Non-rotational Mechanism of Polarization in Alcohols

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Supporting Information

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1. Samples preparation

For our experiments we used five primary alcohols listed in Table S1. All samples were purchased from the same manufacturer (Sigma-Aldrich), except ethanol (Fisher Chemical), and used as received. We used the samples with the highest available purity, i.e. 99.9%, except for decanol with only 98% purity, which explains the dispersion of the corresponding data on dc conductivity (see Fig. 2 of the main text). During the measurements, we found that if part of the probe is in contact with air, absorbed water vapor might affect the dielectric parameters of alcohols. However, this change only applies to static conductivity. The rest of the spectrum, above a few megahertz, was absolutely unaffected by atmospheric moisture over the time interval of the measurements, typically around one hour. Nevertheless, the influence of impurities on the static conductivity of alcohols should in principle be accounted for when considering previous published data on dc conductivity [46,47] (main text), as the samples used in these works had lower purity (see Table S1).

Table S1: List of alcohols used in this study in comparison with those from previous research.

Alcohol	This work	Ref. [46]	Ref. [47]
Methanol	Sigma-Aldrich, 99.9%	Fluka, 99.8%	Panreac, 99.8%
Ethanol	Fisher Chemical, 99.9%	Fluka, 99.8%	Fluka, 99.8%
1-Propanol	Sigma-Aldrich, 99.9%	Fluka, 99.5%	Fluka, 99.5%
1-Butanol	Sigma-Aldrich, 99.9%	Fluka, 99.5%	Fluka, 99.5%
1-Decanol	Sigma-Aldrich, 98%	-	-

2. Measurement procedure

The low- (megahertz), and high-frequency (gigahertz) measurements were performed using different sample holders and measuring cells. Alcohols were placed into measurement cells

using Finnpipette renewed after each usage. The cell was washed with ethanol before each measurement and stored in a liquid to be measured for 5 minutes, heated up to 40°C. The dc measurements cell was thermally stabilized using acetone as a thermal conductive liquid, Peltier cooler for temperature control, and Pt1000 thermocouples for accurate temperature measurements. For the gigahertz region measurements, we used a copper bath, in which the sample in the glass beaker was tightly inserted. The open-end coaxial probe was applied at the liquid-air interface. At low frequencies, we used a cylindrical Teflon cell with two round-flat gold electrodes of 1 cm^2 each and separation about 1 mm. The complex impedance was measured by the four-electrode method [41] (main text), as each alcohol was passing through the space between the electrodes at a constant flow rate controlled by the peristaltic pump.

The measuring rms voltage V_{ac}=100 mV and signal intensity 45 dB were chosen well below the electrolysis stability threshold, 1.23 V, and such that the sample temperature and chemical composition remain stable. The low- and high-frequency measurements show comparable data for the static dielectric constant, and also for the static conductivity, which confirms the validity of our experimental approach. The real, ϵ', and imaginary, ϵ'', parts of the complex dielectric permittivity are calculated from the measured complex impedance $Z^* = Z' + Z''$ with:

$$
\begin{aligned}
\epsilon'(\omega) &= \frac{1}{C_0} \frac{-Z''}{\left(Z'^2 + Z''^2\right)\omega} \\
\epsilon''(\omega) &= \frac{1}{C_0} \frac{Z'}{\left(Z'^2 + Z''^2\right)\omega}
\end{aligned}
$$

where C_0 is the capacitance of the empty cell. The dynamical conductivity is then obtained with its definition: $\sigma(\omega) = \epsilon''(\omega)\epsilon_0\omega$.

3. Self-diffusion and dielectric relaxation

The self-diffusion coefficient of molecules in liquids can be measured independently by two main methods, which give similar results: isotopic substitution, and spin-echo NMR. The data on self diffusion of oxygen, and hydrogen atoms in alcohols, obtained by these methods are available in Refs. [46,47] (main text). For our study, it is important to know the mean square displacement x of atoms on the timescale of the dielectric relaxation time τ_r, which can be obtained using the self-diffusion coefficients D calculated with the Smoluchowski formula $x = (6D\tau_r)^{1/2}$. Values are given in Table S2 for all alcohols considered in our work. As the molecular diffusion in liquids demonstrates hoping-like behavior,[1] it would be informative to compare x with the distance d between centers of molecules. As one can see from Table S2, $x > d$; hence, over the relaxation time τ_r, each molecule covers at least one intermolecular distance as it moves, or, in other words, changes its local environment. This means that inasmuch as dielectric relaxation in associated liquids (including alcohols) is a collective phenomenon, no cluster-like structures made of several molecules can explain the dielectric relaxation, as they simply cannot last sufficiently long for such a relatively long time as τ_r.

Table S2: Self-diffusion and dielectric relaxation parameters of primary alcohols.

n	1	2	3	4	10
τ_r (ps)	54	177	370	549	1989
D (nm$^2\cdot$ns^{-1})	2.44	1.16	0.60	0.50	0.12
x (nm)	0.88	1.11	1.16	1.28	1.21
d (nm)	0.50	0.57	0.62	0.66	0.84

References

(1) J. Frenkel, *Kinetic theory of liquids* (Clarendon Press, Oxford, 1946).