

## Dielectric Relaxation Study of Aqueous Methanol–Butanol Solutions. A Comparison with Higher Homologues

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The dielectric spectra of short-chain alcohol-water mixtures have been studied using dielectric time domain spectroscopy. On addition of water the static dielectric constant  $\epsilon_s$  of the solutions increases, in contrast to what is found in long-chain alcohol-water mixtures. The main relaxation time  $\tau_1$  is successively shortened with increasing water content. For long-chain alcohols the relative change in  $\tau$  follows a common curve. With decreasing chain length the deviation from this curve becomes gradually more pronounced.

Recently the influence of small volume fractions of water on the dielectric spectra of higher n-alcohols was investigated.<sup>1</sup> The static dielectric constant was found to decrease on water addition, a result which cannot be expected if a dielectric mixture formula is applied to these solutions.<sup>2</sup> Strong influence on the dielectric relaxation is also observed, with a shortening of the main relaxation time for all studied alcohols.

The influence of adding non-polar solutes on the dielectric spectra of some n-alcohols has also been reported. The initial addition of cyclohexane to ethanol, propanol and butanol lengthens the main relaxation time  $\tau_1$ , while the opposite effect is found in octanol and decanol.<sup>3,4</sup>

Addition of water to the short-chain normal alcohols, which are completely miscible with water, does not lower  $\epsilon_s$ . On the contrary the C<sub>1</sub>–C<sub>3</sub> homologues show a continuous increase in  $\epsilon_s$  with increasing water content.<sup>5,6</sup> This

behaviour indicates that the dissolution processes when dissolving water in short-chain or long-chain alcohols are different. The results from the cyclohexane-alcohol solutions also point to differences in the association structures. The influence of water addition to ethanol and 2-propanol has been studied at low temperature, where an increase in the principal relaxation time was found.<sup>7</sup> This is the opposite effect to the findings for the long-chain alcohols at room temperature.<sup>1</sup> In view of the above results we have found it important to complete our study of the influence of water addition on the dielectric spectra of normal alcohols, and report in this communication the results for n-butanol, n-propanol, ethanol and methanol solutions at room temperature.

### EXPERIMENTAL

**Chemicals.** The alcohols, methanol (C<sub>1</sub>OH) (Merck AG, *zur Analyse*, 99.5%), ethanol (C<sub>2</sub>OH) (Oy Alko Ab, 99.5%), propanol (C<sub>3</sub>OH) (Merck AG, *zur Analyse*, 99%) and butanol (C<sub>4</sub>OH) (Merck AG, *zur Analyse*, 99.5%) were used without further purification. The water was double-distilled and ion-exchanged immediately before use. Solutions were prepared as described earlier.<sup>1</sup>

**Measurements.** The permittivities were obtained by the total transmission time domain spectroscopy (TDS) method as described in Ref. 1. Spectra were evaluated at forty-five frequencies, evenly distributed on a logarithmic scale between 28 MHz and 10 GHz. In a measuring sequence all alcohol mixtures within a series were consecutively inserted without change of instrument setting or disassembling the coaxial line.

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This ensures the detection of systematic changes in the dielectric parameters on small changes of sample composition. The sample lengths and time windows used were chosen to give good accuracy in the relaxation time determinations. However, the changes in  $\epsilon_s$  with sample composition are well reproduced also with the used sample lengths. For the methanol series the sample length was 10 mm, otherwise 20 mm. The time window used in the butanol series was 20 ns, otherwise 10 ns. Measurements were performed at 20, 40 and 60 °C, except for the methanol solutions due to the low boiling points.

## RESULTS

Measurements on pure, normal alcohols higher than ethanol have shown that the dielectric spectrum <10 GHz can be analyzed in terms of two dispersions.<sup>1</sup> We have therefore analyzed our data at different angular frequencies for the butanol and propanol series in terms of a model function with two relaxation times  $\tau_1$  and  $\tau_2$ ,

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

$\epsilon_s - \epsilon_1$  gives the dielectric increment for the main dispersion, while  $\epsilon_1 - \epsilon_2$  gives the dielectric increment for the high frequency dispersion. The dielectric parameters were determined by an iterative least squares fit of the model function to

Table 1. The dielectric parameters at 20 °C for propanol and butanol at different water contents.

