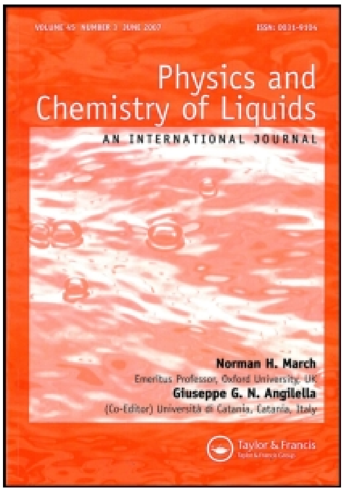

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DIELECTRIC RELAXATION OF GUAIACOL IN SOLUTION AND IN ITS PURE LIQUID STATE

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The dielectric spectrum of guaiacol in toluene solution (mole fraction 0.3 to 1) has been measured over the whole absorption region at 20, 40 and 60 °C. The results are discussed with regard to *intra* and *inter*molecular hydrogen bonding effects. Intramolecular interactions appear to be predominant. Only the 'anomalous' relation between relaxation time and viscosity is indicative of intermolecular interactions which, however, remain comparably weak even in the pure liquid.

Keywords: Dielectrics; hydrogen bonding

It has been shown by various methods that phenolic OH groups are capable of forming intramolecular hydrogen bonds to electron donating substituents in *ortho* position. An example of those compounds is guaiacol (o-methoxyphenol). Its dipole moment as measured in dilute solution indicates a cis orientation of OH with respect to OCH_3. For the pure liquid, on the other hand, a competition of internal and external hydrogen bonding is feasible. Information on the interplay of those interactions can be expected from dielectric relaxation data. Dynamic dielectric studies of guaiacol, however, are sparse and are dealing only with dilute solutions in nonpolar solvents [1–3]. It seems worthwhile to extend those studies to higher concentrations and to the pure liquid in order to find out whether *intra* and *inter*molecular effects are discernible.

We have studied guaiacol from moderately concentrated solutions (mole fraction $x \geqslant 0.3$) up to its pure liquid state, using toluene as diluent since this is a (practically) nonpolar molecule of similar size and structure. The dielectric relaxation spectrum was measured at spot frequencies ranging between some ten MHz and 72 GHz. Temperatures were 20, 40 and 60 °C. Pure guaiacol could be kept liquid at room temperature.

The shape of the loss spectrum $\varepsilon''(\omega)$ is in all cases rather close to the Debye function and can therefore satisfactorily be described by the sum of two Debye type spectral components C_i:

$$\varepsilon''(\omega)=\sum_i S_i \frac{\tau_i\omega}{1+\tau_i^2\omega^2}.$$

Relaxation times τ_i and relaxation strengths S_i are shown graphically in Figure 1. An extrapolation of these parameters to the dilute solution region gives good agreement with the dilute solution data reported for guaiacol in related solvents (p-xylene [1], benzene [2]).

Regarding the overall behaviour which is represented by the total relaxation strength ΣS_i (but could likewise be described by the static permittivity ε_s) it is a remarkable finding that (to within experimental uncertainty) ΣS_i varies in proportion to the concentration c of the polar component, which means that the apparent dipole moment μ_{app}

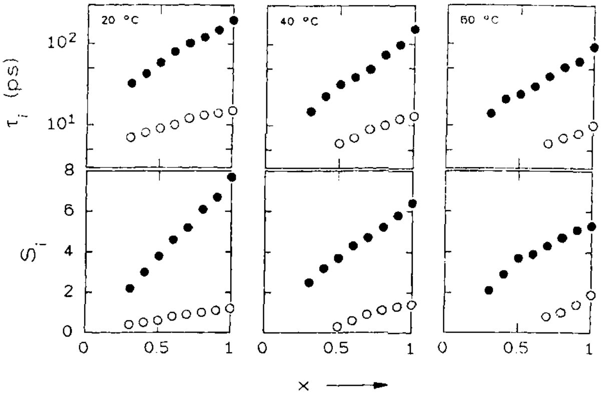

FIGURE 1 Relaxation times τ_i and relaxation strengths S_i of guaiacol in toluene solution, against guaiacol mole fraction x, 20 °C (left) to 60 °C (right). Spectral components: ● C_1, ○ C_2.

stays nearly constant. The moment has been calculated using the Onsager equation (putting $\varepsilon_\infty = n_D^2$) and, for comparison, the immersion model [4] (with $\varepsilon_\infty = \varepsilon_s - \Sigma S_j$). The results differ only little and are practically independent of temperature and concentration: $\mu_{app} = (2.40 \pm 0.05)$ D. This value agrees fairly well with literature data (2.35 [2] to 2.45 D [5] in benzene).

