# Dielectric Behaviour of Some Pure Normal Alcohols and their Binary Mixtures

M. A. M. Eid, I. K. Hakim, K. N. Abd-El-Nour, A. L. G. Saad and M. Stockhausen[a]

National Research Centre, Microwave Physics Department, Cairo (Egypt)
[a] Institut für Physikalische Chemie der Universität Münster, D-48149 Münster (Germany)

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The pure 1-alkanols $C_4$ to $C_{12}$ and seven of their short/long chain binary equimolar mixtures are investigated by static and dynamic dielectric measurements up to 36 GHz at 20, 30 and 40 °C. The apparent dipole moment and the relaxation parameters from a three Debye term analysis of the spectra are discussed. The mixtures are found to behave like a one component alcohol of mean chain length. An odd-even effect is revealed by comparison of mixtures containing $C_{11}$ with those containing $C_{12}$ as long chain mixture component.

## Introduction

Dielectric spectroscopy is a source of information about the structure and dynamics of liquids. The fluctuation-dissipation theorem connects the measured loss spectrum $\varepsilon''(\omega)$ to the polarization fluctuation spectrum of the macroscopic sample [1], and having regard to appropriate macro-micro relations, dielectric spectroscopy is a suitable method to investigate the microscopic stochastic motion of those constituents of the sample matter which are polar. Alcohols are a large class of molecules having in common the polar hydroxy group, thus undergoing essentially the same interactions *via* hydrogen bonding. They have extensively been studied in pure form as well as in mixtures with nonpolar solvents. Remarkably enough, the spectral shape is often close to a Debye function, with some minor additional contribution on the high frequency side. The dynamics of association (in quite a broad sense) rather then single molecule rotational tumbling motion is responsible for the main relaxation contribution of these liquids. There is still some debate in the literature concerning a detailed picture of microdynamics [2]. Nevertheless, valuable information can be drawn in particular from *comparative* dielectric studies of alcohols.

In recent years, mixtures of two alcohols have attracted increasing interest. Most of these studies dealt with mixtures of mono and dihydric alcohols (e.g. [3–5]), while comparatively little information is available on the dielectric behaviour of mixtures of two monohydric alcohols.

In the present work the static permittivity and the dielectric spectrum are studied for the series of pure 1-alkanols $C_4$ to $C_{12}$ (1-butanol to 1-dodecanol, marked by the chain length as **4** to **12**, respectively) and seven of their binary, equimolar mixtures ($0.5\ C_m + 0.5\ C_n$) consisting of a short and a long chain component as given in the following by the short labels *m/n*:

Equimolar mixtures with 1-undecanol:
**4/11, 5/11, 6/11, 7/11;**
with 1-dodecanol:
**4/12, 5/12** and **6/12**.

## Experimental

The dielectric properties were determined for frequencies ranging between 2 MHz and 36 GHz by use of various apparatus at laboratories in Cairo and Münster.

The static permittivity $\varepsilon_s$ was measured at 2 MHz using a WTW dipolemeter with an uncertainty of about 2%.

For frequencies from 100 to 400 MHz an open parallel wire resonator was employed, loaded with the dielectric sample and operated according to Drude's second method [6, 7]. With this device, $\varepsilon'$ as well as $\varepsilon''$ are obtained with an accuracy of about 2%. Covering the frequency range of that apparatus once more, various setups were used for frequencies from 10 MHz to 36 GHz: A VHF bridge up to 90 MHz and coaxial or waveguide resonators above 300 MHz [8], except for 36 GHz, where the reflection of the sample cell was measured directly. These setups were used for the measurement of $\varepsilon''$ only (accuracy about 5%).

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Reprint requests to Prof. Abd-El-Nour; Fax: 0020-2-3370-931.

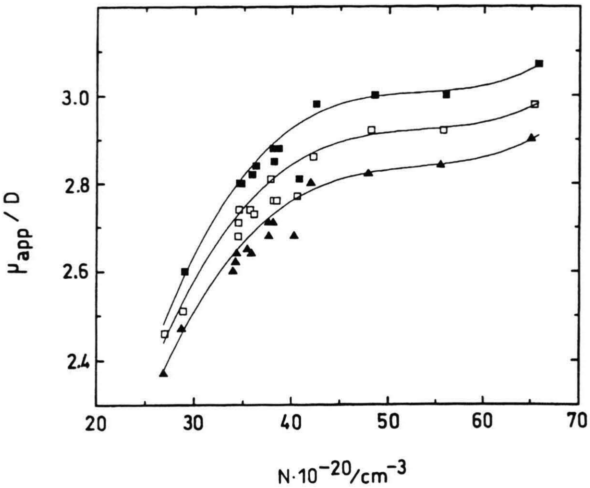

Fig. 1. Apparent dipole moments $\mu_{app}$ vs. dipole density $N$ for the pure alcohols and the equimolar binary mixtures studied. Symbols for temperatures: ■ 20 °C, □ 30 °C, ▲ 40 °C.

