

Dielectric Properties of 4-Cyanobiphenyl in 1,4-Dioxane Solution

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The static and dynamic dielectric properties of the title system are reported for a concentration series from about 8 mmol/l up to 2.3 mol/l at 20°C. The apparent moment (4.2 D, extrapolated to infinite dilution) decreases with increasing concentration, the relaxation time increases proportional to viscosity, that is, somewhat steeper than usually observed. Comparison with other molecules suggests that these features are mainly due to the high dipole moment rather than being specifically related to the prolate shape of the molecule. The broadening of the spectrum toward the high frequency side, on the other hand, may be due to the molecular shape.

Introduction

The molecule 4-cyanobiphenyl (CB, 4-biphenylcarbonitrile) consists essentially of a mesogenic group from which, by substitution in 4 and 4' position, various compounds can be derived which are well known as capable of forming liquid crystals. The question may be raised as to whether 4-cyanobiphenyl itself, at sufficiently high concentration in the liquid state, might exhibit peculiarities due to its prolate shape, pointing already toward the properties of those derivatives. In this regard a closer examination of its dielectric behaviour seems worthwhile. By comparison with other substances one can hope to see whether there are deviations from 'normal' behaviour of both the static permittivity ϵ_s , which yields the apparent molecular moment μ_{app} , and thus structural information, and of the dielectric relaxation spectrum, particularly the relaxation time τ , which yields information on the reorientational motion.

Since CB is solid at ambient temperature, solutions in nonpolar solvents at concentrations as high as possible should be taken into consideration. To our knowledge dynamic dielectric data have been determined only for dilute solutions [1]. The present communication reports therefore the dielectric properties

of CB in 1,4-dioxane solution over a broad concentration range. The solvent dioxane was chosen because of good solubility ($c_{max} \approx 2.4$ mol/l at 20°C). For comparison, we have also measured dielectric spectra of benzonitrile (BN), a molecule containing the same polar group, which, however, is of a more spherical form.

Experimental

The static permittivity ϵ_s of the CB/dioxane system was measured for concentrations $c = 0.008 - 2.3$ mol/l at the frequencies 1.5 kHz and 2 MHz. The dynamic dielectric properties of CB/dioxane were determined for dilute solutions ($c = 0.008 - 0.25$ mol/l) with a swept-frequency transmission spectrometer which could be utilized at frequencies between 200 MHz and 13 GHz. For medium and high concentrations ($c = 0.9, 1.6$ and 2.1 mol/l), several setups were employed, covering the range between 30 MHz and 71 GHz by about 15 spot frequencies. Viscosities η were measured, too, usually with capillary viscosimeters, but at the highest concentration also with a rotation viscosimeter.

For benzonitrile (BN), the dynamic dielectric properties were measured in its pure state and for mixtures with dioxane, n-heptane and cyclohexane at medium and high concentrations similar to those of the CB/dioxane system.

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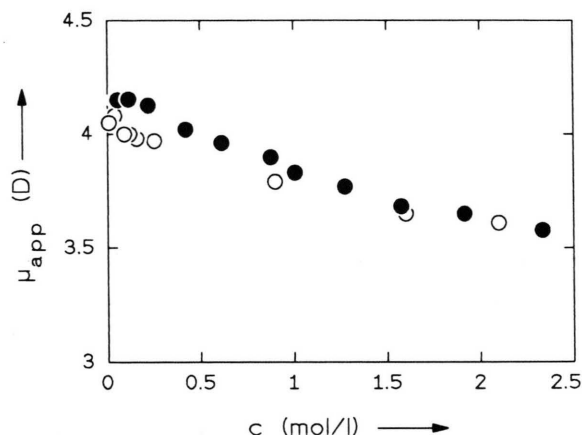


Fig. 1. Apparent dipole moment μ_{app} of 4-cyanobiphenyl in 1,4-dioxane as dependent on concentration c , 20°C. Full symbols: Calculation using the Onsager equation [2], putting $\epsilon_{\infty} = n_D^2$. Open symbols: Calculation using the immersion model [3], putting $\epsilon_{\infty} = \epsilon_s - S$.

