

Dielectric Relaxation Studies of Aqueous Long-chain Alcohol Solutions

BO GESTBLOM^a and JOHAN SJÖBLOM^{b,*}

^a Department of Physics, Uppsala University, Box 530, S-75121 Uppsala, Sweden and

^b Institute for Surface Chemistry, Box 5607, S-114 86 Stockholm, Sweden

Dielectric relaxation processes in long-chain alcohol–water mixtures have been studied using dielectric time domain spectroscopy. The dielectric spectrum has been analysed in terms of two dispersions with relaxation times τ_1 and τ_2 . The study has been performed at three different temperatures.

The influence of a varying water content, of variations in temperature and chain-length of the alcohol, on the static dielectric constant (ϵ_s) and on the main dispersion is reported. ϵ_s is lowered by an increased water content, a higher temperature and an increased lipophilic character of the alcohol. The long relaxation time τ_1 is successively shortened when the content of water is increased in the solution. A higher temperature together with a shorter lipophilic hydrocarbon chain gives a similar trend in τ_1 . The calculated activation energy decreases with an increase in the water content.

Our data are consistent with a structural model, where linear complexes of the alcohol are successively reduced in size when water is added or temperature is raised.

The self-association pattern of pure alcohols together with their structures in diluted hydrocarbon or water solutions has been the objective of intense research. Frequently used methods are spectroscopic^{1–5}, calorimetric,⁶ viscosity⁷ and dielectric^{8–10} methods. Discordant structural proposals and disunited opinions about the level of hydrogen bonding are often results from the

different investigations. Alternatives like “double-bonded” dimers, cyclic specimens, linear polymers or even a water-like structure have been considered possible from the equilibrium measurements.

In order to gain a better understanding of the mechanisms underlying the aggregation of pure aliphatic alcohols, dielectric relaxation has proved to be a powerful tool^{11–16}. In comparing different alcohols the hydrocarbon chain of the molecule should be ascribed an important role. In the case of a short alkyl chain and sufficiently high temperatures and low pressures, the breaking of hydrogen bonds seems to be the rate-determining step in the relaxation process, while the situation for longer aliphatic homologues is much more complicated.

The dielectric spectra of pure alcohols together with alcohol–hydrocarbon solutions have been studied, but for long-chain alcohol–water solutions only static dielectric measurements have been reported.^{8–10, 17–18} No systematic study on the dielectric relaxation of these solutions has been undertaken.

In this paper we report on the dielectric relaxation of n-decanol-, n-nonanol-, n-octanol-, n-heptanol-, n-hexanol- and n-pentanol- water solutions. The investigation is carried out over an interval from 28 MHz to 10 GHz. The whole concentration range up to water saturated alcohol solutions is covered. In order to calculate activation energies we have investigated the dielectric behaviour at three different temperatures, i.e. 20, 40 and 60 °C.

* On leave from Department of Physical Chemistry Åbo Akademi, Porthansgatan 3, SF-20500 Åbo 50, Finland.

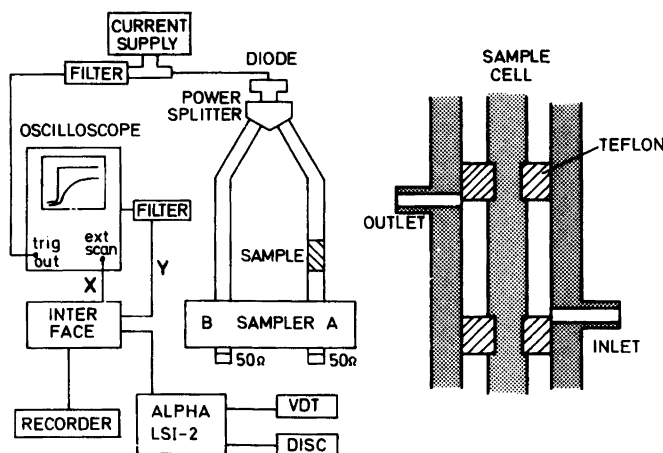


Fig. 1. Schematic diagram of the computer controlled dual channel TDS system and sample cell.

EXPERIMENTAL

Chemicals. The alcohols, n-pentanol (C_5OH) (Merck AG, Zur Analyse, 99 %), n-hexanol (C_6OH) (Merck AG, Zur Analyse, 98 %), n-heptanol (C_7OH) (Merck AG, Zur Analyse, 99 %), n-octanol (C_8OH) (Merck AG, Zur Analyse, 99 %), n-nonanol (C_9OH) (Merck AG, Zur Analyse, 97 %), and n-decanol ($C_{10}OH$) (Ega-Chemie AG, 99.5 %) were used without further purification. The water was double-distilled and ion-exchanged immediately before use.