In addition, the refractive index $n_D$, density $\rho$ and viscosity $\eta$ were determined.

All measurements were done at 20 (except for **12**), 30 and 40 °C.

Substances from Aldrich, Fluka, and Merck were used without further purification.

## Results and Discussion

### *Static Permittivity and Apparent Dipole Moment*

From $\varepsilon_s$ and $\varepsilon_\infty = n_D^2$ the apparent dipole moment $\mu_{app}$ was calculated according to the Onsager relation [9]. To compare the different alcoholic systems, it is useful to refer to the molar concentration or, equivalently, to the number density $N$ of dipoles (here: of molecules). The dependence of $\mu_{app}$ on $N$ is illustrated graphically in Figure 1. The data for each temperature are fitted by a third order polynomial which shall serve as guideline to the eye. It is evident from Fig. 1 that the apparent moment $\mu_{app}$ shows roughly the same correlation with the dipole density $N$ regardless whether it is obtained for a pure alcohol or a binary mixture. This means that the apparent moment depends essentially on the mean distance between the polar groups.

### *Dielectric Spectra and Relaxation Parameters*

The measurements of $\varepsilon'$ and $\varepsilon''$ in the 100 to 400 MHz range cover the main relaxation region of the systems studied. Together with the static permittivity $\varepsilon_s$, they allow for a satisfactory description by one Debye type spectral function. To illustrate this, Fig. 2 shows results for **9** (at three temperatures) which appear as semicircles in the complex permittivity plane.

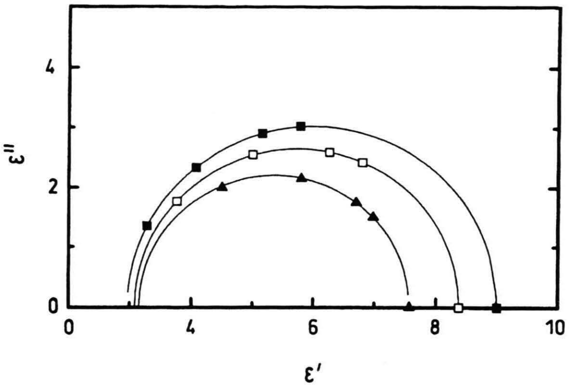

Fig. 2. Cole-Cole plot ($\varepsilon''$ vs. $\varepsilon'$) for 1-nonanol **9**. Frequencies (except for $\varepsilon_s$): 100 to 400 MHz. Symbols for temperatures as Figure 1.

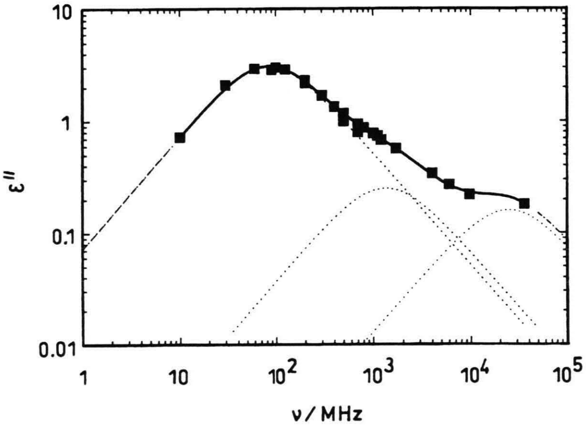

Fig. 3. Absorption spectrum, $\varepsilon''$ vs. frequency $\nu$, of 1-nonanol **9** at 20 °C. The fitting curve shown is the sum of three Debye type components (dotted).

Considering the broader range of frequencies for which $\varepsilon''$ has been measured, a good agreement of $\varepsilon''$ values is found in the overlapping frequency region. However, the results for the extended frequency range can no longer be described by one Debye term. We found that the best fitting of data was obtained by a superposition of three Debye terms, where the lower frequency term (relaxation strength $S_1$, relaxation time $\tau_1$) is the predominating one. An example of the $\varepsilon''$ spectrum and the fitting curve is illustrated in Figure 3. The fitting param-