	$\epsilon_s$	$\epsilon_1$	$\epsilon_2$	$\tau_1/\text{ns}$	$\tau_2/\text{ns}$
<i>w</i> <sub>H<sub>2</sub>O</sub> in C <sub>3</sub> OH					
0.00	19.9	4.1	3.1	0.38	0.04
0.02	19.9	3.9	3.1	0.35	0.03
0.04	20.1	4.1	3.3	0.29	0.03
0.06	20.4	4.5	3.2	0.25	0.03
0.15	23.1	5.9	3.3	0.16	0.02
<i>w</i> <sub>H<sub>2</sub>O</sub> in C <sub>4</sub> OH					
0.00	18.0	3.5	2.8	0.58	0.02
0.02	18.2	3.7	2.8	0.46	0.02
0.04	18.2	4.1	3.1	0.37	0.02
0.06	18.5	4.5	3.2	0.32	0.03
0.10	19.2	5.5	3.6	0.25	0.04
0.14	20.3	6.7	3.7	0.21	0.04

Table 2. The dielectric parameters at 20 °C for methanol and ethanol at different water contents.

<i>w</i> <sub>H<sub>2</sub>O</sub>	C <sub>1</sub> OH			C <sub>2</sub> OH		
	$\epsilon_s$	$\epsilon_1$	$\tau_1/\text{ps}$	$\epsilon_s$	$\epsilon_1$	$\tau_1/\text{ns}$
0.00	33.5	5.6	57	25.2	4.4	0.19
0.02	34.6	5.5	56	26.2	4.5	0.17
0.04	35.9	5.8	57	27.6	5.0	0.16
0.06	36.3	5.7	57	28.1	4.9	0.15
0.15	40.7	6.0	52	31.5	5.8	0.11
0.25	45.4	7.0	47	35.6	6.8	0.08

experimental data. The results are given in Table 1.

For the ethanol and methanol series the secondary dispersion falls outside the studied frequency window<sup>8</sup> and these data were consequently fitted to a single relaxation time model function. These results are given in Table 2.

Treating the dielectric relaxation as a rate process, Kauzmann showed that the temperature dependence of the relaxation time can be represented by<sup>9</sup>

$$\tau_1 = \frac{h}{kT} \exp(\Delta H_a - T \cdot \Delta S_a) / RT \quad (2)$$

$\Delta H_a$  is the molar enthalpy of activation, while  $\Delta S_a$  is the molar entropy of activation for the dipolar reorientation process.  $\Delta H_a$  was determined from straight line plots of  $\ln(\tau_1 \cdot T)$  versus  $T^{-1}$ . The results are given in Table 3, and it is seen that the effect of water addition on the change in  $\Delta H_a$  decreases with chain length.

## DISCUSSION

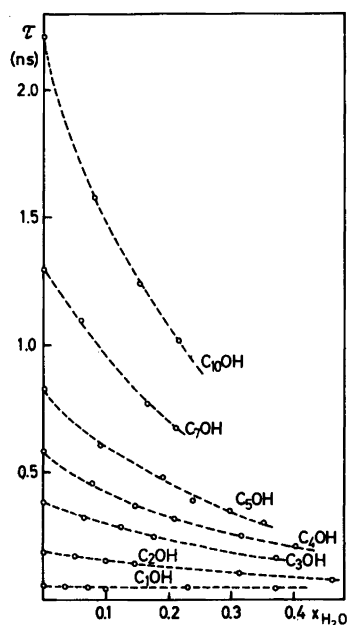
Long-chain alcohols are characterized by a long  $\tau_1$  and a high  $\Delta H_a$ . The dielectric properties of these liquids can be understood in terms of predominantly linear alcohol complexes where the dipoles are highly correlated and possess a limited ability to reorient.<sup>10</sup> The relaxation time  $\tau_1$  is markedly reduced when water is added to the alcohol or the temperature is raised, a consequence of breaking of the structure of the alcohols with an increasing possibility for the molecules to reorient. The observed lowering of  $\epsilon_s$  and reduction in  $\Delta H_a$  is in agreement with this picture.