Preparation of solutions. Samples were made by weighing appropriate amounts of the components in test tubes. These were flame-sealed and thermostated until equilibrium was attained. Usually the tubes were kept for one week at room temperature before the dielectric examination.

Experimental measurements. The total transmission time domain spectroscopy (TDS) method was used to obtain the dielectric spectra.¹⁹ The experimental set-up of the TDS spectrometer is shown in Fig. 1. The TDS measurement is based on the study of the influence of a dielectric sample on a pulse propagating in a coaxial line. The fast rising pulses are generated by a tunnel diode, divided by a power splitter into two coaxial lines, and monitored by a dual channel sampling oscilloscope. One channel serves as the measurement channel, while the other provides a fixed time reference for the proper measurement pulses.

The system is controlled by a minicomputer, which sweeps the time base of the oscilloscope

and stores the registered pulse shapes. This computer also performs the necessary numerical work on the time domain data. Further details on this set-up and the data acquisition has been given in previous papers.²⁰⁻²¹

In the total transmission TDS method an incident pulse transmitted through the empty coaxial line is first registered. The studied liquid is then injected into the sample cell and the pulse transmitted through the sample is registered. The two pulses are Fourier transformed into the frequency domain at chosen frequencies and the transmission coefficient $T(\omega)$ can be evaluated.

The theory of transmission lines gives this transmission coefficient at frequency ω as an equation in $\epsilon^*(\omega) = \epsilon'(\omega) - i\epsilon''(\omega)$. Solution of this equation for experimentally determined values of $T(\omega)$ gives the dielectric spectrum.

The minicomputer which controls the spectrometer also performs the Fourier transformations. The algorithm used is the Samulon modification of the Shannon sampling theorem.²² It also solves the functionality between $T(\omega)$ and ϵ^* using an iterative procedure. The computer first locates an interval on the ϵ' axis inside which the real part of the complex equation has a solution. It then traces the line in the complex plane, where the real part of the equation is satisfied. The point on this line, where it intersects the corresponding line for the imaginary part of the equation, defines the solution.

A sample cell is included in Fig. 1. Holes are drilled in the coaxial line to allow cleaning of the cell and the insertion and change of sample without disassembling the line. A laboratory water suction-pump is used to remove the sample

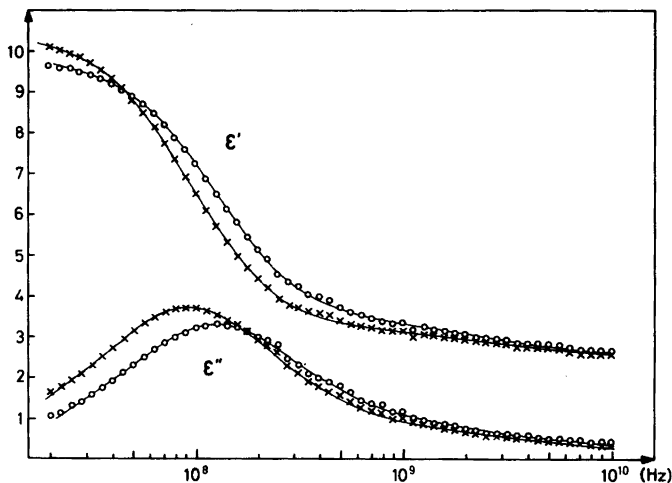


Fig. 2. The dielectric spectra of pure octanol (\times) and octanol containing 1% (w/w) water (\circ). The full drawn lines show theoretical spectra calculated from a two relaxation time model function.

and flush the cell with water, ethanol and acetone between changes of sample. The cell is surrounded by a jacket and held at constant temperature by a Thermomix thermostat. The cell length used in the present measurements is 40 mm.

At a certain temperature the measurement sequence started with the reference pulse, after which all alcohols within a series were consecutively inserted without change of instrument setting or disassembling the line. This ensures the detection of systematic changes in dielectric parameters on small changes of sample composition.

The observational time window used for all measurements was 20 ns. This is sufficiently long to allow the transmitted pulse in all cases to reach its final steady level.

RESULTS

All samples were studied at 20, 40 and 60 °C. The pulse shapes were Fourier transformed and permittivities determined at fifty frequencies between 28 MHz and 10 GHz. The chosen frequencies were evenly distributed on a logarithmic scale. Typical results are displayed in Fig. 2, where the dielectric spectrum of octanol is shown together with the spectrum obtained when 1% H₂O (w/w) is added to the octanol. Theoretical spectra, fitted to the experimental points as discussed below, are included in the figure. The decrease in static dielectric constant on the

addition of water is clearly seen, together with a shift of the main dispersion region to higher frequencies.