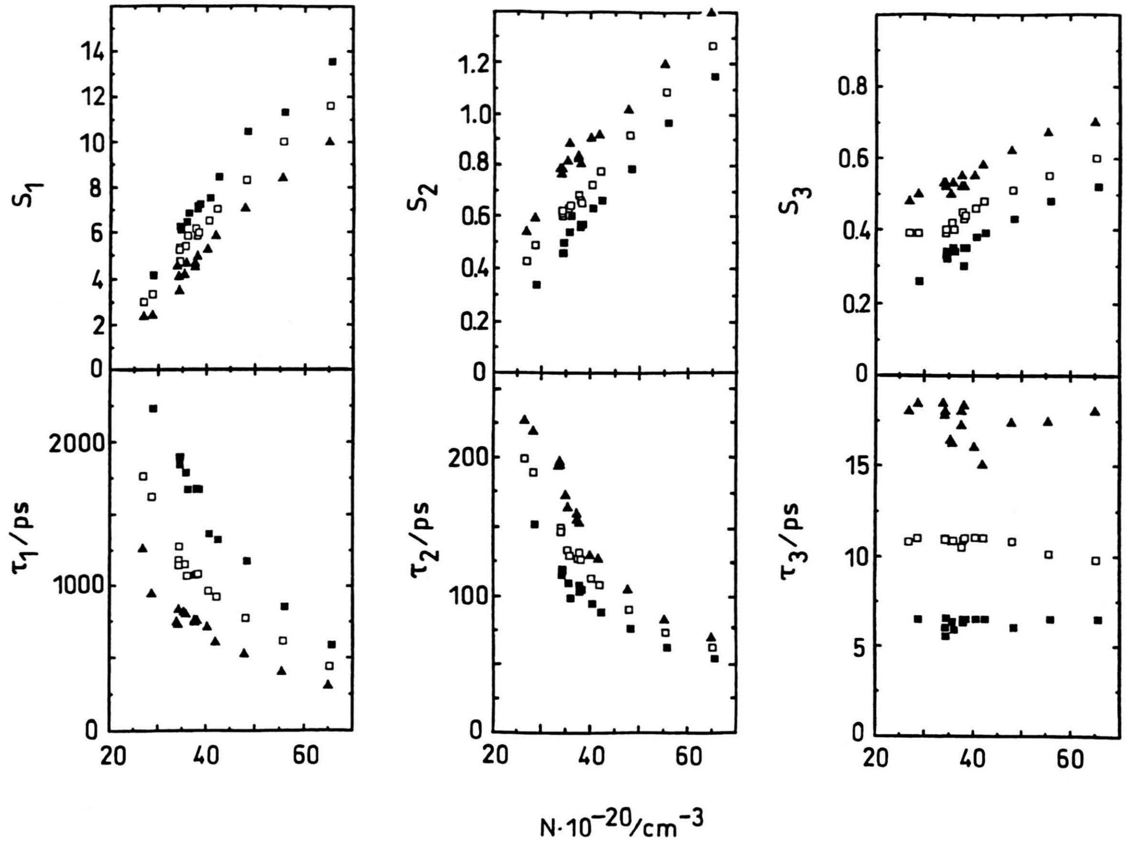

Fig. 4. Collection of the relaxation strengths $S_i$ and relaxation times $\tau_i$ (according to a three Debye term analysis) vs. dipole density $N$ for the pure alcohols and the equimolar binary mixtures studied. Symbols for temperatures as Figure 1.

eters, that are the relaxation strengths $S_i$ and the relaxation times $\tau_i\,(i=1\ldots3)$, are collected for all systems studied (pure alcohols and mixtures) in Figure 4.

Since the $S_i$ are loosely related to the static-optical dispersion step $\varepsilon_s - n_D^2$ and therefore to the apparent moment $\mu_{\mathrm{app}}$, it is not unexpected that the $S_i$ are found to depend essentially on the dipole density $N$. It is, however, a remarkable finding that the relaxation times $\tau_i$ follow such a common trend, too. Thus the equimolar binary mixtures resemble a 'mean' alcohol in their dynamic dielectric behaviour. For example, when 1-hexanol **6** is mixed with 1-dodecanol **12**, the mixture **6/12** behaves dielectrically like 1-nonanol **9**.

The fitting parameters of the minor spectral components have a certain variability range and will therefore not be regarded further. The parameters for the principal spectral term, on the other hand, are fairly certain. The main relaxation time $\tau_1$ from Fig. 4 is displayed in Fig. 5 in semilogarithmic manner against the dipole density $N$ in order to show that there is a surprisingly good correlation of exponential character (with a correlation factor better than 0.99 in ln $\tau_1$). It is interesting to note that a corresponding correlation is found between viscosity $\eta$ and dipole density $N$ (Figure 6).

