

Dielectric Properties of Alkanediol/Water Mixtures

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At 25 °C the complex dielectric permittivity has been measured as a function of frequency ν ($1 \text{ MHz} \leq \nu \leq 56 \text{ GHz}$) and mole fraction x ($0 \leq x \leq 1$) for mixtures of water with 1,3-propanediol, 1,4-butanediol, 1,5-pentanediol, and 1,7-heptanediol. Some parameters like the (extrapolated) static permittivity and the characteristic relaxation time can be directly taken from the spectra. But the spectra can be also analytically represented by semiempirical relaxation spectral functions. A function containing two relaxation terms, a high-frequency Cole–Cole term and a Debye term with smaller relaxation frequency, appears to be appropriate. The relaxation parameters of the water/diol mixtures have been evaluated and compared to other water/organic solvent systems to show that (i) a high degree of permanent electric dipole orientation correlation exists in the diols that is significantly reduced on addition of water, (ii) the characteristic relaxation time reflects a substantial effect of entropy in the mechanism of dielectric relaxation but exhibits also a significant difference from monohydric alcohol/water systems, and (iii) the subdivision of the spectra into two relaxation terms seems to be due to regions of different concentration of hydrogen-bonding sites within the mixtures.

1. Introduction

Because of its outstanding role in chemistry and biology, hydrogen bonding in liquid systems has been intensively studied for long and it is still subject to a lively scientific debate. Among the associating liquids, water is undoubtedly the center of interest. Much attention has been also directed toward the physicochemical properties of alcohols, not only due to their widespread use as solvents but also because of their fascinating features. Alcohols offer the most valuable opportunity to systematically study the combined effects of hydrophilic and oleophilic interactions on stepwise variation of the number density of hydrogen-bonding sites and inert groups.

The influence of the hydrophilic/oleophilic balance on the structure and microdynamics of the liquids is demonstrated by a variety of parameters. Let the relaxation time of the principal dielectric relaxation process at 20 °C serve as an example. For methanol it has a value of 0.057 ns only.¹ It increases monotonously when going to higher normal alcohols to reach 2.21 ns for decanol.^{1,2} Besides the number density of hydroxyl groups and of inert groups, a multitude of other factors is also important in determining the properties of liquid alcohols. Among those factors appear to be the size and overall shape of the molecules and also steric properties. The relevance of the latter may be indicated by the static (electric) permittivity $\epsilon(0)$ of pentanol isomers. The $\epsilon(0)$ value for *n*-pentanol at 25 °C is as high as 15.13 while $\epsilon(0) = 5.78$ only for 2-methyl-2-butanol at the same temperature.³ Since both the concentration of the molecules and the amount of their dipole moment in the gaseous state are almost the same with these isomers, the obvious difference in the static permittivity values has to be taken to reflect a substantial effect of hydrocarbon chain branching on the correlation of permanent electric dipole moment orientation.

Despite such considerable effects in the dielectric parameters and though several alcohol/alcohol,^{4–10} alcohol/water,^{6,7,10–16} and also alcohol/nondipolar solvent^{8,16–18} mixtures have been studied by dielectric spectrometry there is still no generally accepted model of the relaxation mechanism of these liquids. An interesting finding that casts some light on the mechanism

of hydrogen bond network fluctuations is the relation

$$\hat{\tau}/\tau_{w0} \propto \hat{\rho}^{-2.5} \quad (1)$$

which empirically relates the characteristic (model-independent) relaxation time ratio $\hat{\tau}/\tau_{w0}$ of a variety of associating liquids to the normalized number density $\hat{\rho}$ of hydrogen-bonding groups and water molecules.¹⁹ In eq 1 τ_{w0} denotes the relaxation time of pure water and the relaxation time

$$\hat{\tau} = (2\pi\hat{\nu})^{-1} \quad (2)$$

is defined by the frequency $\hat{\nu}$ at which the negative imaginary part $\epsilon''(\nu)$ of the complex dielectric spectrum

$$\epsilon(\nu) = \epsilon'(\nu) - i\epsilon''(\nu) = P(\nu)[\epsilon_0 E(\nu)]^{-1} + 1 \quad (3)$$

adopts its relative maximum

$$d\epsilon''(\nu)/d\nu|_{\hat{\nu}} = 0, \quad d^2\epsilon''(\nu)/d\nu^2|_{\hat{\nu}} < 0 \quad (4)$$

Here $\epsilon_0 (= 8.854 \times 10^{-12} \text{ A s V}^{-1} \text{ m}^{-1})$ denotes the electric field constant and $P(\nu)$ is the amount of the polarization of the sample as responding to an harmonically alternating electric field of field strength $E(\nu)$. Parameter $\hat{\rho}$ in eq 1 is given by the relation

$$\hat{\rho} = (c_w + cZ_{\varphi})/c_{w0} \quad (5)$$

where c and c_w denote the molar concentration of the nonaqueous constituent and water, respectively, $c_{w0} = c_w$ ($c = 0$), and Z_{φ} is the number of hydrogen-bonding groups per organic molecule.

In terms of microscopic models, however, the mechanism of dielectric relaxation that is reflected by relation 1 is still not well understood. Among several reasons, the lack for reliable computer simulations of dielectric relaxation at different number densities $\hat{\rho}$ and also the dearth of relevant measurements of dielectric spectra over a significant frequency band appear to be the most important ones. We, therefore, decided to measure the complex dielectric spectra of mixtures of water with four linear diols of different lengths of their oleophilic part, hence

