Supporting Information

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Micellar Lyotropic Nematic Gels

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The lyotropic nematic N\textsubscript{d} and N\textsubscript{c} phases of the ternary systems H\textsubscript{2}O – n-decanol – SDS and H\textsubscript{2}O – n-decanol – CDEAB were studied using the compositions indicated in the phase diagrams shown in **Figure S1** (SDS-system: \(\omega_{H_2O} = 0.70, \gamma_{N_d} = 0.224, \gamma_{N_c} = 0.176\). CDEAB-system: N\textsubscript{d}: \(\omega_{H_2O} = 0.632, \gamma = 0.15, \) N\textsubscript{c}: \(\omega_{H_2O} = 0.68, \gamma = 0\)).

![Figure S1](image)

**Figure S1.** Room temperature phase diagrams of the ternary systems *(left)* H\textsubscript{2}O – n-decanol – SDS\textsuperscript{[1]} (figure reprinted with permission from [P.-O. Quist, B. Halle, *Liquid Crystals* 1995, *18*, 623.] Copyright 1995 by Taylor and Francis). The black areas indicate the region of the biaxial nematic N\textsubscript{bxx} phase. *(right)* H\textsubscript{2}O – n-decanol – CDEAB (schematically redrawn from Ref\textsuperscript{[2]}), including the molecular structure of the surfactants and the used compositions indicated by red dots (scale in wt%).

The N\textsubscript{d} phase (disk-shaped micelles as mesogenic units) and the N\textsubscript{c} phase (cylindrical micelles as mesogenic units) were distinguished by the way they attach to a polar glass surface and align in a magnetic field. In flat glass capillaries the N\textsubscript{d} phase aligns homeotropic,
while for the N\textsubscript{c} phase a uniform planar director alignment can be observed after four days (see Figure S2). Since the N\textsubscript{d} phase has a negative anisotropy of diamagnetic susceptibility ($\Delta \chi^d < 0$), while for the N\textsubscript{c} phase $\Delta \chi^d > 0$ applies, the global director is oriented perpendicular (N\textsubscript{d}) or parallel (N\textsubscript{c}) to an external magnetic field as confirmed by 2D SAXS (see Figure S3).

**Figure S2.** Polarizing microscopy images of (above) the N\textsubscript{d} and (below) the N\textsubscript{c} phase of the system H\textsubscript{2}O – n-decanol – SDS, (left) directly after filling the sample into flat glass capillaries and (right) four days after filling. After 4 days the N\textsubscript{d} phase appears black between crossed polarizers with the exception of the sample to air interface indicating a homeotropic alignment (appears grey upon tilting), while for the N\textsubscript{c} phase a non-disturbed uniform director alignment can be observed.

**Figure S3.** 2D SAXS diffractograms of (left) the gelator-free N\textsubscript{d} phase and (right) the gelator-free N\textsubscript{c} phase. The samples were oriented for 8 hours in an external magnetic field of 1 T.
before measuring. While the director \( \mathbf{n} \) of the \( N_d \) phase is oriented perpendicular to the magnetic field, the director of the \( N_c \) phase is oriented parallel to it.

The nematic phases were attempted to gel by three LMWGs, namely DBS, DBC and HG1 (see Figure S4). LMWGs form fibers via physical bonds such as H-bonds and \( \pi-\pi \) interactions which then entangle to build-up a 3D gel fiber network. Since all interactions are of the non-covalent kind, the gel formation can be reversibly triggered by temperature (sol-gel transition temperature \( T_{\text{sol-gel}} \)). DBS is known to gel organic solvents and is thus an organogelator, while the water-gelling ability of DBC and HG1 makes them hydrogelators.

![Molecular structure and fiber growth of the LMWGs DBS, DBC, and HG1](image)

**Figure S4.** Molecular structure and fiber growth of the LMWGs DBS, DBC\(^{(3)}\) (Reprinted with permission from F. M. Menger, K. L. Caran, *J. Am. Chem. Soc.* **2000**, *122*, 11679 Copyright 2000 American Chemical Society) and HG1\(^{(4)}\) (Reproduced from Ref.\(^{(4)}\) with permission from The Royal Society of Chemistry).

An overview on our attempts to gel the lyotropic nematic phases of the systems \( \text{H}_2\text{O} – n\text{-decanol} – \text{SDS} \) and \( \text{H}_2\text{O} – n\text{-decanol} – \text{CDEAB} \) with the LMWGs DBS, DBC and HG1 is given in Table S1.
Table 1. Overview on the nematic phases (N\textsubscript{d} and N\textsubscript{c}) of the two lyotropic systems and the three low molecular weight gelators tested in this study to obtain lyotropic nematic gels. The symbols √ and ✗ indicate whether or not the gelation was successful. The numbers in the brackets is the critical gelator concentration (cgc) in wt%, necessary to obtain a nematic gel.

| System          | DBS LMWG (cgc / wt%) | HG1 |
|-----------------|----------------------|-----|
| SDS - n-decanol - H\textsubscript{2}O |                     |     |
| N\textsubscript{d} | √ (0.75)            | √ (2.0) |
| N\textsubscript{c} | √ (0.75)            | √ (2.0) |
| CDEAB - n-decanol - H\textsubscript{2}O |                     |     |
| N\textsubscript{d} | √ (2.0)            | ✗     |
| N\textsubscript{c} | √ (3.5)            | ✗     |

The hydrogelator DBC is known to be responsive to pH-value with gel formation only occurring in acidic medium\textsuperscript{[5]}. We thus tried to gel the nematic phases of the system H\textsubscript{2}O – n-decanol – CDEAB with DBC at pH = 3, 4, and 5, but we were still not able to obtain gels (see Table S1), while for the system H\textsubscript{2}O – n-decanol – SDS gelation at pH = 7 is successful.

