

The relationship between the refractive index and the composition of binary liquid mixtures

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Abstract. The index of refraction as a function of the composition of binary liquid mixtures is examined by means of a two parameter equation. The best linear correlation is obtained by the Debye function corrected by density. Relations to empirical polarity scales are shown.

Zusammenfassung. Der Brechungsindex als Funktion der Zusammensetzung binärer Flüssigkeitsgemische wird mit Hilfe einer Zwei-Parameter-Gleichung untersucht. Die beste lineare Korrelation wird dabei mit der Dichte korrigierten Debye-Funktion erzielt. Zusammenhänge mit empirischen Polaritätsskalen werden dargelegt.

In previous work [1,2] it was shown that the two groups of solvent polarity scales known in the literature [3] applying to slow and fast processes, respectively. The former group includes, for example, the Y [4], $E_T(30)$ [5], Z [6], and χ_B scales [7], which are essentially affected by solvent orientation phenomena, i.e., comparably slow processes. The second group includes the χ_R -scale [7], as well as scales based on the solvatochromism of weakly polar merocyanines [3]. These polarity scales apply more to fast processes and respond preferentially to the polarizability of the medium. A link between the two groups of polarity scales is 4-amino-*N*-methylphthalimide (CAS RN 2307-00-8), whose solvatochromism (for various solvents) correlates linearly with the former scales in fluorescence and with the latter in absorption.

Functions of dielectric constant and refractive index or their combinations are also used as polarity measures for solvents [8-10]. The dielectric constant is the measure for slow processes and the refractive index for fast ones.

$$P_G = E_D \ln(c_p/c^* + 1) + P_G^0 \quad (1)$$

As described in previous works [1,11,12], it was found that the polarity P_G of a binary solvent mixture as a function of its composition quantitatively follows the two-parameter equation (1), where c_p is the molar concentration of the more polar component, and P_G^0 is the P_G value of the less polar component. E_D and c^* are the parameters of the equation. Equation (1), which is generally valid when empirical polarity measures are used [1], in turn offers the

possibility to study the refractive index of solvents or their dielectric constant or functions derived from them as polarity measures.

Results and discussion

Various functions of the refractive index frequently used in the literature [9,10] will be experimentally investigated for their applicability as polarizability measures for binary liquid mixtures. Initially, methanol/water is used as a test mixture for this purpose, which, despite the high polarity of its components and the association via hydrogen bonds, exhibits a continuous change in its solvent structure during the transition from the water-poor to the water-rich mixture [1]. Spontaneous changes in the solvent structure at critical concentrations (c_k) [12,13,14] are not observed [1].

The readily available [15] and precisely measured n_D^{20} values are used as refractive indices. Of further advantage here is the large wavelength difference between the reference wavelength for the refractive index and the absorption sites of the chosen solvents, which lie only in the short-wavelength UV range. Thus, only a small perturbation by components of the anomalous dispersion [16] is to be expected. The interference would be much greater for solvents that have absorption bands near the visible region, e.g., nitrobenzene or 1-methoxynaphthalene.

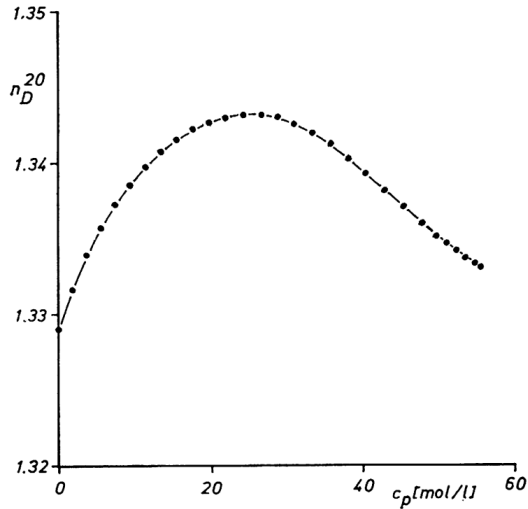


Fig. 1. The refractive index n_D^{20} as a function of the molar concentration of water (c_p) for the binary mixture methanol/water.

Table 1. Application of Eq. (1) to functions [9] of n_D^{20} corrected with density. Investigation of the binary mixture methanol/water.