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TABLE 1: Mole (x) and Volume (v) Fraction of Alkanediol, Concentration of Diol (c) and Water (c_w), Density of Mixture (ρ), and Reciprocal Normalized Hydrogen-Bonding Group Number Density ($\hat{\rho}^{-1}$) According to Eq 5 Displayed for Water/Diol Mixtures at 25 °C

x ($\pm 0.1\%$)	v ($\pm 2\%$)	c (mol/L) ($\pm 0.1\%$)	c_w (mol/L) ($\pm 0.1\%$)	ρ (g cm $^{-3}$) $\pm 0.1\%$	$\hat{\rho}^{-1}$ ($\pm 0.1\%$)
1,3-Propanediol, HO(CH $_2$) $_3$ OH					
0.13	0.374	5.211	34.87	1.025	1.222
0.33	0.664	9.266	18.81	1.044	1.482
0.50	0.800	11.14	11.14	1.049	1.656
0.68	0.895	12.42	5.845	1.051	1.803
1	1	13.79	0	1.050	2.007
1,4-Butanediol, HO(CH $_2$) $_4$ OH					
0.13	0.424	4.820	32.25	1.015	1.321
0.25	0.615	7.004	21.61	1.021	1.554
0.33	0.708	8.065	16.38	1.022	1.702
0.49	0.828	9.372	8.714	1.020	2.015
1	1	11.30	0	1.012	2.449
1,5-Pentanediol, HO(CH $_2$) $_5$ OH					
0.13	0.466	4.467	29.89	1.004	1.425
0.25	0.658	6.429	19.48	1.003	1.711
0.33	0.742	7.116	14.45	1.002	1.929
0.50	0.855	8.178	8.113	0.998	2.262
0.63	0.908	8.670	5.131	0.995	2.463
0.76	0.948	9.030	2.884	0.992	2.642
0.88	0.977	9.297	1.272	0.991	2.786
1	1	9.491	0	0.989	2.915
1,7-Heptanediol, HO(CH $_2$) $_7$ OH					
0.45	0.864	6.283	7.628	0.968	2.740
0.54	0.899	6.519	5.602	0.963	2.969
0.63	0.928	6.701	4.008	0.958	3.179
0.72	0.952	6.873	2.654	0.956	3.374
0.86	0.980	7.076	1.135	0.956	3.620
1	1	7.203	0	0.952	3.841

varying $\hat{\rho}$ by the mole fraction of the organic constituent and also by the hydrophilic/hydrophobic balance of the alcohol molecules. These measurements complement some former studies of the dielectric properties of water/diol systems.^{20–27} We predominantly aim at a comparison of the $\hat{\epsilon}$ vs $\hat{\rho}$ relations of water/diol systems to those of mixtures of water with monohydric alcohols. In order to, in addition, look for structural properties of the liquids and for fine details of the relaxation process, attention has been also paid to the static permittivity and to the shape of the dielectric spectra under consideration. We thus conducted the measurements over the wide frequency range from 1 MHz to 56 GHz.

2. Experimental Section

Binary Mixtures. In this paper, results for mixtures of water with four diols following the structure formula



are reported. 1,3-Propanediol ($n = 3$, trimethylene glycol, 98%), 1,4-butanediol ($n = 4$, tetramethylene glycol, 99%), 1,5-pentanediol ($n = 5$, pentamethylene glycol, 99%) and, 1,7-heptanediol ($n = 7$, heptamethylene glycol, 98%) as purchased from Merck (Darmstadt, FRG), Aldrich (Steinheim, FRG), Alfa (Karlsruhe, FRG), and Sigma (Deisenhofen, FRG), respectively, were used as delivered. Water was distilled and deionized by mixed-bed ion exchange. The mixtures were prepared by weighing appropriate amounts of the constituents into suitable flasks. The density ρ of the liquids was measured at 25 °C using a pycnometer that had been calibrated before against deionized and degassed water. A survey of the liquids is presented in Table 1. Also given in this table are concentration

TABLE 2: Experimental Errors in the Complex Permittivity Data

ν (GHz)	$\Delta\epsilon'/\epsilon'$	$\Delta\epsilon''/\epsilon''$
0.001–0.03	0.02	0.1
0.03–1	0.01	0.04
1–2	0.05	0.07
2–5	0.05	0.02
5–27	0.01	0.02
27–56	0.04	0.04

data, the volume fraction v of diol, the density ρ , and the quantity $1/\hat{\rho}$ (eq 5).

Complex Permittivity Measurements. Between 1 MHz and 3 GHz the complex permittivity $\epsilon(\nu)$ of the samples was measured as a function of frequency ν using sample cells of the cutoff variety.^{27,28} The sample volume of these cells is formed from a coaxial line/circular waveguide transition that, with the aid of a coaxial feeding line, is connected to a reflection test set (HP 85044A) of a computer-controlled network analyzer (HP 8753A). Measurements consisted in the determination of the complex reflection coefficient of the cell. In all measurements the circular waveguide section was excited below its cutoff frequency so that according to a careful modal analysis of the device²⁸ a simple lumped-element network representation of the cell was possible. The parameters of this network were derived from calibration procedures using the cell filled with dry air ($\epsilon = 1$) and with liquids of well-known dielectric spectrum (water, acetone). In order to reach maximum sensitivity in the measurements, the length l of the inner conductor of the coaxial line/circular waveguide transition was varied between 1 and 20 mm matching the cell characteristics to the permittivity of the sample under test and also to a particular frequency range. The permittivity data measured at the same frequency but at different cell lengths l agreed within the limits of experimental error.

At frequencies above 1.7 GHz a traveling wave transmission method has been employed in which the electromagnetic field transmitted through a specimen cell is interferometrically probed at variable sample thickness.^{27,29} We used seven double-beam interferometers to cover the frequency range. One interferometer was constructed with coaxial line components ($\nu < 5$ GHz) the others with waveguide devices ($5.3 \leq \nu \leq 56$ GHz). The cells consisted of a piece of coaxial line ($\nu < 5$ GHz) or a circular waveguide section ($\nu > 4$ GHz) sealed by a dielectric window made of Teflon or silicone rubber. A coaxial line or circular waveguide immersed in the liquid was precisely shiftable along the direction of wave propagation in order to probe the electromagnetic field within the liquid column.

The specific electric dc conductivity σ of the liquids was measured in the usual manner at 1 and 10 kHz. With all samples the σ values were just in the order of 10^{-4} S m $^{-1}$. Hence only small corrections

$$\epsilon''(\nu) = \epsilon''_{\text{tot}}(\nu) - \sigma(\epsilon_0\omega)^{-1} \quad (7)$$

were necessary to derive the desired dielectric loss number $\epsilon''(\nu)$ from the measured total loss number $\epsilon''_{\text{tot}}(\nu)$. Here and in what follows $\omega = 2\pi\nu$ denotes the angular frequency.