**Table 3.** Activation enthalpies in kJ/mol for the main relaxation process in some alcohol water solutions.

$w_{\text{H}_2\text{O}}$	$\Delta H_{\text{C}_2\text{OH}}$	$\Delta H_{\text{C}_3\text{OH}}$	$\Delta H_{\text{C}_4\text{OH}}$
0.00	17	26	26
0.02	17	26	25
0.04	17	25	25
0.06	18	25	24
0.10			23
0.14			21
0.15	17	24	
0.25	17		

Structurally, the short-chain homologues deviate from the long-chain homologues by their ability to form cyclic units with a high exchange probability, which decreases the correlation of the dipoles. The reduced tendency of parallel alignment of dipoles is accompanied by a shorter relaxation time  $\tau_1$  and a lower activation enthalpy  $\Delta H_a$ .

In contrast to the effect of adding cyclohexane,<sup>3,4</sup> the addition of water to ethanol,

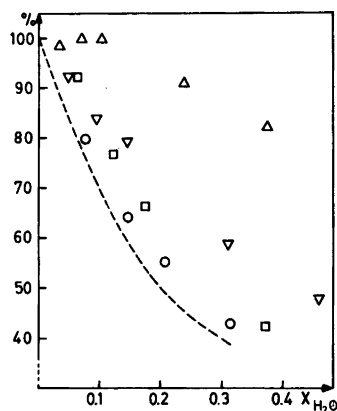


**Fig. 1.** Relaxation time for the main dispersion ( $\tau_1$ ) versus mol fraction water for the different alcohols at 20 °C.

propanol and butanol shortens the relaxation time (Fig. 1). The effect is similar to that of the higher alcohols, although its magnitude is markedly lower. The curves in Fig. 1 display the influence of the water molecules on the self-association of the alcohols. In this respect the derivative,  $d\tau_1/dx_{\text{H}_2\text{O}}$  as  $x_{\text{H}_2\text{O}}$  approaches zero, can be taken as a measure on the strong initial interaction between alcohol and water molecules. The lower alcohols are characterized by numerically small derivatives which can even be zero as for methanol-water solutions.

Fig. 2 summarizes the effects of adding water to different n-alcohols. With a decreasing chain length the deviation from the curve for the long-chain alcohols becomes gradually more pronounced. The divergent behaviour of methanol is also found in  $\epsilon_s$  where the methanol-water solutions are characterized by a linearity in the increase of  $\epsilon_s$  on water addition, as seen from Table 2 and earlier shown in Ref. 6.

Deviating from the other alcohols the methanol-water solutions have a constant  $\tau_1$ . This could indicate that this alcohol has a self-association pattern similar or at least reminiscent of that of water. The linearity in  $\epsilon_s$  of these solutions also gives rise to a speculation regarding an ideal behaviour, *i.e.* the solution obeys dielectrically an additivity rule  $\epsilon_s = \epsilon_1^0 \phi_1^0 + \epsilon_2^0 \phi_2^0$ , where  $\phi_i$  is the volume fraction and  $\epsilon_i^0$  is the dielectric constant of the pure component *i*. From this behaviour one



**Fig. 2.** Relative change in  $\tau_1$  versus mol fraction water for butanol (○), propanol (□), ethanol (▽) and methanol (△) at 20 °C. The dotted line summarizes the result for all the higher alcohols, see Ref. (1).

could postulate larger coexisting domains of water and methanol. The constancy of  $\tau_1$  of  $C_1OH$  upon water addition does not contradict this picture. On the other hand a model with complete interchangeability of the methanol and water molecules leaving the local dipolar environments essentially unaltered cannot be ruled out in the interpretation of Fig. 1.

The opposing effects on the dielectric relaxation when adding cyclohexane or water to the short-chain alcohols indicate that different mechanisms influencing the structure are operative in these two cases. The lengthening in  $\tau_1$  can be due to a restricted rotation of the alcohol molecules in the presence of the bulky cyclohexane molecules.<sup>4</sup>

The increase of relaxation times on addition of water, observed at low temperatures, for ethanol and 2-propanol solutions,<sup>7</sup> on the other hand, was suggested to show that the water molecules inhibit the alcohol relaxation by forming bonds between chains. It can be expected that such an effect can only dominate at very low temperatures, near or below the melting point.

It is clear that quantitative details about the associated structure of alcohols and its variation with chain length are difficult to obtain. However, it is also clear that systematic dilution studies of dielectric relaxation can add valuable information.<sup>4</sup> Further work in this direction should be pursued, to complete the now somewhat patchy picture.

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