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Local viscosity and solvent relaxation experienced by rod-like fluorophores in AOT/4-chlorophenol/m-xylene organogels

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ABSTRACT

Organogels prepared from AOT/4-chlorophenol/m-xylene are immobile in the macroscopic sense, with a well-characterized internal structure. However, the molecular level dynamics inside the gels is not too clear, although a very slow structural relaxation has been reported previously. Using a set of rod-like fluorophores, we find that the rotational mobility of a small guest molecule inside the gel can be extremely fast, indicating presence of sufficiently low-microviscosity domains. These domains consist of m-xylene solvent molecules trapped in the interstices of fiber bundles comprising columnar stacks of 4-chlorophenol surrounded by AOT molecules. However, interstitial trapping of m-xylene does retard its own dynamics, which explains the slow solvent relaxation inside the gels. Hence, the state of m-xylene in the organogel may be characterized as "bound", in contrast to the "free" state in neat m-xylene.

1. Introduction

Organogels are often produced in a dry non-polar hydrocarbon solution of low molar mass gelators consisting of the anionic surfactant molecule sodium bis-ethylhexylsulfosuccinate (commercially known as AOT) and certain low pK_a phenols [1–9]. An AOT/hydrocarbon solution at an AOT concentration above its cmc is itself a low-viscosity liquid comprising of nanoscopic spherical AOT reverse micelles dispersed in the hydrocarbon solvent [8], as shown in Fig. 1a. However, when the phenol is added under appropriate conditions, the liquid turns into an immobile gel. High resolution NMR and FTIR, SAXS, XRD and AFM studies of these gels have revealed that the planar phenol molecules are stacked in columnar "strands", surrounded by the AOT molecules [4,5]. Supported by a scaffold of favorable H-bonding between the $—SO_3^-$ headgroups of AOT and the —OH groups of the phenol, the strands self-assemble into "fibers", that are further aggregated into "fiber bundles" [5], as shown in Fig. 1b. In other words, the AOT reverse micelle structure totally disintegrates in the presence of the phenols, and is replaced by an extended three-dimensional network of cross-linked fiber bundles capable of trapping the hydrocarbon solvent and forming the organogel. These organogels are most stable when the phenol:AOT molar ratio is unity [5].

A large number of studies over the years have helped to elucidate the structure of these organogels down to the nanometer level of detail [3–7]. As the next step forward, several groups have very recently begun to probe how the molecular length-scale dynamics in these gels is affected by the local structure. For example, we showed that FRET in AOT organogels depends critically on the spatial distribution of the donor and acceptor fluorophores in and around the fibers and fiber bundles [8]. In a previous work, solvation dynamics of a small guest fluorophore, Coumarin 153 (C153), in AOT/ 4-chlorophenol/*m*-xylene organogels was found to occur with a 3.9 ns time constant which is ~1000-fold slower than that in a pure aromatic solvent like toluene [9]. Since the gel is apparently immobile with an extremely large macroscopic viscosity, the very slow solvation dynamics looks quite natural, seemingly suggesting decreased molecular mobility inside the gel.

However, a more reliable estimate of mobility inside the gel is afforded by the measurement of local microviscosity. For this purpose, we decided to study the time-resolved fluorescence anisotropy of a set of three guest fluorophores: DOCI, DODCI and DCM (all shown in Fig. 2) in the AOT/4-chlorophenol/*m*-xylene organogel, and to compare the results with those obtained in pure *m*-xylene and in AOT/*m*-xylene reverse micelle solution. Fluorescence anisotropy loss in picosecond time-scales arises mainly from rotational reorientation of the fluorophore. Since the rotational motion is opposed by the friction exerted by molecules in the immediate vicinity of the guest fluorophore, the anisotropy loss directly reports on the microviscosity in the host medium [10]. From Fig. 2, it is evident that the chosen fluorophores have a structural similarity: in the ground-state, each of the double bonds has a *trans*-configuration, so that the overall molecule may be described as rod-like, where the aspect ratio of lengths measured along the longitudinal and transverse axes is rather large. The advantage of using a "rod-like" probe molecule as against a more rounded, "spherical" probe molecule is that the former displaces a larger number of surrounding molecules during its reorientational movement, and hence is more sensitive to microviscosity. Moreover, each of the molecules carries two bulky terminal groups connected by a cyanine-type bridge.

