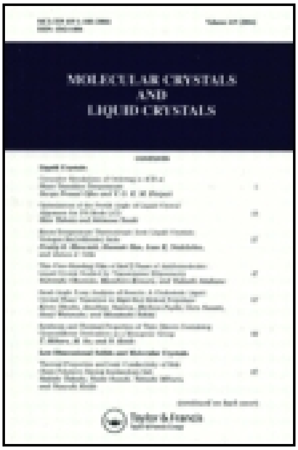

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# Characteristics of Solvation Dynamics of Rhodamine 700 in Cyanobiphenyls

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# Characteristics of Solvation Dynamics of Rhodamine 700 in Cyanobiphenyls

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The results of solvation dynamics measurements of rhodamine 700 in the isotropic phase of two different liquid crystalline substances, 8CB and 4CB, are presented. It is shown that solvation takes place on a length scale shorter than the orientational correlation length of the pseudonematic domains. Two processes contribute to the solvation. The slower process can be described by dielectric relaxation. The faster component is interpreted in terms of intermolecular interactions specific to liquid crystalline samples.

*Keywords:* solvation dynamics; nematogenic liquid; dynamical Stokes shift; cyanobiphenyl; liquid crystal

## INTRODUCTION

The special interest in the dynamics of liquid crystals is mostly based on the unusual anisotropy caused by the macroscopic alignment of the molecules[1]. Even in the macroscopically isotropic phase of liquid crystals long range interactions lead to orientationally ordered, so-called pseudo-nematic domains which can be observed by light scattering [2] or optical Kerr effect (OKE)[3] experiments. As predicted by the Landau-de Gennes theory[4] for phase transitions of weakly first order, the size of these pseudo-nematic domains shows a critical increase approaching the isotropic-nematic phase transition from higher temperatures. Parallel to this the time constant of the collective reorientational dynamics of these domains diverges.

The investigation of the solvation dynamics of such a microscopically structured liquid is a new approach to learn more about the length scale of solvation. Solvation dynamics is monitored via the dynamical Stokes shift of a fluorescing probe molecule. If upon excitation the probe molecule changes its dipole moment or structure, the solvent reorganizes around the excited molecule. While the excitation and other internal relaxation processes can be regarded as instantaneous, the evolution of the solvent rearrangement can be observed with a 1.5 ps time resolution by monitoring the shift of the fluorescence spectrum. The solvation dynamics in liquid crystals will be discussed under three aspects in this paper: Observation of different kinds of solvation processes and their interpretation, length scale of solvation and comparison of solvation in two liquid crystalline substances with similar structure.

A description of the experimental setup and a detailed discussion of the data analysis can be found in the literature[5].

## SAMPLE

As probe molecule for solvation dynamics rhodamine 700 perchlorate (Rh700) was used. This cationic dye was chosen because of its high absorptivity at 650nm, which is necessary to avoid two photon absorption of the liquid crystalline solvents. Rh700 was purchased from Radiant Dyes and was used without further purification. We worked with concentrations of ~ $5x10^{-4}$ mol/l. The absorption spectra in the isotropic phase showed no temperature dependence. A strong degradation above 350 K, resulting in a fast decoloration of the solution, prevented us from taking data at higher temperatures. Rh700 has its fluorescence maximum at 687 nm.

The liquid crystalline solvents 4-octyl-4'-cyanobiphenyl (8CB) and 4-buty-4'-cyanobiphenyl (4CB) were purchased from MERCK England and were used without further purification. 8CB, the first solvent investigated forms two liquid crystalline phases, between 294.5 K and 306.5 K a smectic A phase and between 306.5 K and 313.5 K a nematic phase. In contrast to 8CB, 4CB does not form liquid crystalline phases in the pure liquid and since it crystallizes at 289 K the virtual isotropic-nematic phase transition temperature must consequently lie below 289 K. The melting point of 4CB is at 321 K.

## RESULTS AND DISCUSSION

In solvation dynamics measurements solvents are usually classified by H-bonding, dipole-dipole or van-der-Waals interactions. While the influence of H-bonding is still discussed[6], it is found that the solvation dynamics of small polar solvent molecules are determined by the frequency dependent dielectric constant of the solvent[7]. Its relaxation time is closely related to the longitudinal relaxation time and therefore its temperature dependence is given by the Debye-Stokes-Einstein relation. For the case of a single Debye dispersion regime this is expressed by

$$\varepsilon(\omega)=\varepsilon_\infty+\frac{\varepsilon_0-\varepsilon_\infty}{1-i\omega\tau_D} \qquad (1)$$

$$\tau_D\propto\frac{\eta(T)}{k_BT} \qquad (2)$$

$$\eta(T)=\eta_0\exp(E_a/k_BT)$$

where $\varepsilon_0$ and $\varepsilon_\infty$ are the static and infinite frequency dielectric constants, $\tau_D$ is the Debye relaxation time and where $k_B$ is the Boltzmann constant, $\eta$ is the viscosity with activation energy $E_a$ and T is the temperature.

