be explained by means of percolation theory, as in binary mixtures of solids three sections can be distinguished (see chapter 1.4). The fact that these three sections can only be found in the case of

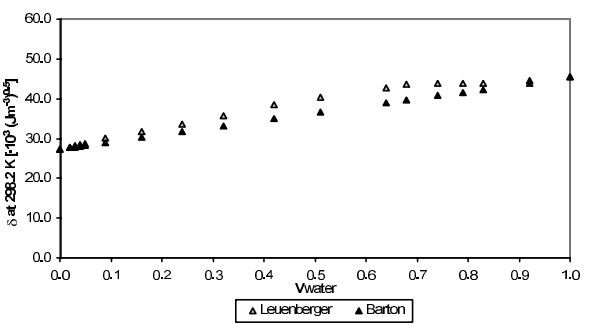

Fig. 4. The Hildebrand solubility parameter δ calculated according to Barton and via $(E_i/E)f(1/T)$ (Leuenberger) for the binary mixture of ethanol/water.

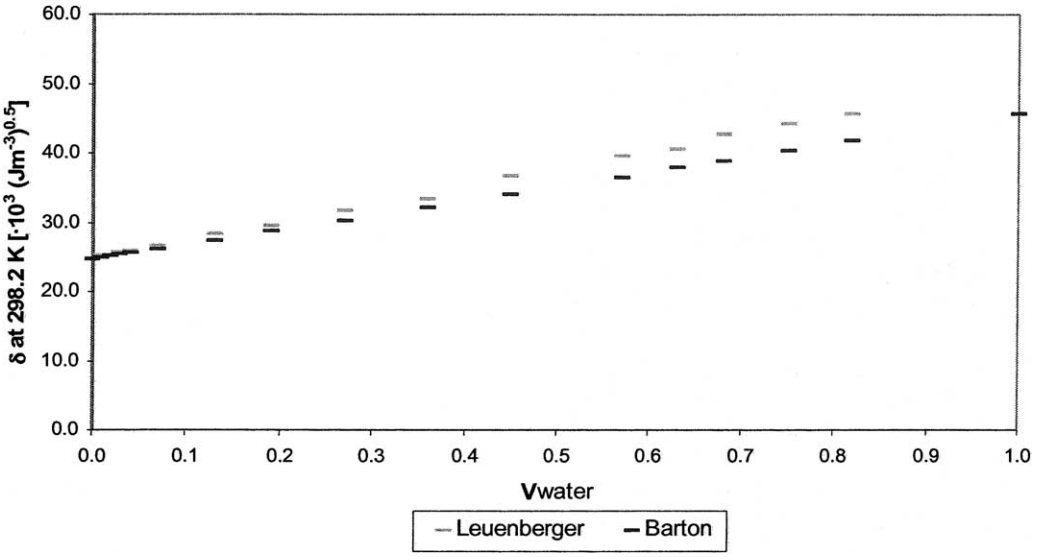

Fig. 5. The Hildebrand solubility parameter δ calculated according to Barton and via $(E_i/E)f(1/T)$ (Leuenberger) for the binary mixture of 1-propanol/water.

glycerol/water and 1,2-propanediol/water may have its origin in polyols being flexible molecules, capable of forming three-dimensional networks. Alcohols with one OH-group are believed to form only two-dimensional chains (Minami et al., 1980).

4.2. Calculation of g-values according to the Kirkwood-Fröhlich equation

As a first approximation, the curves of the investigated binary mixtures of two polar liquids can be subdivided into three segments (Fig. 2):

The addition of water to the examined pure polar liquids leads to a decrease of g with a minimum at a water volume fraction $V_{\text{water}} \approx 0.3$. This decrease is more prominent for 1-propanol/water than for ethanol/water, more pronounced for glycerol/water than for 1,2-propanediol/water. The decrease of g can be explained by structure breaking (Hasted, 1973). It may be assumed that the addition of water leads to a less marked structure breaking for liquids whose properties are more 'water-like'. This would explain the smaller decrease of g in ethanol compared to 1-propanol, and in glycerol compared to 1,2-propanediol. A further contribution to the stronger decrease of g for glycerol compared to 1,2-propanediol could be found in glycerol forming a more marked three-dimensional structure than 1,2-propanediol.

For $V_{\text{water}} \approx 0.3 - 0.75$ the curves can be described by weakly rising straight lines. From view of percolation theory this concentration range seems to correspond to Section 2 (see chapter 1.4): at $V_{\text{water}} \approx 0.3$ water starts to form infinite clusters, both water and the polar liquid percolate the system up to $V_{\text{water}} \approx 0.75$ (for $V_{\text{water}} >$ approximately 0.75, the polar liquid is embedded in water as isolated clusters of molecules). Both liquids determine the properties of the mixture in this concentration range. Nevertheless, with increasing water concentrations the influence of water grows; this explains the positive slope of the straight line.