In addition to the main dispersion region an additional dispersion can be discerned in the microwave range. This can be more clearly²³ seen by plotting ϵ' against $\nu\epsilon''$. For a single relaxation process this plot would show a single straight line, while for several relaxation processes several straight line segments should be obtained. Fig. 3 shows such a plot for the 1% octanol–water spectrum in Fig. 2. The presence of one (or several) relaxation process(es) besides the main relaxation is clearly seen.

Garg and Smyth¹² have made frequency domain measurements on normal primary alcohols extending down to mm wavelengths. They analysed their data in terms of three different relaxation times for each alcohol. The shortest relaxation time in their analyses is of order 1ps, and the corresponding dispersion consequently falls outside the frequency range (≤ 10 GHz) accessible in TDS measurements. We have therefore chosen to analyse our data in terms of a model function with two relaxation times τ_1 and τ_2

$$\epsilon^* = \epsilon_2 + \frac{\epsilon_s - \epsilon_1}{1 + i\omega\tau_1} + \frac{\epsilon_1 - \epsilon_2}{1 + i\omega\tau_2} \quad (1)$$

In this equation ϵ_2 gives the limiting permittivity at high frequencies, $\epsilon_s - \epsilon_1$ gives the dielectric

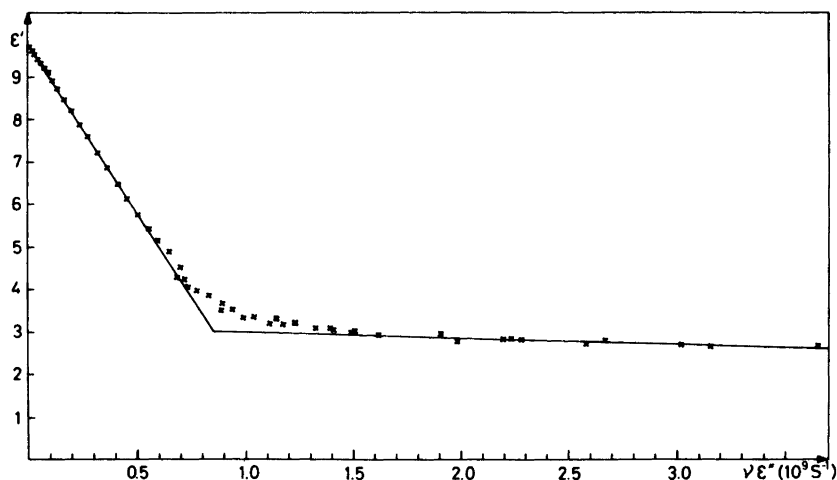


Fig. 3. Plot of ϵ' versus $\nu\epsilon''$ for the aqueous octanol solution data in Fig. 2.

increment for the main dispersion while $\epsilon_1 - \epsilon_2$ gives the dielectric increment for the high frequency dispersion.

The dielectric parameters for all samples were determined by an iterative least squares fit of calculated to measured permittivities at the 50 frequencies. A typical example of such a fit is included in Fig. 2. The root mean square deviation $|\epsilon_{\text{exp}}^* - \epsilon_{\text{theor}}^*|$ for these spectra is 0.07.

The dielectric parameters for the studied alcohol-water solutions at the three temperatures are given in Table 1.

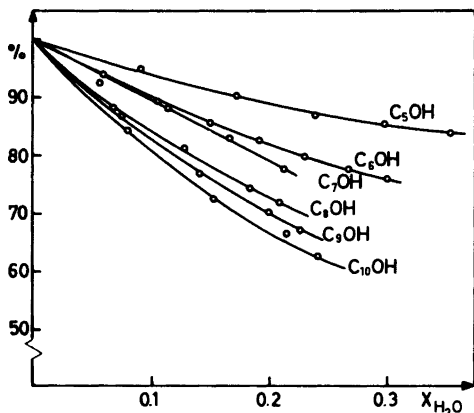


Fig. 4. Ratio between the dielectric increment $\epsilon_s - \epsilon_1$ of the aqueous alcohol solution and that of the pure alcohol versus mol fraction of water at 20 °C.

The decrease of the static dielectric constant on the addition of water, as previously reported¹⁰ is reproduced. A measure of the influence of the addition of water can be obtained from the changes in the dielectric increment $\epsilon_s - \epsilon_1$. Such a plot is given in Fig. 4, where the relative values of $\epsilon_s - \epsilon_1$ (as related to the pure alcohols) are given as function of the mol fraction of H₂O for the different alcohols.