The frequency of measurement was known and kept constant during the measurements with an uncertainty of less than $\pm 0.1\%$. The temperature of the samples was controlled to within ± 0.05 K. The errors in the complex permittivity data depend on the measuring frequency as shown by the data listed in Table 2. These data result from a careful analysis of sources of errors, particularly from measurements in which liquids of known dielectric spectrum have been used as sample. Also

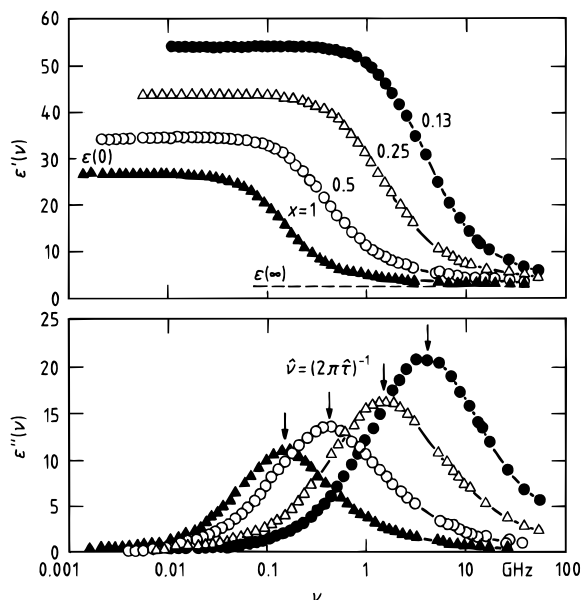


Figure 1. Real part $\epsilon'(\nu)$ and negative imaginary part $\epsilon''(\nu)$ of the complex dielectric spectrum at 25 °C displayed for water/1,5-pentanol mixtures with different mole fractions x of diol.

TABLE 3: Model-Independent Parameters of Water/Diol Dielectric Spectra. Static Permittivity (Eq 8) and Characteristic Relaxation Time $\hat{\tau}$ (Eq 2) at 25 °C

x	$\epsilon(0) (\pm 0.1)$	$\hat{\tau} \text{ (ns)} (\pm 5\%)$	x	$\epsilon(0) (\pm 0.1)$	$\hat{\tau} \text{ (ns)} (\pm 5\%)$
1,3-Propanediol			1,4-Butanediol		
0.13	64.3	0.032	0.13	59.6	0.039
0.33	52.2	0.087	0.25	50.6	0.090
0.50	46.1	0.15	0.33	46.1	0.13
0.68	41.6	0.22	0.49	40.5	0.28
1	34.9	0.33	1	31.4	0.74
1,5-Pentanol			1,7-Heptanediol		
0.13	54.2	0.044	0.45	27.1	0.40
0.25	44.0	0.11	0.54	25.9	0.57
0.33	39.7	0.16	0.63	24.6	0.78
0.50	34.3	0.38	0.72	23.8	1.05
0.63	31.9	0.50	0.86	23.0	1.38
0.76	29.8	0.79	1	22.4	1.88
0.88	28.3	0.86			
1	26.9	1.12			

considered in the estimation of errors are possible systematic deviations in the permittivity data measured with different cells, with different electronic instruments or with different microwave devices.

3. Results and Analytical Description of the Complex Permittivity Data

Obvious Characteristics of the Dielectric Spectra. In Figure 1 a plot is given of the real part $\epsilon'(\nu)$ and negative imaginary part $\epsilon''(\nu)$ of the complex dielectric spectrum for pure 1,5-pentanol and for three mixtures of water with that diol. All spectra shown in Figure 1 exhibit one dispersion ($d\epsilon'(\nu)/d\nu < 0$)/dielectric loss ($\epsilon''(\nu) > 0$) region only. Hence in the aqueous systems there do not seem to exist well-separated relaxation regions for the water and the alkanediol in the mixtures. This finding is common to all liquids measured in this study. The extrapolated static permittivity

$$\epsilon(0) = \lim_{\nu \rightarrow 0} \epsilon'(\nu) \quad (8)$$

is well-defined by the measurements at lower frequencies and has, therefore, been directly taken from the spectra (Table 3). As expected on grounds of the static permittivity values of the

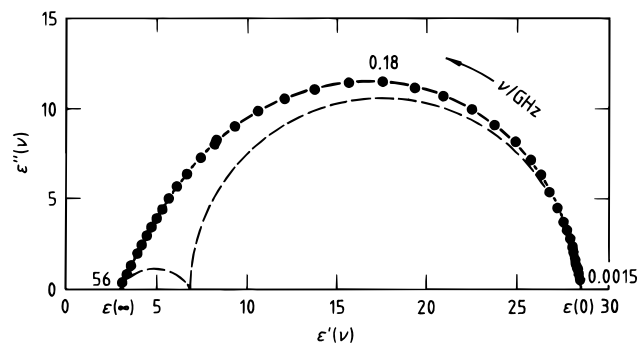


Figure 2. Cartesian plot of the dielectric loss number $\epsilon''(\nu)$ as a function of the real part $\epsilon'(\nu)$ of the complex permittivity shown for a water/1,5-pentanol mixture with mole fraction $x = 0.88$ of diol at 25 °C. The full curve is the graph of the model relaxation spectral function $RF_m(\nu)$ defined by eq 17 with the parameter values as found by the regression analysis (Table 4). The dashed curves indicate the individual relaxation terms.

constituents, within each series of mixtures $\epsilon(0)$ increases with the water content of the samples. Also directly available from the measured spectra, for instance by the use of suitable analytical expressions, is the frequency $\hat{\nu}$ at which the dielectric loss $\epsilon''(\nu)$ adopts its relative maximum. Hence, for comparison with relevant literature data, the values for the model-independent characteristic relaxation time $\hat{\tau}$ (eq 2) are also included in Table 3.

Treatment of Data. On a second view the $\epsilon''(\nu)$ spectra for the diols and also for the water/diol mixtures appear to be somewhat unsymmetric. This is more obviously demonstrated by Figure 2 where a complex plane representation for the spectrum of another water/1,5-pentanol mixture is shown as an example. In this Cartesian plot of $\epsilon''(\nu)$ as a function of $\epsilon'(\nu)$ the data clearly do not follow a semicircle as characteristic for a Debye-type relaxation term $R_D(\nu)$ with discrete relaxation time τ_D ³⁰

$$R_D(\nu) = \frac{\Delta\epsilon_D}{1 + i\omega\tau_D} \quad (9)$$

Within the limits of experimental error, the dielectric relaxation of water at 25 °C can be represented by a Debye term,³¹ hence

$$\epsilon(\nu) = \epsilon(\infty) + R_D(\nu) \quad (10)$$

Here

$$\epsilon(\infty) = \lim_{\nu \rightarrow \infty} \epsilon'(\nu) \quad (11)$$

is the permittivity extrapolated to frequencies well above the relaxation region as illustrated by Figures 1 and 2. If subscript w0 is used to indicate parameters of pure water, its microwave complex permittivity may be written as

$$\epsilon(\nu) = \epsilon_{w0}(\infty) + \frac{\epsilon_{w0}(0) - \epsilon_{w0}(\infty)}{1 + i\omega\tau_{w0}} \quad (12)$$

where $\epsilon_{w0}(0) - \epsilon_{w0}(\infty) = \Delta\epsilon_{w0} (= \Delta\epsilon_D)$ is the dispersion step. The values for the parameters of eq 12 are given in Table 4.