Some semiquantitative considerations may be based on the assumption of independent group moments $\mu_1 = \mu(OH)$ and $\mu_2 = \mu(OCH_3)$. For the purpose of rough estimations we assume that $\mu_1 = 1.60$ D, moment angle $\vartheta_1 = 60°$ (as for phenol [6–9]), and $\mu_2 = 1.25$ D, $\vartheta_2 = 65°$ (as for methoxybenzene [9–16]). The moment torsion about the bond directions is denoted by α_1, α_2, where $\alpha_{1,2} = 0$ means moments in the plane of the phenyl ring, the OH moment pointing towards OCH_3 and the OCH_3 moment in a corresponding direction, *i.e. trans* with respect to OH.

The experimental $\mu_{app} = 2.40$ D is consistent with $\alpha_1 = 0$, independent of α_2, which is the *cis* orientation of OH conjectured already in the literature. However, all combinations of α_1 and α_2 feasible with an angle of 65° between the group moments will yield the same μ_{app} value.

The approximate constancy of μ_{app} indicates that this describes essentially a single molecule property. The moment does not give any significant hint at orientational correlation and, correspondingly, at *inter*molecular hydrogen bonding effects, even not in the pure liquid case.

Turning to the dynamic parameters, the order of magnitude of τ_1 suggests that the major spectral component C_1 reflects the tumbling motion of whole molecules (subsequently, this will be regarded further), while the minor component C_2 (with $\tau_2 \approx 5 \cdots 15$ ps), the weight of which tends to increase with increasing temperature, is likely to originate in some uncorrelated internal motion of the OH and/or OCH_3 groups. Some group motion relaxation times reported in the literature may be quoted for comparison: OH (phenol) $\approx 1 \cdots 2$ ps in dilute solution [17]; OCH_3 (methoxybenzene) $\approx 5 \cdots 9$ ps in dilute solution as a result of hindered rotation [11, 18–21], but only $\approx 2 \cdots 3$ ps in the pure liquid [22, 23].

The Arrhenius activation enthalpy derived from the main relaxation time τ_1 is in the order as usually found with non-associating liquids. For pure guaiacol: $\Delta H_{\tau 1} \approx 14$ kJ/mol (while, for example, often values

> 30 kJ/mol are observed with associating liquids such as alcohols). The activation enthalpy for viscous flow is clearly higher: $\Delta H_\eta \approx 23$ kJ/mol for pure guaiacol.

For an assessment of the relaxation time τ_1 it is informative to regard its relation to viscosity η, as represented in Figure 2. This figure shows also values for two reference molecules which are unlikely to undergo specific interactions, namely benzonitrile and benzophenone. The former was chosen as a benzene derivative of similar size as guaiacol, while the latter was added because data are available for a broader viscosity range so that it can serve as an illustrative example. It may be seen from these comparative data that they obey a rough correlation of the $\tau_1 \sim \eta^a$ type, where $a < 1$, thus less than the value $a = 1$ predicted by Debye's hydrodynamic model. Empirically, $a < 1$ has been found to be the 'normal' case for numerous quasi-rigid molecules relaxing by single molecule rotational tumbling motion [4, 30, 31]. The present guaiacol data, however, exhibit a markedly