Relaxation times for the pure alcohols have been given by Garg and Smyth,¹² based on bridge measurements. Our data differ slightly from these values. However, their data have been shown to be slightly in error^{4,24} and a satisfactory comparison cannot be made. An exception is given by heptanol for which a revised bridge analysis²⁶ gave dielectric parameters which are in excellent agreement with the heptanol data in Table 1.

The table reveals a progressive decrease of the relaxation time of the main dispersion for all studied alcohols on the addition of water to the sample. This is further brought out in Fig. 5, which plots τ_1 against mol fraction H₂O at 20 °C.

The ratio of the relaxation time on dilution with water relative to that of the pure alcohol at 20 °C is given for the whole series in Fig. 6. This relative change in relaxation time with mol fraction H₂O seems to follow a master plot as indicated in the figure. Similar master plots are found at 40 and 60 °C, however these are successively displaced a few per cent towards

Table 1. The dielectric parameters for the normal alcohols pentanol-decanol at different water contents and temperatures.

w_{H_2O}	20 °C					40 °C					60 °C				
	ϵ_s	ϵ_1	ϵ_2	$\tau_1(ns)$	$\tau_2(ns)$	ϵ_s	ϵ_1	ϵ_2	$\tau_1(ns)$	$\tau_2(ns)$	ϵ_s	ϵ_1	ϵ_2	$\tau_1(ns)$	$\tau_2(ns)$
C₅OH															
0.000	15.6	3.3	2.7	0.83	0.03	13.6	3.3	2.6	0.37	0.02	11.7	3.3	2.6	0.18	0.01
0.020	15.3	3.6	2.8	0.61	0.03	13.4	3.6	2.7	0.28	0.02	11.6	3.6	2.9	0.15	0.02
0.040	15.1	4.0	2.9	0.48	0.03	13.4	4.0	3.0	0.23	0.03	11.8	4.0	3.0	0.12	0.02
0.060	15.2	4.5	3.1	0.39	0.03	13.5	4.3	2.9	0.19	0.02	11.9	4.6	3.2	0.11	0.02
0.080	15.3	4.8	3.1	0.35	0.04	13.7	4.8	3.3	0.17	0.03	12.2	5.0	3.3	0.10	0.02
0.100	15.7	5.4	3.2	0.30	0.04	14.1	5.4	3.6	0.15	0.03	12.6	5.4	3.6	0.08	0.02
C₆OH															
0.000	13.5	3.2	2.6	1.09	0.04	11.7	3.2	2.6	0.47	0.02	10.0	3.2	2.6	0.22	0.02
0.010	12.9	3.4	2.6	0.89	0.04	11.4	3.4	2.7	0.39	0.03	9.8	3.4	2.6	0.19	0.02
0.020	12.8	3.6	2.7	0.74	0.04	11.3	3.5	2.7	0.33	0.03	9.8	3.6	2.7	0.16	0.02
0.030	12.7	3.9	2.8	0.64	0.04	11.2	3.7	2.8	0.29	0.03	9.8	3.8	2.9	0.15	0.02
0.040	12.6	4.1	2.9	0.57	0.04	11.2	4.0	2.9	0.26	0.03	9.9	4.0	2.9	0.13	0.02
0.050	12.6	4.4	3.0	0.52	0.04	11.2	4.2	3.0	0.24	0.03	9.9	4.1	2.9	0.12	0.02
0.060	12.6	4.6	3.0	0.48	0.04	11.2	4.4	3.0	0.22	0.03	10.0	4.5	3.2	0.12	0.02
0.070	12.6	4.8	3.1	0.44	0.04	11.3	4.6	3.1	0.21	0.03	10.0	4.8	3.0	0.11	0.02
C₇OH															
0.000	11.6	3.2	2.6	1.29	0.05	10.0	3.2	2.6	0.53	0.04	8.5	3.3	2.6	0.24	0.02
0.010	11.3	3.4	2.6	1.10	0.05	9.8	3.3	2.7	0.46	0.04	8.5	3.4	2.6	0.21	0.02
0.020	11.0	3.6	2.7	0.91	0.06	9.6	3.5	2.7	0.38	0.04	8.4	3.5	2.6	0.18	0.02
0.030	10.8	3.8	2.8	0.77	0.06	9.5	3.7	2.8	0.33	0.03	8.4	3.7	2.8	0.16	0.02
0.040	10.6	4.1	2.9	0.68	0.06	9.4	3.9	2.8	0.29	0.03	8.4	3.9	2.8	0.14	0.02
C₈OH															
0.000	10.5	3.1	2.5	1.73	0.06	8.9	3.1	2.5	0.66	0.03	7.5	3.1	2.5	0.27	0.02
0.010	9.8	3.3	2.6	1.28	0.06	8.5	3.3	2.6	0.51	0.03	7.4	3.3	2.6	0.22	0.02
0.020	9.5	3.5	2.6	1.01	0.06	8.3	3.5	2.6	0.41	0.03	7.4	3.4	2.6	0.19	0.02
0.030	9.2	3.7	2.7	0.88	0.06	8.2	3.6	2.7	0.35	0.03	7.4	3.6	2.7	0.16	0.02
0.035	9.1	3.8	2.7	0.80	0.06	8.1	3.7	2.7	0.33	0.03	7.3	3.6	2.7	0.15	0.02
C₉OH															
0.000	9.1	3.1	2.5	1.91	0.08	7.9	3.1	2.5	0.72	0.04	6.8	3.2	2.6	0.30	0.03
0.010	8.5	3.3	2.5	1.43	0.07	7.5	3.3	2.6	0.55	0.04	6.6	3.4	2.7	0.25	0.03
0.020	8.1	3.5	2.6	1.10	0.07	7.3	3.5	2.7	0.44	0.04	6.6	3.6	2.8	0.21	0.03
0.030	7.9	3.7	2.7	0.93	0.07	7.2	3.7	2.7	0.38	0.04	6.5	3.8	2.8	0.18	0.03
0.035	7.8	3.8	2.7	0.86	0.07	7.2	3.8	2.8	0.36	0.04	6.5	3.9	2.9	0.17	0.03
C₁₀OH															
0.000	8.1	3.0	2.5	2.21	0.08	7.0	3.0	2.5	0.81	0.05	6.0	3.1	2.5	0.32	0.03
0.010	7.5	3.2	2.5	1.58	0.09	6.6	3.2	2.5	0.60	0.05	5.8	3.2	2.6	0.25	0.03
0.020	7.2	3.5	2.6	1.24	0.09	6.5	3.4	2.6	0.48	0.05	5.8	3.4	2.6	0.20	0.03
0.030	7.0	3.6	2.7	1.02	0.07	6.4	3.6	2.6	0.40	0.04	5.8	3.5	2.7	0.17	0.02
0.035	6.9	3.7	2.7	0.93	0.07	6.3	3.7	2.7	0.37	0.04	5.8	3.6	2.7	0.17	0.03