In order to analytically represent the measured permittivity data of the diols and the water/diol mixtures, various other relaxation functions RF of the type

$$RF = \epsilon(\infty) + \sum_{i=1}^I R_i(\nu) \quad (13)$$

TABLE 4: Parameters of the Model Relaxation Spectral Function $RF_m(\nu)$ Defined by Eq 17 for Water³¹ and for Mixtures of Water with Diols at 25 °C

x	$\epsilon(\infty)$ (± 0.2)	$\Delta\epsilon_{CC}$ ($\pm 7\%$)	τ_{CC} (ns) ($\pm 5\%$)	α ($\pm 10\%$)	$\Delta\epsilon_D$ ($\pm 7\%$)	τ_D (ns) ($\pm 5\%$)
0	5.2	$\equiv 0$			73.2	0.0083
1,3-Propanediol, HO(CH ₂) ₃ OH						
0.13	4.3	27.0	0.016	0.09	33.0	0.034
0.33	4.4	10.8	0.028	0.07	37.0	0.095
0.50	3.5	6.4	0.031	0.21	36.2	0.16
0.68	3.4	4.7	0.036	0.25	33.5	0.23
1	3.3	3.3	0.035	0.25	28.3	0.34
1,4-Butanediol, HO(CH ₂) ₄ OH						
0.13	4.7	26.0	0.021	0.09	28.9	0.048
0.25	4.4	15.0	0.034	0.10	31.2	0.11
0.33	4.4	15.0	0.059	0.09	26.7	0.16
0.49	3.7	8.1	0.092	0.17	28.7	0.31
1	2.8	4.1	0.12	0.40	24.5	0.76
1,5-Pentanediol, HO(CH ₂) ₅ OH						
0.13	4.5	25.0	0.023	0.11	24.7	0.057
0.25	4.0	19.0	0.050	0.15	21.0	0.15
0.33	3.9	15.2	0.069	0.16	20.6	0.20
0.50	3.5	8.6	0.13	0.21	22.2	0.43
0.63	3.3	6.8	0.17	0.27	21.8	0.55
0.76	3.1	3.9	0.13	0.28	22.8	0.83
0.88	2.9	3.8	0.15	0.36	21.6	0.90
1	2.8	3.0	0.12	0.39	21.1	1.15
1,7-Heptanediol, HO(CH ₂) ₇ OH						
0.45	4.0	10.4	0.17	0.13	12.7	0.56
0.54	3.7	8.9	0.23	0.15	13.3	0.72
0.63	3.4	6.5	0.28	0.19	14.7	0.91
0.72	3.3	4.3	0.27	0.19	16.1	1.15
0.86	3.0	3.5	0.32	0.30	16.5	1.46
1	3.0	2.4	0.32	0.30	17.0	1.95

with $I = 1, 2$ have been fitted to the spectra using a nonlinear least-squares regression analysis to minimize the variance

$$\chi^2 = \frac{1}{N - P - 1} \sum_{n=1}^N w(\nu_n) |\epsilon(\nu_n) - RF(\nu_n; \xi_1, \dots, \xi_P)|^2 \quad (14)$$

Here denote R_i ($i = 1, 2$) different relaxation terms, ν_n ($n = 1, \dots, N$) are the frequencies of measurements, and $w(\nu_n)$ are weighing factors that consider the experimental error of $\epsilon(\nu_n)$. The quantities ξ_p ($p = 1, \dots, P$) are the adjustable parameters of the model relaxation function RF. The uncertainty $\Delta\xi_p$ in the values ξ_p of these parameters ($p = 1, \dots, P$) have been derived from additional runs in which sets of pseudodata $\tilde{\epsilon}'(\nu_n)$, $\tilde{\epsilon}''(\nu_n)$ were considered in the regression analysis. These sets of pseudodata have been generated by varying the original permittivity values within their limits of experimental errors using the relations

$$\tilde{\epsilon}'(\nu_n) = \epsilon'(\nu_n) + a' \Delta\epsilon'(\nu_n) \quad (15)$$

$$\tilde{\epsilon}''(\nu_n) = \epsilon''(\nu_n) + a'' \Delta\epsilon''(\nu_n) \quad (16)$$

where $a', a'' \in [-1, 1]$ are random numbers. We tried to minimize both in the regression analysis, the variance χ^2 (eq 14) and the uncertainty in the parameter values of the relaxation spectral function.

Model Relaxation Spectral Function. In order to account for the shape of the measured spectra, a variety of relaxation terms has been used in the spectral function RF (eq 13). Besides a double Debye term model ($R_{D1} + R_{D2}$) a Cole–Cole (R_{CC}^{32}), Davidson–Cole (R_{DC}^{33}), Havriliak–Negami (R_{HN}^{34}), and a Dissado–Hill (R_{DH}^{35}) term have been considered and also the combinations of these terms with an additional Debye term. In view of the aforementioned χ^2 and $\Delta\xi_p$ criteria and a self-

consistent description of all spectra the model function

$$RF_m(\nu) = \epsilon(\infty) + R_{CC}(\nu) + R_D(\nu) \quad (17)$$

was found to appropriately account for the measured permittivity data if the Debye term represents the low-frequency part of the relaxation spectral function and the Cole–Cole term the high-frequency part. The Cole–Cole term is defined by the relation

$$R_{CC}(\nu) = \frac{\Delta\epsilon_{CC}}{1 + (i\omega\tau_{CC})^{1-\alpha}} \quad (18)$$

where parameter α measures the width of the underlying relaxation time distribution function. The values for the parameters of the model function $RF_m(\nu)$ are also collected in Table 4.