No.	Function P_G^a	Correlation coefficient ^b	N^c
1	$\frac{n_D^{20}}{\rho}$	-0.999978	71
2	$\frac{(n_D^{20})^2}{\rho}$	-0.999982	71
3	$\frac{(n_D^{20})^2 - 1}{\rho[(n_D^{20})^2 + 2]}$	-0.999992	71
4	$\frac{(n_D^{20})^2 - 1}{\rho[2(n_D^{20})^2 + 1]}$	-0.999987	71
5	$\frac{(2(n_D^{20})^2 + 1)(n_D^{20})^2 - 1}{\rho((n_D^{20})^2 + 2)^2}$	-0.999996	71
6	$\frac{1}{\rho(n_D^{20})^2}$	-0.999032	71
7	$\frac{1}{\rho n_D^{20}}$	-0.999638	71

a see ref. [9], b correlation coefficient when applying Eq. (1), c number of measured values.

Figure 1 shows the refractive index of the binary mixture methanol/water as a function of the molar concentration of water (c_p ; water as the component with the larger refractive index). A strongly curved curve with a maximum is obtained. A direct linearization using Eq. (1) is not possible. However, it is noticeable that the maximum of this curve lies just in the region where the methanol/water mixture exhibits a strong volume contraction. Since it is well known that refractive index is sensitive to changes in density, functions of refractive index corrected with density might be a better measure than a function of refractive index itself (cf. the definition of molar

refraction). Eq. (1) is now used to examine the functions of refractive index commonly used in the literature [9], where all functions are corrected with density. For a selection, this is given in Tab. 1 for the mixture methanol/water. Eq. (1) is very well satisfied by the Debye function (No. 3): Correlation coefficient of -0.999992 for 71 measured values. In Fig. 2, this function is plotted against $\ln(c_p/c^* + 1)$ according to Eq. (1). Over the entire experimentally accessible range, the linear relationship is satisfied with high precision.

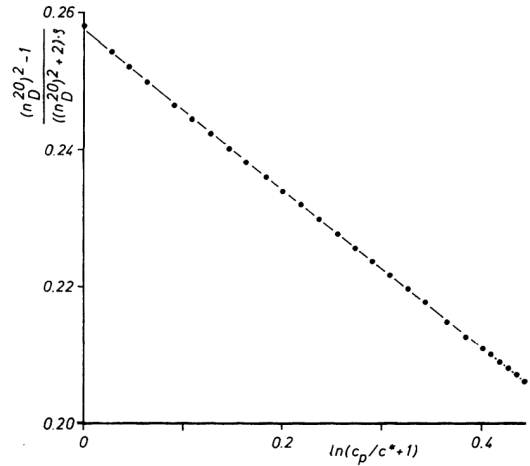


Fig. 2. The corrected Debye function (No. 3) is plotted against $\ln(c_p/c^* + 1)$ for the methanol/water mixture according to Eq. (1). (For better clarity, not all points have been plotted).

The much more complex function No. 5 yields only a slightly better correlation coefficient. The Kirkwood function No. 4, which is also frequently used, correlates significantly worse according to Eq. (1). Less favorable is also the function No. 6, which is used as a simplification. The simple linear function n_D^{20}/ρ (No. 1) provides an already surprisingly good correlation coefficient. This can be explained by a Taylor series expansion of the Debye function. If one develops the Debye function according to n_D^{20} and breaks off the series after the linear term, this must already be a good approximation because of the small numerical interval of the refractive indices.

Although the differences in the linear correlations of the functions according to Table (1) are not very pronounced, and it has also been pointed out in the literature [9] that different functions represent a useful description of the polarizability, the clear preference for the Debye function is found. Just as with the typical binary mixture of water/methanol, the preference is found with all other suitable mixtures studied. It is therefore unlikely to be due to chance, such as systematic measurement error.

$$\frac{(n_D^{20})^2 - 1}{e[(n_D^{20})^2 + 2]} = E_D \ln(c_p/c^* + 1) + P_G^0 \quad (2)$$

Using the Debye function and taking into account the density correction, the general Eq. (1) thus passes into Eq. (2), which describes the concentration dependence of the refractive index for binary liquid mixtures. [P_G^0 in Eq. (2) is the corrected Debye function for $c_p = 0$, analogous to Eq. (1)]. Equation (2) is used in the following for the study of the other binary mixtures.