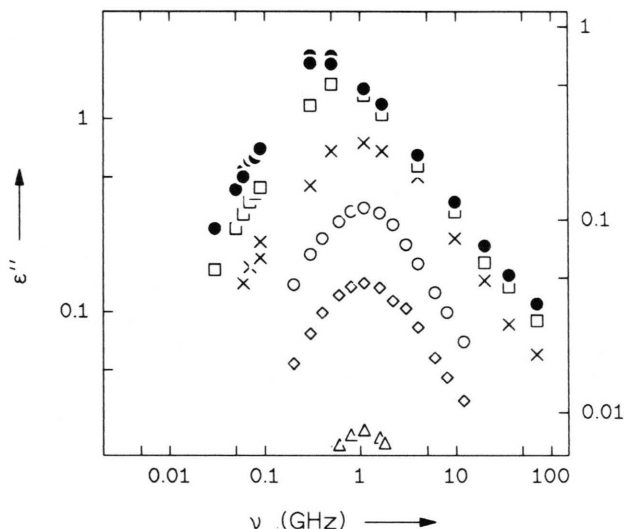


Fig. 2. Imaginary part of permittivity, ϵ'' , vs. frequency ν (log-log-plot) for 4-cyanobiphenyl solutions in 1,4-dioxane, 20°C. — Concentrations \bullet 2.1, \square 1.6, and \times 0.9 mol/l: left scale. Concentrations \circ $118 \cdot 10^{-3}$, \diamond $47 \cdot 10^{-3}$, and \triangle $8.1 \cdot 10^{-3}$ mol/l: right scale (which is shifted by the factor 3).

Chemicals from Aldrich were used as obtained. The temperature was 20°C in all cases.

Results

The static properties are summarized in Fig. 1, which shows the apparent moment μ_{app} of CB as de-

Table 1. Relaxation parameters τ , S , and β (Cole-Davidson fit) of 4-cyanobiphenyl in 1,4-dioxane at 20°C. First group of data: Measurements up to 13 GHz. Second group of data: Measurements up to 71 GHz.

c mol/l	τ ps	S	β
$8.14 \cdot 10^{-3}$	155	$16.5 \cdot 10^{-3}$	0.92
$38.8 \cdot 10^{-3}$	165	$80.5 \cdot 10^{-3}$	0.90
$47.3 \cdot 10^{-3}$	160	$100 \cdot 10^{-3}$	0.89
$90.7 \cdot 10^{-3}$	150	$180 \cdot 10^{-3}$	0.95
$118 \cdot 10^{-3}$	170	$245 \cdot 10^{-3}$	0.92
$158 \cdot 10^{-3}$	155	$315 \cdot 10^{-3}$	0.94
$253 \cdot 10^{-3}$	165	$515 \cdot 10^{-3}$	0.94
0.90	240	1.90	0.71
1.60	330	3.40	0.72
2.10	420	4.55	0.73

duced from ϵ_s and $\epsilon_{\infty} = n_D^2$ by use of the Onsager formula [2]. Values obtained with $\epsilon_{\infty} = \epsilon_s - S$ according to the immersion model [3], where S is the relaxation strength found by dynamic measurements, are added for comparison.

The dynamic properties of CB/dioxane are represented by some $\epsilon''(\omega)$ spectra in Figure 2. It may be noted that the maximum stays at practically constant frequency for dilute solutions but is shifted toward lower frequencies at higher concentrations. The spectra can well be fitted within experimental uncertainties by a Cole-Davidson (CD) function, notwithstanding that in the double logarithmic plot there is a very slight positive curvature at the highest frequencies measured, indicating a weak additional absorption region (possibly the onset of Poley absorption as found with dilute solutions at still higher frequencies [1]).