4. Discussion

Shape of Relaxation Spectra. A similar situation as with the water/diol mixtures has been found for a variety of associating organic solvents and their mixtures with water. It is the finding of only one dispersion/dielectric loss region (Figure 1) that may, however, be favorably represented by a superposition of two relaxation terms (eq 17). Our own studies of such liquids over a similar frequency range include alcohols¹⁴ as well as unbranched³⁶ and branched³⁷ poly(ethylene glycol) monoalkyl ethers. Most spectra of those systems can be alternatively discussed, assuming either a two-subphase relaxation model or an almost homogeneous dielectric relaxation mechanism with a continuous distribution of relaxation times. The finding that the present water/diol spectra appear to be not in conformity with the assumption of only one continuous relaxation time distribution could reflect the lack for suitable theoretical models. On the other hand, the fact that the measured spectra do not exhibit two well-separated relaxation regions could be simply a reflection of the broadness of relaxation terms that just on favorable conditions allow for a clear separation from one another. Such conditions have been found with carboxylic acid/water mixtures.³⁸

Besides the aforesaid inherent limitations of relaxation spectrometry, the present complex permittivity data point at another interesting point to which little attention has been directed so far. Though measured in a reasonable frequency range around the characteristic relaxation frequency $\hat{\nu}$, the data do not comply with the requirements in the low- and high-frequency behavior as predicted for physical reasons.³⁹ From fundamental theoretical considerations follows that the limiting slopes

$$S(0) = \lim_{\nu \rightarrow 0} (d\epsilon''(\nu)/d\epsilon'(\nu)) = -\infty \quad (19)$$

$$S(\infty) = \lim_{\nu \rightarrow \infty} (d\epsilon''(\nu)/d\epsilon'(\nu)) = -0 \quad (20)$$

should hold. As illustrated by the complex plane representation of the dielectric spectrum for 1,4-butanediol in Figure 3, within the frequency range of measurements the data do not follow the relations (19) and (20). Hence also in this respect the description by the relaxation function $RF_m(\nu)$ should be considered an empirical representation of data rather than a theoretical evaluation.

It is nevertheless interesting to notice that in various previous studies [e.g., refs 27, 36, 37] $S(0) = -\infty$ had been found in conformity with a Davidson–Cole relaxation spectral term $R_{DC}(\nu)$ instead of a Cole–Cole term $R_{CC}(\nu)$. The unsymmetric relaxation time distribution reflected by $R_{DC}(\nu)$ has been related

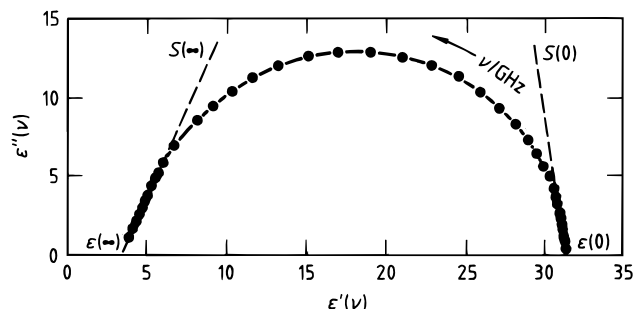


Figure 3. Complex plane representation of the dielectric spectrum of 1,4-butanediol at 25 °C.

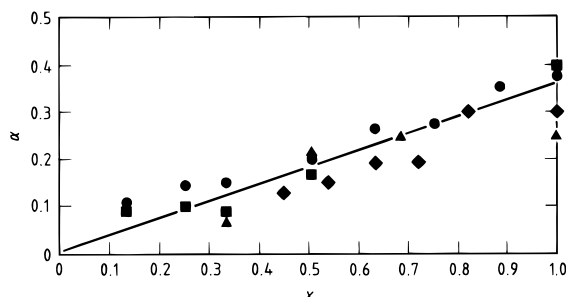


Figure 4. Relaxation time distribution parameter α at 25 °C shown as a function of mole fraction x of alkanediol for mixtures of water with diols $\text{HO}(\text{CH}_2)_n\text{OH}$: (▲) $n = 3$; (■) $n = 4$; (●) $n = 5$; (◆) $n = 7$.

to the fluctuating free-volume model^{40,41} and also the defect diffusion model^{41,42} of dielectric relaxation. Within the framework of the free-volume model an unsymmetric relaxation time distribution function points at a structure relaxation time that nearly agrees with the dipole reorientation time whereas a symmetric relaxation time distribution function as underlying a Cole–Cole term is an indication for the structure relaxation to be slower than the dipole reorientation. Quite remarkably, the Cole–Cole term describes the faster relaxation process here. It is only briefly mentioned in this context that the Cole–Cole relaxation time distribution parameter α almost linearly increases with the mole fraction x of diol (Figure 4).

Extrapolated Permittivities: Dipole Orientation Correlation. With the restriction that the model relaxation function $\text{RF}_m(\nu)$ used to extrapolate the measured data does not follow the limiting slopes as given by eqs 19 and 20, the values of both the low- and high-frequency permittivity $\epsilon(0)$ and $\epsilon(\infty)$ are well-defined by the measurements. In Figure 5 these values are displayed versus the mole fraction x of diol to show that the $\epsilon(\infty)$ values of the four series of mixtures rather uniformly decrease from the water value $\epsilon(\infty, x=0) = \epsilon_{w0}(\infty) (=5.2)$ to the value $\epsilon(\infty, x=1) (=2.8, \dots, 3.3)$ for the diols. However, due to the distinctly different static permittivity $\epsilon(0, x=1)$ of the diols each of the water/diol systems exhibits its own $\epsilon(0)$ vs x relation.