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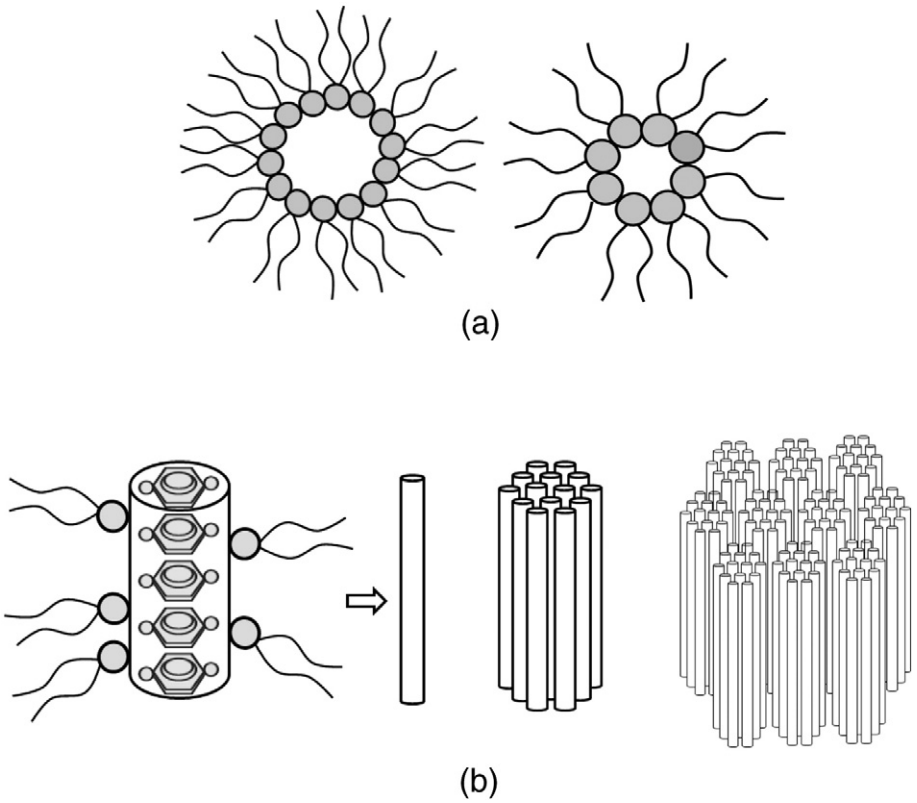
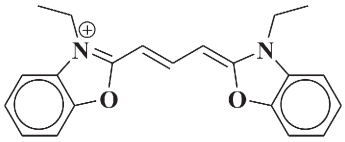
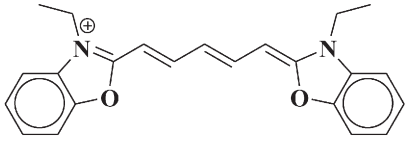


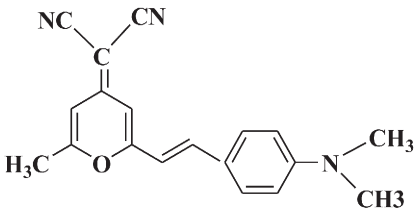
Fig. 1. Pictorial representation of (a) AOT reverse micelles in AOT/m-xylene solution and (b) strands, fibers and fiber bundles in AOT/4-chlorophenol/m-xylene organogels.



3,3'-Diethyloxacarbocyanine iodide (DOCI)



3,3'-Diethyloxadicarbocyanine iodide (DODCI)



4-(dicyanomethylene)-2-methyl-6-(p-dimethylamino-styryl)4H-pyran (DCM)

Fig. 2. Structure of the fluorophores under study: DOCI, DODCI and DCM. The iodide counterion has not been shown for DOCI and DODCI.