Closer inspection of the data reveals an interesting peculiarity within the general $\tau_1 - N$ correlation. Let the equimolar mixture of two alcohols $C_n$ and $C_m$ be considered. The corresponding 'mean' alcohol is $C_x$, with $x=(n+m)/2$. If $x$ is not an integer, some property to be discussed may be taken as average from the next neighbouring alcohols on both sides of $x$. Now, regarding $\tau_1$ as property under discussion, the relaxation time $\tau_1^{(m,n)}$ calculated as $\tau_1^{(m,n)}=(\tau_1^{(m)}+\tau_1^{(n)})/2$ may generally be unequal to the value $\tau_1^{(x)}$ as found empirically for the 'mean' alcohol $C_x$ or from the correlation illustrated in Figs. 4, 5 for the corresponding density $N^{(x)}$. (Note that $N^{(x)}$ is approximately obtainable as weighted average from the *inverse* of densities $N^{(m)}$ and $N^{(n)}$, so that the ef-

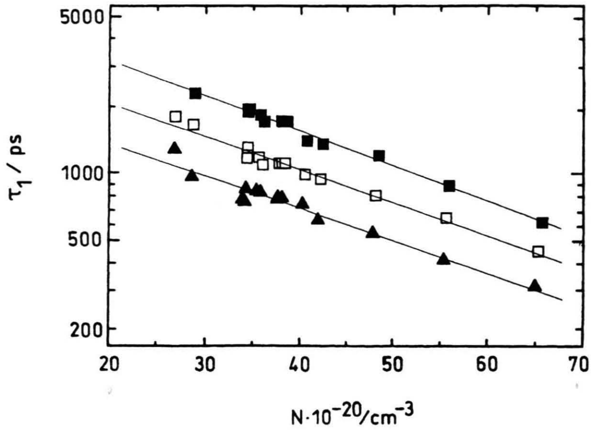

Fig. 5. Main relaxation time $\tau_1$ vs. dipole density $N$. Same $\tau_1$ as Fig. 4, but semilogarithmic plot. Symbols for temperatures as Figure 1.

Table 1. Ratio of the relaxation times $\tau_1^{(m,n)}$ and $\tau_1^{(x)}$ defined in the text. The values given are averaged for the three temperatures at which the equimolar $C_m/C_n$ mixtures have been studied.

| Mixture | $\tau_1^{(m,n)}/\tau_1^{(x)}$ | Mixture | $\tau_1^{(m,n)}/\tau_1^{(x)}$ |
|---|---|---|---|
| **4/11** | $0.96_5$ | **4/12** | $0.73_2$ |
| **5/11** | $0.96_2$ | **5/12** | $0.75_3$ |
| **6/11** | $0.96_7$ | **6/12** | $0.78_0$ |
| **7/11** | $0.95_4$ | | |

fect to be described is not directly evident from Figs. 4, 5.) Table 1 summarizes some ratios of the fictitious relaxation time $\tau_1^{(m,n)}$ and the experimental $\tau_1^{(x)}$ for short/long chain mixture combinations. It is obvious that the mixtures containing **11** behave different from those containing **12**. The chain length of the shorter mixture component seems to be of insignificant influence. Attempts to correlate these findings on $\tau_1^{(m,n)}/\tau_1^{(x)}$ to other properties of the mixtures, e.g. to the excess volumes [10], were not successful. Probably the differences between **11** and **12** are to be considered as an odd-even effect, which conclusion is in agreement with previous results [11–15].

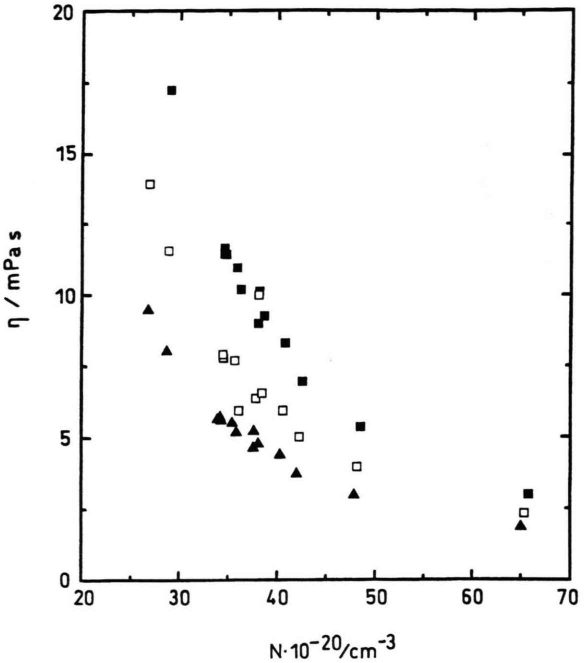

Fig. 6. Viscosity $\eta$ vs. dipole density $N$ for the pure alcohols and the equimolar binary mixtures studied. Symbols for temperatures as Figure 1.

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