The $\epsilon(0, x=1)$ data are shown as a function of hydroxyl group concentration $c_{\text{OH}} (=2c)$ in Figure 6 where for comparison data for some monohydric alcohols ($c_{\text{OH}} = c$) are also given. According to our expectations the static permittivity increases with the concentration of dipolar groups. Quite surprisingly, however, both series of data follow nearly the same $\epsilon(0)$ vs c_{OH} relation. Hence as compared to the monohydric alcohols there do not seem to exist other structure effects in the static permittivity of the diols. Notice, however, that this conclusion is not generally valid. Going from 1,3-propanediol ($\epsilon(0) = 34.9$, Table 3) to 1,2-propanediol the static permittivity is substantially reduced ($\epsilon(0) = 29.2$, 20 °C²³) though the concentration of hydroxyl groups is similar in the isomers. In this context it is worth mentioning that the value for the static permittivity of

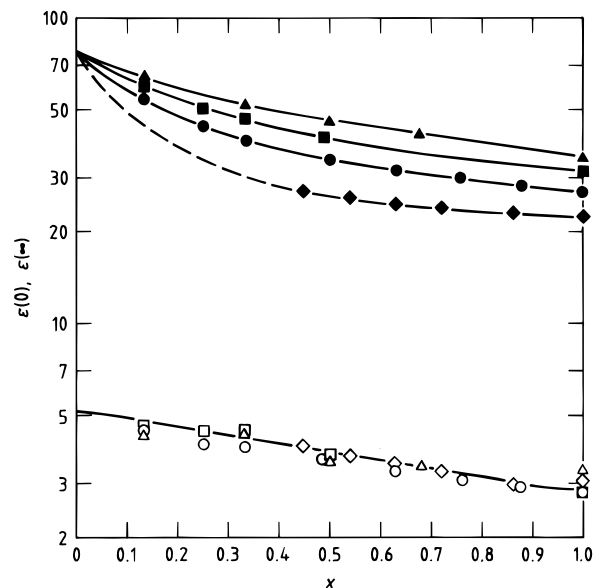


Figure 5. Logarithmic plot of the static permittivity $\epsilon(0)$ (closed symbols) and extrapolated high-frequency permittivity $\epsilon(\infty)$ (open symbols) vs the mole fraction x of alkanediol for mixtures of water with diols $\text{HO}(\text{CH}_2)_n\text{OH}$ at 25 °C: (▲) $n = 3$; (■, □) $n = 4$; (●, ○) $n = 5$; (◆, ◇) $n = 7$.

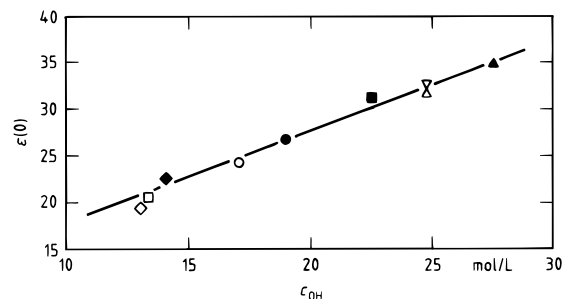


Figure 6. Static permittivity $\epsilon(0) = \epsilon(0, x=1)$ of diols (closed symbols) and monohydric alcohols (open symbols) at 25 °C displayed as a function of the concentration c_{OH} of hydroxyl groups: (▲) 1,3-propanediol; (■) 1,4-butanediol; (●) 1,5-pentanediol; (◆) 1,7-heptanediol; (△) methanol;¹⁴ (▽) methanol;⁴³ (○) ethanol;⁴³ (□) 1-propanol;⁴³ (◇) 2-propanol.¹⁴

highly branched *tert*-butyl alcohol ($\epsilon(0) = 12.2 \pm 0.2$, $c_{\text{OH}} = 10.66 \text{ mol/L}$ ¹⁵) does not fit to the linear dependence of $\epsilon(0)$ upon c_{OH} as shown in Figure 6.

Structural properties of a dipolar liquid are reflected by the static permittivity if these properties include a correlation in dipole orientations. In the present associating liquids, particularly in the binary mixtures, a variety of correlations between different molecular dipoles might be present. We thus restrict the evaluation of the $\epsilon(0)$ data to the calculation of a global *effective* dipole orientation correlation factor g_{eff} . Based on the Fröhlich theory of the static permittivity,^{44,45} this g_{eff} factor may be defined by the relation

$$\frac{\epsilon(0) - \epsilon_{\infty}}{\epsilon(0)} \frac{2\epsilon(0) + \epsilon_{\infty}}{(\epsilon_{\infty} + 2)^2} = g_{\text{eff}} \frac{N_A}{9kT\epsilon_0} D_L(c_l \mu_l) \quad (21)$$

where $N_A = 6.02 \times 10^{23} \text{ mol}^{-1}$, $k = 1.38 \times 10^{-23} \text{ A s V K}^{-1}$, and

$$D_L(c_l \mu_l) = \sum_{l=1}^L c_l \mu_l^2 \quad (22)$$

Here, c_l and μ_l denote the concentration and dipole moment in

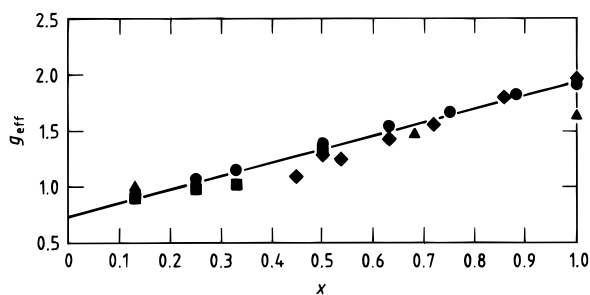


Figure 7. Effective dipole orientation correlation factor g_{eff} as defined by eq 21 displayed against mole fraction x of alkanediol for mixtures of water with diols $\text{HO}(\text{CH}_2)_n\text{OH}$ at 25 °C: (\blacktriangle) $n=3$; (\blacksquare) $n=4$; (\bullet) $n=5$; (\blacklozenge) $n=7$.

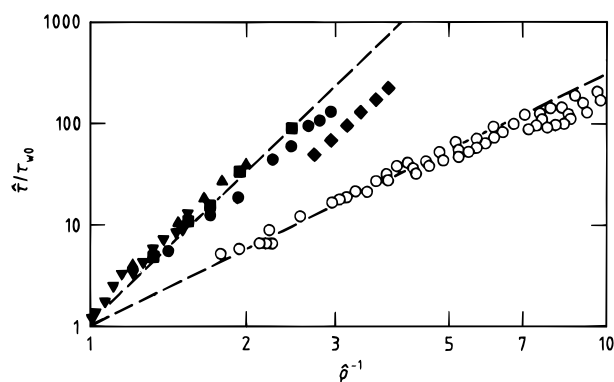


Figure 8. Relaxation time ratio $\hat{\tau}/\tau_{w0}$ displayed as a function of $\hat{\rho}^{-1}$ (eq 5, Table 1) for mixtures of water with diols (closed symbols) and monohydric alcohols (open symbols^{1,2}). Also included are data for ethanediol⁵ and butanediol²⁷ from the literature. (∇) 1,2-ethanediol; (\blacktriangle) 1,3-propanediol; (\blacksquare) 1,4-butanediol; (\bullet) 1,5-pentanediol; (\blacklozenge) 1,7-heptanediol.