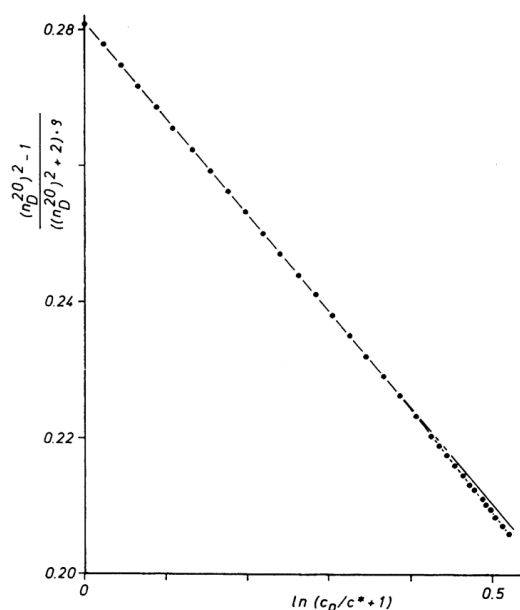


Fig. 3. Function No. 3 for the ethanol/water mixture plotted against $\ln(c_p/c^* + 1)$ according to Eq. (2), c^* for $c_p < c_k$.

In the binary ethanol/water mixture, the components also have absorption sites only in the shortwave UV region. However, there is a significant difference from the methanol/water mixture: at about 50% by volume water (c_k), the solvent structure changes abruptly [1,12,14] (double straight line). For empirical polarity scales, Eq. (1) holds above and below c_k with different parameters E_D and c^* . This property of the ethanol/water mixture is also reflected when Eq. (2) is applied. In Fig. 3, the Debye function according to Eq. (2) is plotted against $\ln(c_p/c^* + 1)$ for the range of low water concentrations ($c_p < c_k$). A straight line with a correlation coefficient of -0.999987 is obtained for 40 readings, which changes to a second, steeper one for concentrations $c_p > 40$ mol/L. However, the differences in the slopes are not as pronounced here as with other polarity scales [1]. When comparing the different functions of Table 1, a completely analogous result is obtained as for the methanol/water mixture.

The validity of Eq. (2) is not limited to mixtures with alcohols. Table 2 gives some binary mixtures with water as examples, for which density and refractive index are known with high precision. It should also be emphasized that Eq. (2) is valid for binary mixtures of liquids and solids, as shown by some examples in Table 2. From Table 1 and 2 it can be concluded that the concentration dependence of the refractive index in binary mixtures is best reproduced by the Debye function corrected with the density in combination with Eq. (1). The dielectric constant of binary mixtures exhibits an analogous dependence on composition as does the refractive index. This will be reported in another context.

Table 2. Application of Eq. (1) to the Debye function [9] for binary mixtures [Eq. (2)].

No.	mixture ^a	E_D ^b	c^* ^{b,c}	N ^d	r ^c	c_k ^{e,f}
1	Water - methanol	-0.115	99.09	71	-0.999992	--
2	Water - ethanol ^g	-0.141	81.10	40	-0.999987	43
3	Water - ethanol ^h	-0.2302	>150	31	-0.999998	43
4	Acetic acid - water ^g	0.342	48.95	53	0.999969	11.5
5	Water - citric acid	0.082 ⁱ	>150	22	0.999901	--
6	Water - dextran	2.024 ⁱ	>150	21	0.999999	--
7	Sucrose - water	-0.3366 ⁱ	2.529	63	-0.999985	--
8	Glycerol - water	0.0306	19.16	36	0.999989	--
9	Glucose - water	-0.3571 ⁱ	4.82	51	-0.999998	--
10	D-fructose - water	-0.3406 ⁱ	4.834	56	-0.999993	--
11	Formic acid - water ^g	-0.1294	150	21	-0.999719	9

a The component to which c_p refers is listed first, b parameter of Eq. (2), c in mol/L, d the number of measuring points, e correlation coefficient when applying Eq. (2), f critical concentration [1], g $c_p < c_k$, h $c_p > c_k$, i function No. 1 from Table 1.

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