The solvation by nonpolar solvent molecules however is described as structural relaxation due to mechanical stress[8]. This model was mainly developed for the description of nonpolar but polarizable molecules like aromatic compounds. It predicts a temperature dependence of the solvation times analogous to that of the viscosity.

Fig. 1 shows the temporal evolution of the the fluorescence maximum for three different temperatures, normalized according to

$$S_\nu(t)\equiv\frac{\nu_{\max}(t)-\nu_{\max}(\infty)}{\nu_{\max}(0)-\nu_{\max}(\infty)} \qquad (3)$$

This time-dependent spectral shift can be fitted by a triple exponential function. Two relaxation times can clearly be attributed to solvation dynamics while the third relaxation process on the time scale of the life time could not be measured with a sufficient reliability and consequently could not be interpreted. Fig. 2 shows the temperature dependence of the slow component in 8CB and 4CB. The fit of the temperature dependence is obtained on the basis of Eq. (1). To test the validity of the dielectric model we compared the activation energies with the values listed in the literature[9]. The results of this comparison are shown in Table 1.

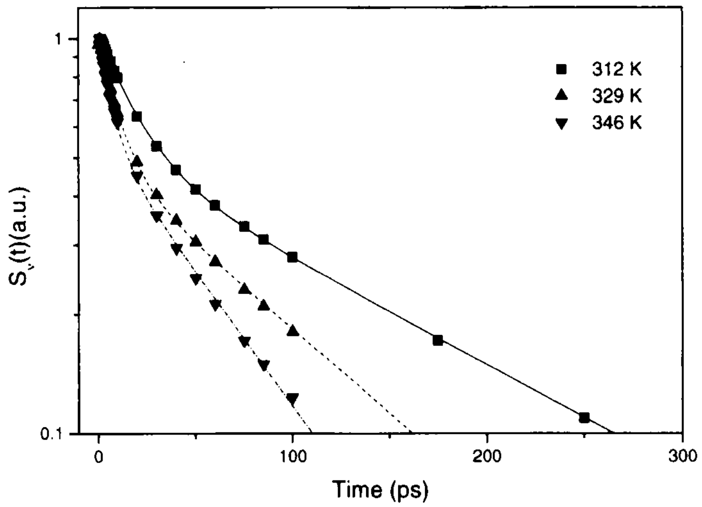

FIGURE 1 $S_v(t)$ of Rh700 in 8CB at 312 K(■), 329 K (▲), 346 K (▼) and corresponding fits

TABLE 1 Comparison of the activation energies in the isotropic phase

| | $E_a$ (kJ/mol)[9] | $E_a$ (kJ/mol) (solvation) |
|---|---|---|
| 8CB | 32 | 28±5 |
| 5CB | 33 | - |
| 4CB | - | 34±5 |

A more stringent test of the validity of dielectric theory is a direct comparison of the solvation time constants $\tau_F$ of 8CB with its Debye relaxation time $\tau_D$ which should obey eq. 4. $\tau_D$ was obtained from reorientational data[3] of 5CB molecules in n-heptane (as 8CB data are not available) and eq. 4 was applied to obtain $\tau_{F5CB}$ as shown in Table 2.

$$\tau_F = \left(\frac{\varepsilon_\infty}{\varepsilon_0}\right) \cdot \tau_D \qquad (4)$$

Form the good agreement of the values we can conclude that the solvation dynamics of both liquids on the tens to hundreds of picoseconds timescale is governed by the dielectric friction of the solvent.

TABLE 2 Comparison of relaxation times

| $\eta/T$ (cp/K) | $\tau_{F5CB}$(calc)$^{(1)}$ (ps) | $\tau_{F8CB}$(meas)$^{(2)}$ (ps) |
|---|---|---|
| $2 \cdot 10^{-2}$ | 49 | 50 |
| $5 \cdot 10^{-2}$ | 122 | 100 |
| $8 \cdot 10^{-2}$ | 194 | 150 |

$^{(1)}$ $\tau_{F5CB}$ with Eq. (4) $^{(2)}$ $\tau_{F8CB}$(meas) solvation dynamics results