the gaseous state, respectively, of the l th contributing species. We do not know the dipole moment of the diols. We therefore tentatively assume the group moment $\mu_{\text{OH}} (=1.7 \text{ D}^{45})$ of the hydroxyl groups of a diol molecule to be equal to that of monohydric alcohols. Hence we simply use

$$D_L(c_l\mu_l) = 2c_{\text{OH}}\mu_{\text{OH}}^2 + c_w\mu_w^2 \quad (23)$$

where $\mu_w = 1.84 \text{ D}^{46}$ is the dipole moment of an isolated water molecule.

With the $\epsilon(0)$ and ϵ_∞ ($=\epsilon(\infty)$) data from Tables 3 and 4, respectively, $g = g_{\text{eff}}$ values are found which slightly increase from about 1.7 to 2 when going from 1,3-propanediol to 1,7-heptanediol. The g_{eff} data of the mixtures of water with diols (Figure 7) monotonously increase with mole fraction x of alcohol. Again a uniform behavior results for the four series of mixtures. Obviously, the length of the oleophilic part of the diol molecules is of low importance for the arrangement of the dipolar groups and water molecules within the aqueous systems. It is still an open question which high-frequency permittivity ϵ_∞ has to be used in eq 21. From a theoretical point of view a value between the squared optical refractive index n^2 and the extrapolated high frequency $\epsilon(\infty)$ might be appropriate.⁴⁷ Since we preferred to use $\epsilon_\infty = \epsilon(\infty)$, leading to the smallest possible g_{eff} values (e.g. $g_{\text{eff}} (=g) = 0.76$ for water at 25 °C), there can be no doubt that a strong effect of dipole orientation correlation exists in the diols. This effect is gradually reduced on addition of water molecules which due to their four hydrogen-bonding sites offer the possibility for many local structures.

Characteristic Relaxation Time. Comparison to Monohydric Alcohols. In Figure 8 the model-independent relaxation time $\hat{\tau}$ (normalized to τ_{w0}) is displayed as a function of the

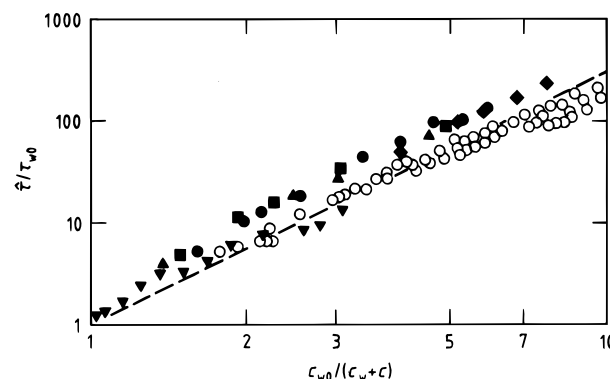


Figure 9. Same data as in Figure 8 but $Z_\phi = 1$ used in $\hat{\rho}^{-1}$ (eq 5) of the diol systems.

reciprocal normalized number density $\hat{\rho}^{-1}$ of hydrogen-bonding groups and water molecules. Besides the results for the water/diol mixtures also shown in that diagram are data for pure monohydric alcohols as well as for mixtures of water with some monohydric alcohols. Two different groups of liquids clearly emerge from these relaxation time data, those containing monohydric alcohols and those containing diols as organic solvent. The $\hat{\tau}$ values of both groups follow a

$$\hat{\tau}/\tau_{w0} = \hat{\rho}^{-n_\tau} \quad (24)$$

relation. However, the empirical exponent is $n_\tau = 2.5$ with the monohydric alcohols, as already mentioned in the Introduction, while the relaxation times of the diol systems can be represented rather by the exponent $n_\tau = 5$. If it is assumed that the dipole reorientation rate of an OH group is influenced by neighboring OH groups, but not by the OH group of the same diol molecule and only by one of the two OH groups of other molecules at the same time, then $Z_\phi = 1$ could be appropriate in eq 5. Consequently, the $\hat{\tau}$ values of the water/diol systems should agree with the $\hat{\tau}$ vs $\hat{\rho}^{-1}$ relation for the monohydric alcohol/water systems. As shown by Figure 9 ($n_\tau = 2.5$) this is indeed the case in fair approximation.

In the light of this empirical dependence of $\hat{\tau}$ upon $\hat{\rho}^{-1}$ the relaxation time data could be taken to indicate that only one hydroxyl group per diol molecule is available for the mechanism of (comparatively slow) dielectric relaxation. Such conclusions may be questioned, however, in view of the flexibility of the diol molecules. If the relaxation characteristics of mixtures of water with poly(ethylene glycol) monoalkyl ethers, for which $2 \leq n_\tau \leq 4.7$ resulted at $\hat{\rho}^{-1} < 1.5$,³⁷ are also taken into account, then the finding of $n_\tau \approx 5$ for the water/diol mixtures appears to be a less uncommon result. Nevertheless, the characteristic relaxation times of the alkanol/water systems reveal a substantial effect of entropy in the dielectric relaxation of associating liquids. Within a homologous series of associating organic solvents there are only small changes in the hydrogen bond energy but there is an increasing effect of the interactions of hydrocarbon groups. The substantial increase in the dielectric relaxation time at increasing oleophilic part of the alcohols clearly reflects the decreasing probability density for the formation of new bonds.