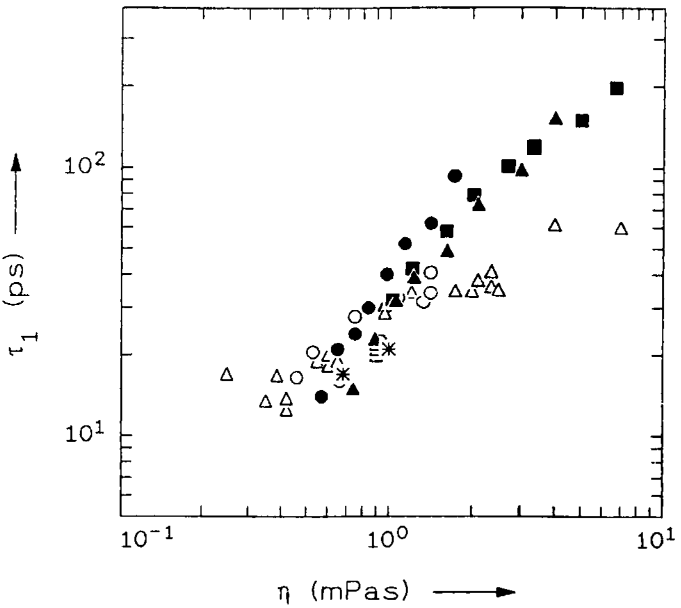

FIGURE 2 Main relaxation time τ_1 against viscosity η, ■ 20 °C, ▲ 40 °C, ● 60 °C. Dilute solution values from [2] (solvents benzene and CCl_4, 20 °C) are denoted by ∗. -For comparison: ○ benzonitrile (dilute solutions to pure liquid), 20 °C [24]; Δ benzophenone (dilute solutions only), 20 or 25 °C [25–29].

steeper increase of τ_1 with η, in particular in the higher temperature case.

Before discussing that peculiarity, it should be stressed that the range of absolute τ_1 values found is still consistent with the assumption that the tumbling motion of single molecules is the main relaxation mechanism. For *low* guaiacol concentrations this is obvious from the comparative data shown in Figure 2. But even for *high* concentrations, where, in comparison, τ_1 appears to be too long, a rough estimate on the basis of $\tau_1 - \eta$ values from the above-mentioned body of empirical data [31] shows that a tumbling entity should have an effective radius of about 0.48 nm, which is not unreasonable for a single guaiacol molecule but rules out the involvement of distinct higher complexes such as guaiacol dimers.

The apparently 'anomalous' viscosity dependence of τ_1 is therefore likely to relate to relaxation mechanisms which are operative in addition to the 'normal' tumbling motion. These may be of (i) *intra*molecular or (ii) *inter*molecular character.

(i) Assuming 'normal' single molecule motion for the *high* concentration range, the unexpectedly steep decrease of τ_1 on dilution could be ascribed to *internal* fluctuations. One has to invoke an additional process somewhat faster than, but practically indistinguishable from, the overall tumbling motion. Indeed, an intermediate spectral component C_x of that kind can formally be found in a modified analysis of spectra by introducing a *constrained* relaxation time τ_1 as extrapolated according to 'normal' behaviour from the $\tau - \eta$ values at high concentration. Such an additional process, if existent, is likely to differ in character from an uncorrelated group fluctuation since this is suspected to give rise to the minor component C_2 rather than contributing to the C_1 region. Although according to semiempirical (PCILO) calculations [32] the planar conformation is the most stable one, it may therefore tentatively be assumed that there is a secondary out-of-plane direction of the OCH_3 moment (as found for methoxybenzene [33]), perhaps even of the OH moment. If so, a concerted inversion mechanism could be taken into consideration. We have estimated the amplitude necessary to account for the relaxation strength of C_x, using the group moments quoted above but restricting α_1 and α_2 to those combinations which keep the total moment equal to the experimental

μ_{app}. Under these assumptions a sufficient moment component perpendicular to the ring plane is found only for unreasonable torsion angles ($\alpha_1 \approx 70°, \alpha_2 \approx 35°$). Thus internal motion alone can scarcely account for the 'anomalous' behaviour.

(ii) Assuming 'normal' behaviour for the *low* concentration range, the unexpectedly steep increase of τ_1 on increasing concentration could be interpreted as due to some kind of weak *inter*molecular interaction, slowing down the tumbling motion otherwise related to viscosity as usual. A behaviour of similar kind has been found in some cases of solute-solvent interactions [31]. For the present system it would be a matter of weak solute-solute (*viz.* guaiacol) interactions, possibly arising from the competition of *inter* and *intra*molecular hydrogen bonding. Naturally deviations from the planar conformation of guaiacol are prerequisite for those interactions, too.

In conclusion, since it is not possible to make a distinction on the basis of dielectric results, mechanisms according to assumptions (i) and (ii) may both contribute to the peculiar relaxation behaviour of guaiacol. Concerning the introductory question both assumptions lead to the same qualitative inference anyway: The *intra*molecular interaction between OH and OCH_3 group is seemingly somewhat loosened on increasing concentration, but it remains strong enough to withstand the formation of hydrogen bonds to neighbouring guaiacol molecules to a dielectrically ascertainable degree even in the bulk state. Because of that the overall dielectric behaviour of guaiacol resembles that of non-associating rather than associating substances for its whole concentration range.

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