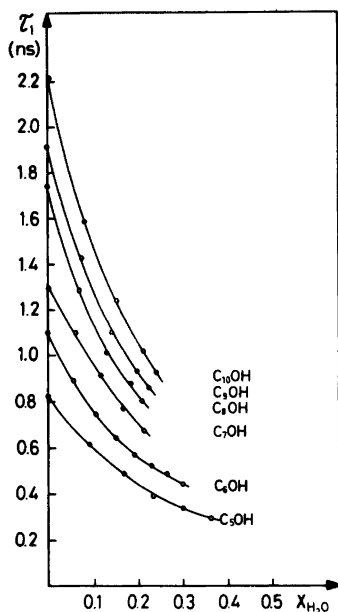


Fig. 5. Relaxation time τ_1 for the main dispersion versus mol fraction water for the different alcohols at 20 °C.

higher values with rising temperature.

Treating the dielectric relaxation as a rate process, Kauzmann²⁷ gave for the relaxation time

$$\tau = \frac{h}{kT} e^{(\Delta H_a - T \cdot \Delta S_a)/RT} \quad (2)$$

Here ΔH_a is the molar enthalpy of activation and ΔS_a is the molar entropy of activation for the dipolar reorientation process. A plot of $\ln \tau T$ against $1/T$ should therefore give a straight line from the slope of which the activation enthalpy ΔH_a can be obtained.

Typical plots are given in Fig. 7, showing results for the extremes of the studied alcohols, *i.e.* decanol and pentanol. The activation enthalpies for the whole series are summarized in Table 2.

DISCUSSION

The dielectric spectrum of the investigated pure alcohols and the alcohol-water systems is informative with respect to the static dielectric constant as well as to the relaxation processes.

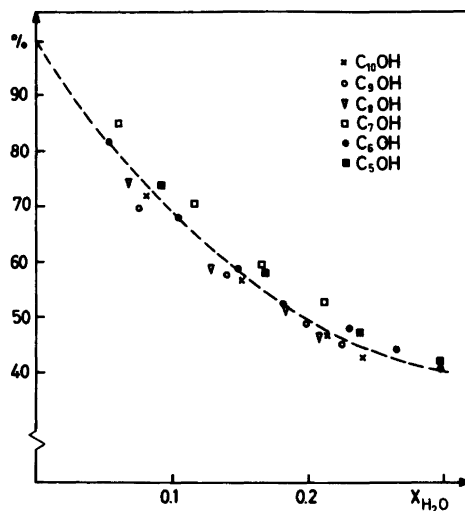


Fig. 6. Ratio between the relaxation time τ_1 of the aqueous alcohol solution and that of the pure alcohol versus mol fraction water at 20 °C.