Globally, the effect of entropy can be explained by ideas on the mechanism of dielectric relaxation in hydrogen-bonded liquids^{19,27,37} that are based on computer simulation studies of water^{48–51} and methanol.⁵² Within the hydrogen-bonded network the bonding strength fluctuates rapidly. For water, for example, the correlation time of network fluctuations is as small as 0.1–1 ps.^{53,54} A reduction in the bond strength, however, does not necessarily result in a reorientation of a dipolar group

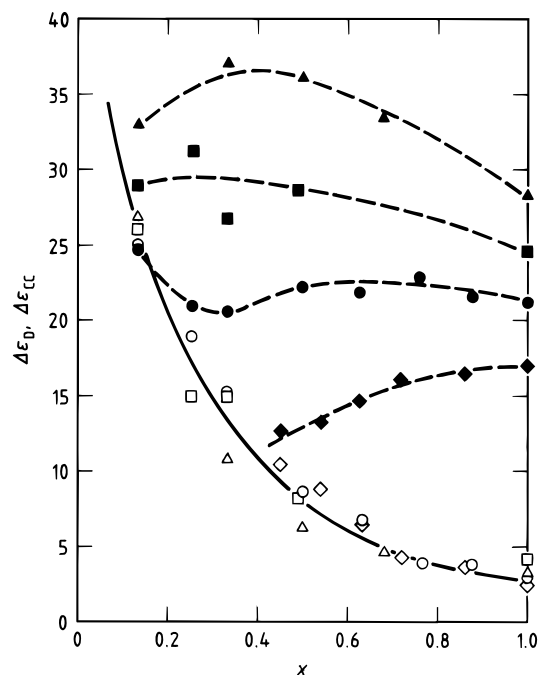


Figure 10. Relaxation amplitudes $\Delta\epsilon_D$ (closed symbols) and $\Delta\epsilon_{CC}$ (open symbols) vs mole fraction x of alkanediol for mixtures of water with diols $\text{HO}(\text{CH}_2)_n\text{OH}$ at 25 °C: ($\blacktriangle, \triangle$) $n = 3$; (\blacksquare, \square) $n = 4$; (\bullet, \circ) $n = 5$; (\blacklozenge, \lozenge) $n = 7$.

or molecule. Orientational motions of the dipole vector through a significant angle are only performed if a network defect exists so that a new suitable hydrogen-bonding site is offered. Computer simulation studies of water show that the necessary defect in the tetrahedral network structure is normally an additional water molecule, the so-called “fifth neighbor”,⁴⁸ at an intermediate position of the lattice. For alcohols, the nature of such defects is not completely clear at the present, particularly since there do not exist computer simulations for alcohols with predominating oleophilic part. The assumption of an additional hydrogen bond partner as the cause for dipole reorientation, however, seems to be nevertheless a promising basis for further considerations.

In conformity with computer simulation studies for water,^{53,54} let us additionally assume that the reorientation process itself resembles a switching so that it occurs in a short time compared to the dielectric relaxation time. The dielectric relaxation time is thus predominantly governed by the time for which a dipolar species has to wait until (due to thermal fluctuations) an appropriate defect, namely a suitably located and orientated additional hydrogen bond partner, exists at a given position of the network. The probability density for the occurrence of such defects decreases, of course, with increasing oleophilic part of the organic solvent molecules.

The trends in the dielectric relaxation time of associating liquids as following from this idea of dipole reorientation mechanism are confirmed by results for a variety of systems, including mixtures of monohydric alcohols with diols.⁵ Details of the relaxation mechanism are still subject to discussion and have to be clarified by further relevant measurements and computer simulation studies.

Individual Relaxation Terms. Our analysis of the measured spectra in terms of two different relaxation processes allows for some more sophisticated conclusions on the structure and microdynamics of water/diol systems. As illustrated by Figure 10, within each series of mixtures the amplitude $\Delta\epsilon_D$ of the low-frequency Debye-type relaxation term depends only weakly on the mixture composition. Due to the dilution of dipolar

species by oleophilic groups the relaxation strength decreases when going from lower to higher diol homologues. The relaxation amplitude $\Delta\epsilon_{CC}$ of the high-frequency Cole–Cole term decreases monotonously with increasing mole fraction x of diol (Figure 10). In correspondence with the relaxation time distribution parameter α_{CC} (Figure 4) and the dipole orientation correlation factor g_{eff} (Figure 7) the $\Delta\epsilon_{CC}$ values do not noticeably depend on the length of the diol molecules. Obviously, both relaxation terms contain contributions from both constituents of the mixtures. Addition of water to mixtures with high content of diol ($x \geq 0.7$) leads to a growth of the regions with higher concentration of hydrogen-bonding groups of water molecules.

Not just with respect to the form of the spectra but also in view of the relative importance of the two relaxation terms the water/diol mixtures exhibit characteristics that are different from those of the aforementioned mixtures of water with carboxylic acids. In the spectra of the latter the high-frequency relaxation is completely absent at low water content, thus suggesting a liquid structure that is formed by droplets of high carboxylic acid concentration in a suspending phase of high water concentration. However, carboxylic acids associate predominantly to cyclic dimers at small water content,^{55–60} while diols are expected to form almost fuzzy hydrogen-bonded chain structures, probably with high degree of branching. The tendency toward the formation of subphases seems, therefore, to be less pronounced in water/diol systems. This view is supported by the fact that the τ_{CC} and τ_D data for each series of alkanediol/water mixtures show an almost analogous behavior (Table 4). Both series of data nearly monotonously increase at increasing x from the water value $\tau_{w0} = 8.27$ ps to the value for the alkanediol, with a weak relative maximum in the Cole–Cole relaxation times of the propanediol and pentanediol mixtures.

5. Conclusions

Addition of water to diols has a strong influence on the dielectric spectrum. The static permittivity increases in close correspondence to water/monohydric alcohol mixtures. This increase is due to the increasing concentration of dipolar species. The effective dipole orientation correlation factor decreases with increasing water concentration, indicating that the diol structure with high degree of parallel ordering of dipole moments is successively disturbed. The characteristic relaxation times of the water/diol mixtures appear to be mainly governed by the number density of hydrogen-bonding groups or molecules. A similar behavior has been already found for mixtures of water with various other organic solvents and also with associating organic liquids. It has been discussed in terms of an entropy effect in the dielectric relaxation. However, with the diol mixtures the dependence of the relaxation time upon the number density of hydrogen-bonding species is much stronger than with mixtures of monohydric alcohols, a finding that still deserves for an explanation.

When investigated in detail the spectra of the diols and also of the water/diol mixtures reveal two relaxation processes, of which the one with longer relaxation time is attributed to regions of low density of hydrogen-bonding species. The other relaxation process, the amplitude of which decreases with diol concentration, is assumed to be due to dipole reorientational motions in regions of higher density of hydrogen-bonding groups or water molecules. The hydrogen bond network, however, seems to form a fuzzy structure rather than clear subphases of high and low diol content, respectively.

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