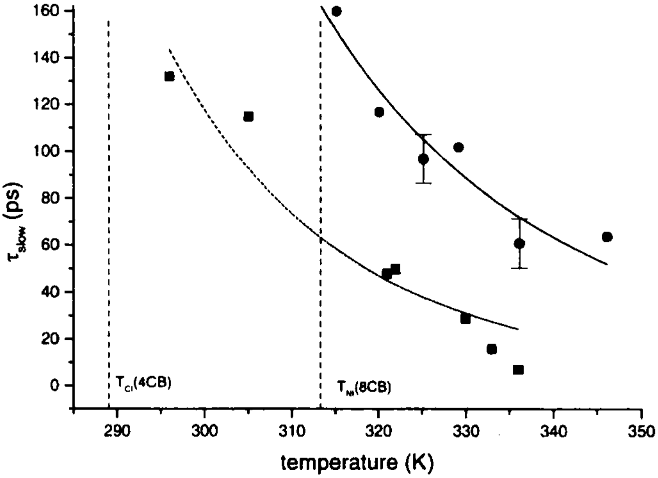

FIGURE 2 Temperature dependence of the slow solvation component of 8CB (•) and 4CB (▪), also the phase transitions for 4CB (isotropic - crystalline) and 8CB (isotropic – nematic ) are shown. The full lines are fits according to the dielectric theory.

A slower component which we observed in our experiment and which may as well be attributed to a dielectric relaxation mechanism could not be analysed due to its poor reproducibility.

We do not observe any peculiar temperature dependence which could be attributed to solvation processes on a length scale longer than the correlation length of the pseudo-nematic domains. This leads us to the conclusion that the observed solvation dynamics takes place in a solvation shell not larger than three molecular lengths.

The faster relaxation process, however, shows a completely different temperature dependence (Fig. 3). Up to at least 20 K above the nematic-isotropic phase transition these dynamics show no temperature

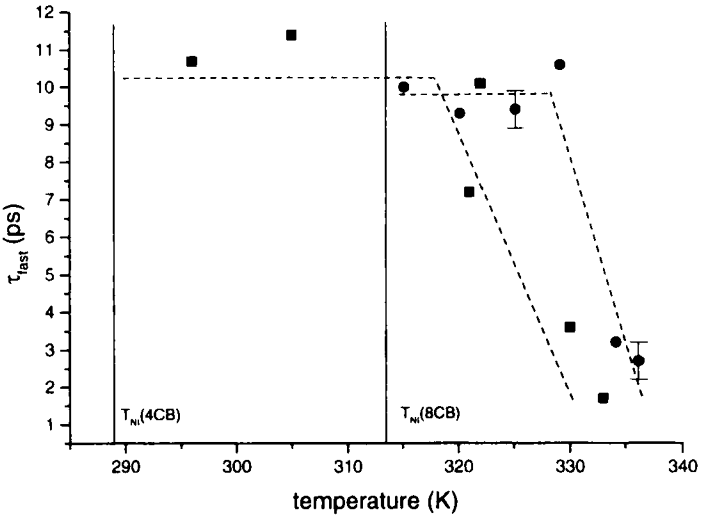

FIGURE 3 Temperature dependence of the fast solvation component of 8CB (•) and 4CB (▪), also the phase transitions for 4CB (isotropic - crystalline) and 8CB (isotropic – nematic) are shown. The dashed line are eyeguids.

dependence within our time resolution. At higher temperatures a drastical acceleration of these dynamics is seen. A very important observation is the fact that not only the temperature dependence in the two systems 8CB and 4CB is very similar, but the absolute relaxation times are identical as well for the two solvents.

Since up to now there is no theory predicting such a temperature dependence and since there exists no special model for solvation dynamics in liquid crystalline systems, only a preliminary interpretation of these data can be given. Internal relaxation processes of the probe molecule Rh700 could be possibly temperature independent. However, there are no such processes for Rh700 on the timescale of our measurements. Thus this fast decay component has to be interpreted as a relaxation associated with the solvent.

A comparison of the temperature dependence of the solvation process with the one found for reorientational processes in neat 5CB[3] and in neat MBBA[10] shows a remarkable coincidence. In both experiments a temperature independent component is observed over a broad temperature range above the phase transition and the relaxation is quantitatively the same for all investigated liquid crystals. Due to this observation this component must be attributed to the specific structure in liquid crystalline fluids. Experimental results have shown that in liquid crystals dimer or even larger cluster formation occurs[11]. A possible explanation for temperature independent dynamics is then found in solid-like surroundings created by the cluster, which reorients itself on a much slower time scale.

## CONCLUSIONS

Solvation dynamics in liquid crystals display a complex behavior. With a time resolution of 1.5 ps we observe two dynamical regimes, where the slower one can be attributed to the dipolar relaxation expected for polar molecules. The change of the pseudo-nematic domain size does not influence the temperature dependence of this component. Thus we believe that solvation takes place on the range of not more than three molecular lengths. The second, faster component shows a temperature dependence similar to the one observed in optical Kerr effect experiments in neat liquid crystals and which is characterized by a temperature independence near the phase transition. The relaxation times in both investigated liquid crystals have the same absolute values. We interpret this in terms of a solvation process characteristic for liquid crystals, however there is no satisfactory theory yet.

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