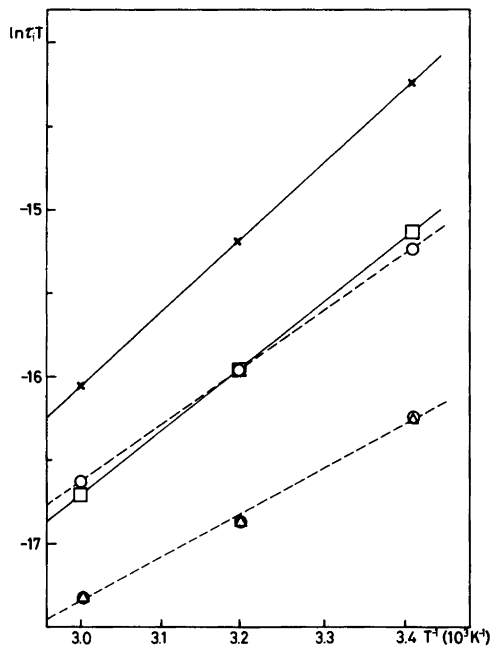


Fig. 7. Plot of $\ln \tau_1 T$ versus T^{-1} for the main dispersion in the pure decanol (\times), the 3.5 % water-decanol solution (\square), the pure pentanol (\circ) and the 10 % water-pentanol solution (Δ) respectively.

Table 2. Activation enthalpies in kJ/mol for the main relaxation process in the normal alcohol–water solutions.

$w_{\text{H}_2\text{O}}$ in	C_{10}OH	C_9OH	C_8OH	C_7OH	C_6OH	C_5OH
0.000	36.5	35.3	35.3	31.6	30.0	28.3
0.010	34.8	32.6	33.3	31.0	28.6	
0.020	34.4	30.8	31.5	30.4	28.4	26.2
0.030	33.7	30.6	31.8	29.2	26.8	
0.035	31.8	30.0	31.4			
0.040				29.2	27.4	25.6
0.050					27.2	
0.060					26.4	23.5
0.070					25.5	
0.080						22.7
0.100						21.9

Static dielectric constants. As far as the actual value of ϵ_s is considered we notice an expected increase in the dielectric constant with an increasing weight fraction of hydroxylic groups in the normal alcohol. The increase in ϵ_s for the pure alcohol is linear with respect to w_{OH} , but the slope is different for the short-chain (methanol–butanol) and long-chain alcohols (pentanol–decanol).¹⁰ Thus the number of –OH-groups seems to be important for the degree of self-association. The liquid self-associated state, stabilized by hydrogen bonds, consists of linear polymers and cyclic aggregates. The probability of cyclization decreases as the molecular weight increases.

Usually one tries to visualize the short-range dipole–dipole interactions in terms of the Kirkwood correlation factor²⁸ g given by the Kirkwood – Fröhlich equation

$$g = \frac{9kTV}{4\pi N_A \mu^2} [(\epsilon_s - \epsilon_\infty)(2\epsilon_s + \epsilon_\infty)/\epsilon_s(\epsilon_\infty + 2)^2] \quad (3)$$

where k is Boltzmann's constant, T is the absolute temperature, V is the molar volume, μ is the gas phase dipole moment, N_A is Avogadro's constant, ϵ_s and ϵ_∞ is the static dielectric constant and the optical dielectric constant, respectively. A deviation of g from unity is thus a measure of the degree of hindered molecular rotation due to short-range intermolecular forces. For associated liquids the correlation factor is generally >1 due to a predominantly parallel alignment of neighbouring dipoles. A $g < 1$ should be attributed to an antiparallel alignment. We have estimated g -values for the different pure alcohols according to eqn. (3) and found them to increase with

increasing molar mass, all values exceeding unity. Further, we found that a higher temperature reduces the value of g . Notice, however, that actual values of g should be taken with caution due to uncertainties in ϵ_∞ . We have determined ϵ_∞ according to $\epsilon_\infty = 1.1n_D$, where n_D is the refractive index at 436 nm as determined previously.²⁹ The added 10 % accounts for the contribution of the atomic polarization. The trend in the values of g indicates a more pronounced parallel alignment of the dipoles in higher alcohols. One should thus expect a predomination of linear complexes over cyclic structures as the molar mass of the normal alcohol increases. Dannhauser *et al.*^{15,25} have thus underlined the possibility of finding complexes with an open chain for normal octanol from studies on isomeric octylalcohols.