The fitting parameters, that is relaxation time τ , relaxation strength S and CD skewness parameter β , are recorded in Table 1. The noticeable difference between the β parameters of the low concentration group of data and that for medium and high concentration is due to fitting both groups of data by one CD function, although they cover different experimental frequency ranges; it could formally be evaded by using a higher β value and introducing an extra high frequency term with about 25–30 ps relaxation time in case of the latter group of data. The 'effective' relaxation time τ_{eff} which describes the $\epsilon''(\omega)$ maximum, however, is unaffected by the type of analysis. In case of the CD function, $\tau_{eff} \approx \tau\beta$.

Discussion

The monotonous decrease of the apparent Onsager moment μ_{app} on increasing concentration (Fig. 1), which is substantiated by the apparent moment estimated by use of the simple immersion model, resembles the findings with other highly polar molecules (e.g. acetonitrile) and should therefore not be regarded as a peculiarity of CB. It can be ascribed to orientational correlation with increasing preference of opposite moment directions, very probably as a result of dipole–dipole interactions. Extrapolated to infinite dilution, the Onsager moment is $\mu_{app} = 4.2_0$ D, in satisfactory agreement with literature data (4.3_4 D in benzene, 25°C [4]).

An assessment of the relaxation behaviour is facilitated by consideration of the relaxation time in its relation to viscosity. The appropriate quantity for that purpose is the 'effective' relaxation time τ_{eff} which describes the $\epsilon''(\omega)$ maximum. For a broad variety of quasi-rigid, non-associated molecules relaxing via their tumbling motion, a correlation between τ_{eff} and the viscosity η was found empirically, which in a double log representation is roughly linear, τ_{eff} values for a given molecule lying within an octave bandwidth for different concentrations in quite different solvents and even for the pure state [3, 5, 6]. The main parameter of that correlation is the 'effective' molecular radius, so that molecules of similar shape and size exhibit similar relaxation times in liquids of similar viscosity. Accordingly, we compare in Fig. 3 the $\tau_{eff} - \eta$ data for the nitriles under consideration with those available for closely related substances. Figure 3 represents (a) the data for 4-cyanobiphenyl (CB) solutions and (b) for benzonitrile (BN) in the pure state and in solution, as measured in this work, both together with literature values also for related compounds, where the CN group is replaced by another, less polar substituent (Cl, Br or NH_2).

A $\tau_{eff} - \eta$ comparison would be complicated if the viscosity, as feasible in case of concentrated solutions of rod like solute molecules, should be an ill defined quantity. We have therefore measured the rheological behaviour of a concentrated CB/dioxane solution with a rotation viscosimeter. It appeared to be of Newtonian type; to within experimental uncertainty there is no deviation from linearity in the shear stress vs. angular velocity plot.

Part (a) of Fig. 3 shows points for biphenyl derivatives. It may first be seen that the $\tau_{eff} - \eta$ literature