Between $V_{\text{water}} \approx 0.75 - 1.00$, we find for the polyols a linear segment with a more pronounced positive slope, contrary to the monoalcohols with a slightly decreasing line. The fact that for ethanol and 1-propanol g is larger at $V_{\text{water}} \approx 0.75$ than for pure water, can be tentatively explained by monoalcohols forming two-dimensional chains (Minami et al., 1980), contrasting the three-dimensional structures of 1,2-propanediol and glycerol. For aqueous ethanol and 1-propanol

solutions in the water-rich concentration range this could therefore mean that water clusters cannot fully interconnect, taking a more parallel alignment than in pure water.

It must be emphasised that the subdivision of the curves into linear segments leads to an approximate description. The fact that the transitions between two segments are not very abrupt can be explained by liquids being dynamic systems.

4.3. Comparison of results: modified Debye model and Kirkwood-Fröhlich approach

(E_i/E) can be seen as a parameter for the extent of close range molecular interactions. g describes the arrangement of molecules, the preference for either parallel or nonparallel alignment.

For ethanol/water as an example, we see a linear dependence of (E_i/E) on the volume fraction of water, probably due to the fact that the network-building water is replaced with the chain-building ethanol reducing the number of hydrogen bonds. On the other hand, we can clearly distinguish three sections for $gf(V_{water})$, reflecting the structural changes of the liquid.

This shows that (E_i/E) and g supply complementary informations about the properties of a liquid system.

4.4. Modified Debye model and Hildebrand solubility parameter δ

The Hildebrand solubility parameter δ of the mixtures 1,4-dioxane/water, ethanol/water, and 1-propanol/water derived via $(E_i/E)f(1/T)$ are compared to those calculated according to Barton (1991).

For all three mixtures,δ calculated according to Leuenberger showed near-linear dependence on the volume fraction of water. Nevertheless, marked deviations can be found.

For 1,4-dioxane/water, deviations from linear behaviour occur in the region of $V_{water} \approx 0.1 - 0.4$, approximately corresponding to the concentration range where no three-dimensional network of water molecules is expected. δ according to Leuenberger are found to be smaller than those according to Barton, i.e. they show a more 'dioxane-like' character.

For ethanol/water and 1-propanol/water, positive deviations from the Barton values are found.

The fact that the correlation between $|m|$ and δ, previously found in pure liquids, was confirmed in binary mixtures leads to suggesting the replacement of δ with $|m|$, as $|m|$ is more accessible through experiment than δ, especially for non-volatile compounds (e.g. polymers).

The difference between the δ-values obtained with the calculation according to Barton and those determined according to (Eq. (7)) can be explained by the fact that the linear approach of Barton does not take into account percolation phenomena. Thus, the calculation of δ via Eq. (1) leads to a more accurate description of the properties of liquid mixtures.

4.5. Percolation phenomena

It could be shown that critical concentrations, i.e. percolation thresholds can be observed both in the case of (E_i/E) as well as in the case of g-values. These thresholds are compiled in Table 1.

Table 1
Percolation thresholds found for (E_i/E) and g as a function of the volume fraction of water in the investigated binary mixtures

Mixture	Percolation threshold (V_{water})	
	(E_i/E)	g
1,4-Dioxane/water	≈ 0.3	–
Ethanol/water	nil	0.29 0.69
Glycerol/water	0.21 0.62	0.29 0.70
1,2-Propanediol/water	0.20 0.63	0.33 0.54
1-Propanol/water	nil	0.21 0.80

Note that the Kirkwood-Fröhlich-equation should be used for polar compounds only, non-applicability of (Eq. (2)) is indicated by dashes (–).

According to percolation theory, at most three segments subdividing the curves for $(E_i/E)f(V_{water})$ and $g\ f(V_{water})$ are expected. This was confirmed for the mixtures of water with ethanol (g), 1-propanol (g), 1,2-propanediol ((E_i/E), g), and glycerol ((E_i/E), g).

For 1,4-dioxane/water, only one critical concentration ($p_{c(1,4\text{-dioxane})}$) can be found for $(E_i/E)f(V_{water})$. This may be explained by the close range interactions being strongly dominated by water, leading to a linear behaviour in the concentration range of percolating water structure ($V_{water} \approx 0.3 - 1.0$).

$(E_i/E)f(V_{water})$ of both ethanol/water and 1-propanol/water show a linear behaviour over the whole concentration range. While the structural changes are reflected by $gf(V_{water})$, the strong influence of water leads for these mixtures to a linear dependence of close interaction forces on the amount of water present.

It is well known that different properties may yield slightly different percolation thresholds. Also, it has to be kept in mind that percolation phenomena become much more pronounced for binary systems, where the property examined is very different for each pure component. The made findings show clearly that the percolation theory leads to a better understanding of the properties of liquid mixtures.

4.6. Conclusions

The examinations showed that the modified Debye equation according to Leuenberger can be applied for the description of both pure polar and nonpolar solvents and aqueous binary mixtures. The values of the Hildebrand solubility parameter δ calculated via (E_i/E) leads to results comparable to those according to Barton (1991). Marked deviations were found (see Figs. 3–5) due to the fact that percolation phenomena are taken into account. Thus, a more accurate description of the behaviour of liquid mixtures is possible.

To our knowledge, this is the first experimental evidence of percolation phenomena in binary fully miscible liquids. Further investigations of binary liquid mixtures and of solubility properties are necessary.

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