With increasing temperatures the value of g diminishes which is also the case with the static dielectric constant of each alcohol. Obviously an enhanced temperature increases the thermal energy of the monomeric units inside the polymeric species with a more frequent breakdown of the linear hydrogen bonded complexes. Lawrence *et al.*⁹ have investigated normal heptanol and branched isomers. They concluded from the decrease in ϵ_s for the pure $n\text{-C}_7\text{OH}$ with increasing temperature, that the linear multimers are reduced to smaller units. D'Aprano has come to similar conclusions from his study of the temperature dependence of the static dielectric constant of n -propanol, n -butanol, n -pentanol and n -hexanol.⁷

When water is added to a long-chain alcohol

we observe a decrease in ϵ_s in analogy with previous data. This trend in the measured dielectric constant cannot be predicted by any mixture model allowing the alcohol and water to have similar dielectric properties as in the bulk phase. It is quite obvious that the original self-associated structures of the liquids undergo remarkable changes upon mixing. This is also indicated by viscosity measurements.³⁰

From studies on n-butanol-water solutions where the static dielectric constant is almost horizontal for the lowest water contents, Brown and Ives¹⁷ have suggested a structure where each water molecule should bind four alcohol molecules. This tetrahedral structure should have a vanishing dipole moment.

According to our opinion linear complexes might predominate for the normal long-chain alcohols. Rupturing this degree of self-association, i.e. adding water or raising the temperature (see Table 1) results in lower molecular complexes which are more dynamical in nature and thus less hindered to reform hydrogen bonds. These conclusions can be drawn from the static dielectric constant and its temperature and concentration dependence.

Dielectric dispersion. The dielectric spectrum of pure, normal alcohols in their liquid forms is characterized by three different relaxation regions.¹² Of these the predominating one is the low frequency Debye-like dispersion with a long relaxation time τ_1 . The fast relaxation with the shortest relaxation time τ_3 ($\tau_3 \approx 3$ ps) is usually concentration independent.¹² The intermediate relaxation with τ_2 25–50 ps is dependent on the alcohol concentration.¹² As seen from Table 1 τ_1 is usually of the order 1–2 ns for the long-chain alcohols but decreases fast as the chain-length of the alcohol is reduced.

Physically τ_3 has been interpreted in terms of monomeric $-\text{CH}_2\text{OH}$ or $-\text{OH}$ group rotation. The magnitude of τ_3 is independent of molecular size and agrees with the relaxation due to the fast rotation of the hydroxylic group in phenols.³¹ Thus it seems that evidence for an interpretation of τ_3 in terms of hydroxylic group rotation about the C–O bond in monomer alcohol molecules has been obtained. The magnitude of τ_2 is dependent on the molecular size suggesting some type of molecular rotation for this relaxation process. The simplest model for this intermediate process is a monomer rotation.¹² This process has

also been claimed to represent a weighted average of a monomer and one or more polymer species.²⁵ The short relaxation times τ_2 and τ_3 also exist in solutions of isomeric alcohols, where the hydroxylic group is sterically hindered and prevents an association to linear complexes. Thus it seems that the short relaxation times τ_2 and τ_3 should, despite some unexpected behaviour in concentration dependence of the dispersions, primarily represent monomeric $-\text{OH}$ rotation about a C–O bond, and a monomeric molecular relaxation, respectively.

The low-frequency relaxation τ_1 has been the subject of much discussion and speculation. It has been shown from studies on octyl alcohol isomers, that this process does not occur in solutions where the $-\text{OH}$ group is effectively shielded like 3-methyl-3-heptanol.¹⁵ In order to predominate the dielectric spectrum this low-frequency dispersion is accompanied by high g -values of the alcohol. According to several authors^{14,15,32} τ_1 is a relaxation time connected with a break-up of linear alcohol complexes. Probably this takes place in such a way that a breaking of hydrogen bonds together with a monomer molecular reorientation is involved. The theory based on linear alcohol polymers has been opposed. If a solution should be built up by this kind of aggregate one should naturally expect a size distribution among the species and hence the main dispersion should also reveal a certain distribution of relaxation times. However, such a distribution has not been reported. Furthermore it does not seem to be within the scope of this theory that the found activation energy of the process clearly exceeds 20 kJ mol^{-1} , which is the usually accepted value for a break-up of hydrogen bonds. These facts have rendered Bordewijk *et al.*³³ to introduce highly polar cyclic tetramers in order to account for the absence of a distribution in τ_1 . For alcohols with low g -values and an absence of the low-frequency dispersion the same authors suggest a lower degree of association, i.e. no higher multimers than dimers should be present in these solutions. Although the nature of this process giving rise to τ_1 is not in detail clarified, it should involve a breaking of hydrogen bonds together with a monomeric or polymeric reorientation. The breaking of the hydrogen bond is a prerequisite for dipolar reorientation, but the whole process is cooperative and the interaction depends on the local

environment. In this way one can account for the long relaxation time together with the functionality between τ_1 and the hydrocarbon chain length of the alcohol.