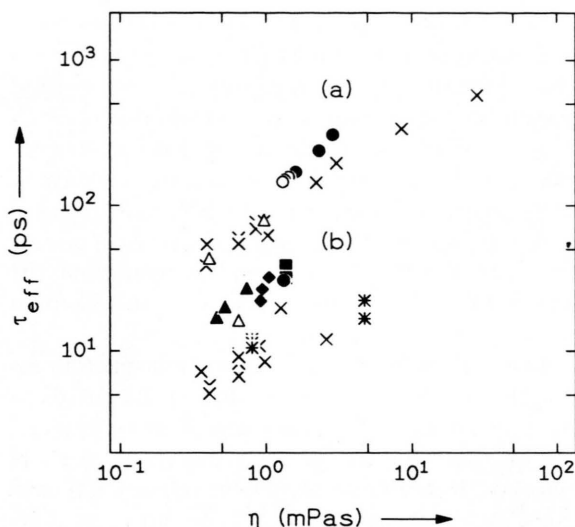


Fig. 3. Effective relaxation time τ_{eff} (characterizing the maximum of $\epsilon''(\omega)$) vs. viscosity η , 20°C (log-log-plot). – (a) Biphenyl derivatives $\text{Ph}_2\text{-X}$. Cyanobiphenyl, $\text{X}=\text{CN}$: ● conc./dioxane, ○ dil./dioxane, △ dil./other solvents [1]. – For comparison, $\text{X}=\text{Br}$, NH_2 : × dil./various solvents [5–10]. – (b) Phenyl derivatives Ph-X . Benzonitrile, $\text{X}=\text{CN}$: ■ pure [11, 12], ● conc./dioxane, ▲ conc./n-heptane, ◆ conc./cyclohexane, △ dil./other solvents [13]. – For comparison, $\text{X}=\text{Cl}$, NH_2 : * pure [14–18], × dil./various solvents [1, 13, 19–23].

data for dilute solutions of CB and of comparative substances with Br or NH_2 substituents obey a good correlation. The slightly different size of these molecules does not play a significant role. It should be mentioned that molecules of differing shape and moment direction (e.g. benzophenone derivatives [24]) which, however, have a long semiaxis of similar magnitude, exhibit a long relaxation time in accord with this correlation even in concentrated solutions or as pure substances. Thus it seems permissible to compare CN compounds with related ones where the polar substituent is similar in size.

Regarding now the CB/dioxane concentration series (Fig. 3), the dilute solutions exhibit slightly increased τ_{eff} values which, however, are still consistent with those of the comparative systems to within the scatter of the empirical $\tau_{eff} - \eta$ correlation. It is remarkable, however, that the log-log slope is clearly larger (≈ 1) than expected from that correlation. On increasing concentration the τ_{eff} values tend to exceed the comparative values significantly.

To see whether those features are peculiar to CB, it is sufficient to take a glance at the data of phenyl

systems depicted in part (b) of Fig. 3: They exhibit qualitatively similar features. Comparing solutions of similar viscosity, the τ_{eff} values of benzonitrile (BN) appear to be longer than for the other derivatives in all cases. The BN/dioxane mixture series is not very noticeable in the $\tau_{\text{eff}} - \eta$ representation since it stays at nearly constant values, but with BN/cyclohexane a steep slope is found, as for the CB/dioxane concentration series. For BN/heptane, on the other hand, the slope is smaller. The nature of the solvent is likely to play a role in that respect.

In view of these findings it seems unjustified to ascribe the above-mentioned features of the CB/dioxane system principally to the *shape* of the polar molecule involved. Rather the high *moment* of the CN group may have an influence on the relaxation time in case of both biphenyl and phenyl derivatives by slowing down the reorientational motion more than expected from the usual $\tau_{\text{eff}} - \eta$ correlation. This effect may for the most part be due to solute-solute dipole forces as the variation of the apparent moment of CB in dioxane solution, but it may reflect solute-solvent interactions in addition.

Concerning the introductory question, we conclude from those comparisons that the dielectric behaviour of CB even in concentrated dioxane solution is 'normal' in the sense that the features regarded so far are unlikely to be specifically related to its prolate shape.

Finally we remark briefly upon the non-Debye character of the CB spectrum. If one changes to its

above-mentioned description employing an additional higher frequency spectral component, this appears in roughly the same range as the BN spectrum (considering comparable viscosities). Assuming that the additional component relates to a physically distinguishable process, it can therefore be ascribed to a tumbling motion determined by an effective radius in the order of approximately one phenyl ring, that is tumbling of the CB molecule around its long axis. Even a weak, though non-vanishing, moment component μ_{\perp} perpendicular to that axis may suffice to cause a noticeable relaxation contribution, provided that the tumbling motion does not simply correspond to the semimacroscopic molecule-in-continuum model, since then it is possible that the respective contribution may be intensified in comparison with its 'normal' weight $(\mu_{\perp}/\mu)^2$ [24]. This assumption is not unlikely to be applicable in the case of CB. Consequently, the *broadening* of the CB spectrum might be regarded as due to the prolate *shape* of the 4-cyanobiphenyl molecule, in accordance with the observation that, on the other hand, BN spectra can be described by a Debye function.

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