Tables 1 and 2 and Figs. 4–7 summarize the effects of water addition on the dielectric spectra of the alcohols. The reduction of ϵ_s is accompanied by an increase in ϵ_1 , when adding water, leading to reduction in the dielectric increment as seen in Fig. 4. The immediate interpretation would be in terms of a break-up of linear chains with a reduction in polymer species and a concomitant increase in low molecular moieties. This effect is most pronounced for the alcohol with the longest hydrocarbon chain, *i.e.* decanol.

The variations in ϵ_2 in Table 2 cannot be molecularly interpreted since it does not represent the true optical dielectric constant given by n_D^2 . In order to do so the complete spectrum >10 GHz must be analysed and a third relaxation time introduced.

The present study gives a detailed picture of the main relaxation in the normal alcohols and its variation with chain length of the alcohol, temperature and water content. The main feature of τ_1 as seen from Table 1 and Fig. 5, is a lengthening of the relaxation time with increasing chain length. An addition of water causes a marked shortening of τ_1 . This shortening of the relaxation time is also observed on temperature increase. The calculated activation enthalpies are given in Table 2. For the studied alcohols we find an activation energy which is larger than the simple hydrogen bond energy of 20 kJ/mol, increasing from 28 kJ/mol for pentanol to a value of 37 kJ/mol for decanol. This trend in ΔH_a suggests that for the higher alcohols the bond breaking cannot be the rate-determining step in the relaxation process. The long relaxation time together with the high activation energy point also at the importance of the local structure in the polymeric unit when determining the details of the relaxation process.

Fig. 5 shows the successive shortening of the relaxation time τ_1 , on the addition of water, again with the largest absolute effect for the longest chain alcohol, decanol. On a relative scale, however, the changes are comparable as seen in Fig. 6. Taking the derivative $d\tau_1/dx_{H_2O}$ as an indicator on the influence of water on the alcohol structure, the initial addition brings about the largest change in all investigated alcohols. The

reduction in τ_1 on water addition further supports the conclusion drawn from Fig. 4, *i.e.* an effective rupturing of the original hydrogen bonds in the linear chains. In the activation energies (Table 2) this is observed as a marked reduction in ΔH_a on dilution with water.

CONCLUSIONS

The addition of small amounts of water to the long-chain normal alcohols pentanol–decanol has a strong influence on the dielectric spectrum. The static dielectric constant ϵ_s decreases with increasing water content, the effect augmenting with the lengthening of the alkyl chain. Together with the reduction in ϵ_s the dielectric increment $\epsilon_s - \epsilon_1$ for the low frequency dispersion is reduced on water addition, this effect on a relative scale again increasing with the alkyl chain length.

The relaxation time τ_1 for the main dispersion shortens on the addition of water. The initial introduction of water causes the largest effect in all alcohols studied. Although in absolute terms the change in relaxation time increases with increasing chain length, the relative change on water addition seems to be nearly the same for all studied alcohols.

On increasing temperature the static dielectric constant ϵ_s drops for both the pure alcohols as well as for the alcohol–water solutions. The relaxation τ_1 shortens on temperature increase and the activation enthalpy for this process is increased with alkyl chain length. Addition of water reduces the activation enthalpies the effect being largest for the longest chain alcohols. The strong influence of water on the dielectric properties of the alcohols can be understood as an effect of the rupturing of the linear complexes believed to predominate in pure long-chain alcohols. Rupturing these complexes reduces the correlation of molecular dipoles, leading to a lowering of the static dielectric constant. The increase in monomeric units simultaneously reduces the relative importance of the dielectric increment of the low frequency dispersion. This relaxation requires the breaking of hydrogen bonds in the molecular complexes, and is dependent on the local environment as due to different chain lengths of the alcohols. The rupturing of the molecular chains increases the probability of a molecular reorientation on the

breaking of hydrogen bonds, leading to the observed shortening of relaxation times.

In the frequency range studied we observe changes in the alcohol structure. Although our study does not directly permit us to draw so detailed conclusions about the structural changes in water, we have not disregarded these in the discussion. The specific changes in water should be investigated at higher frequencies as reported previously.³⁴

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