In the following, only the results of the system H\textsubscript{2}O – n-decanol – SDS will be discussed. Similar results on the gelation of the nematic phases of the system H\textsubscript{2}O – n-decanol – CDEAB can be found in the Bachelor thesis of Friedrich Stemmler\textsuperscript{[6]}.

The phase sequences and the sol-gel transition temperatures \( T_{\text{sol-gel}} \) of the examined samples of the system H\textsubscript{2}O – n-decanol – SDS are shown in Table S2. \( T_{\text{sol-gel}} \) is measured by inversion of the test tube at different temperatures in a water basin and checking for flow. Please note that the gel to sol transition is not a sharp phase transition since the gel state is not a thermodynamic stable state. During the melting of a physical gel network several processes take place. The net points and junction zones of the network (inter-fiber interactions) as well as the physical bonds holding together one single fiber (intra-fiber interactions) must be
overcome. Thus, the $T_{\text{sol-gel}}$ specified in Table S1 rather indicates a broad melting range of at least $T_{\text{sol-gel}} \pm 3\text{K}$.

A transition of the $N_d$ phase into a lyotropic lamellar $L_\alpha$ phase with increasing temperature is found. The appearance of a phase with long-range translational order at higher temperatures than a phase with solely long-range orientational order is highly untypical but already reported for the studied system $H_2O$ – $n$-decanol – SDS$^{[7,8]}$. The phase sequence of the lyotropic liquid-crystalline phases is only slightly influenced by the presence of the gel networks made of DBS and DBC. An exception are the gels obtained with HG1. Gelation of the $N_c$ phase with HG1 leads to an isotropic gel, while gelling the $N_d$ phase results in a chiral nematic gel. For all obtained nematic gels the gel network is stable up to higher temperatures than the nematic phase ($T_{\text{sol-gel}} > T_{N\alpha} / T_{N\iota}$).

**Table S2.** Phase sequences of the gelator-free and gelled nematic phases of the system $H_2O$ – $n$-decanol – SDS (studied up to 105°C), as well as $T_{\text{sol-gel}}$ of the nematic gels.

| sample           | Phase Sequence [°C] | $T_{\text{sol-gel}}$ [°C] |
|------------------|---------------------|---------------------------|
| Gelator-free $N_d$ | $N_d$ 33 $L_\alpha$ 90 isotropic | -                         |
| $N_d$, 1 wt% DBS  | $N_d$ 36 $L_\alpha$ 94 isotropic | 78                       |
| $N_d$, 2 wt% DBC  | $N_d$ 40 $L_\alpha$  | 69                       |
| $N_d$, 2 wt% HG1  | $N_d$ 40 $L_\alpha$ 66 isotropic | 44                       |
| Gelator-free $N_c$ | $N_c$ 30 isotropic  | -                         |
| $N_c$, 1 wt% DBS  | $N_c$ 31 isotropic  | 85                       |
| $N_c$, 2 wt% DBC  | $N_c$ 42 $2\phi$ ($N_c / \text{iso}$) | 75                       |
| $N_c$, 2 wt% HG1  | isotropic           | -                         |

We studied the nematic gels (for HG1 good images could be obtained for the binary gel $H_2O / 0.5$ wt% HG1 only) by freeze-fracture electron microscopy (FFEM). Twisted gel fibers with an average thickness of 6.5 nm for DBS, 10 nm for DBC and on average 4.5 nm for HG1 were observed (see Figure 1h and Figure S5.)
Figure S5. FFEM images of (a) the N$_d$ phase gelled with 1 wt% DBS, and (b) the binary gel H$_2$O / 0.5 wt% HG1. Please note the orientational alignment of the fibers in (a).

Analogous to the results for the gelling of the N$_d$ phase shown in Figure 2 and 3, here the results obtained when gelling the N$_c$ phase are presented. The nematic nature of the gels obtained when gelling the N$_c$ phase with DBS and DBC is proven by polarizing microscopy and SAXS, due to the observed schlieren texture and broad diffraction maxima, respectively (see Figure S6). Nevertheless, we cannot fully exclude the formation of a biaxial nematic gel. Here, measurements of the birefringences ($n_2$-$n_1$ and $n_3$-$n_2$) by e.g. laser conoscopy$^{[7,9]}$ would be necessary to ultimately determine whether a calamitic nematic phase has formed. But since the range of the N$_{bx}$ phase in the ternary phase diagram is very narrow we believe the formation of a biaxial nematic gel is rather unlikely. A macroscopic aligned nematic gel is demonstrated by 2D SAXS and the corresponding schematic drawing is shown in Figure S7.
Figure S6. Comparison of the gelator-free N_c phase with the N_c phase gelled with the different LMWGs. (left) POM images of a) the gelator-free N_c phase and of the gels obtained with c) 12-HOA, e) DBS, g) DBC and i) HG1. (right) X-ray diffraction profiles of b) the gelator-free N_c phase and of the gels obtained with d) 12-HOA, f) DBS, h) DBC and j) HG1.
Gelation of the lyotropic nematic $N_c$ phase with the gelator 12-HOA leads to a lamellar gel. Contrary, gelation of the $N_c$ phase with the LMWGs DBS and DBC results in a nematic gel. When using HG1 to gel the $N_c$ phase, the formation of an isotropic gel is observed.

**Figure S7.** (a) 2D SAXS diffractogram of the DBC gelled $N_c$ phase. Although the gel fibers form first, an oriented director configuration is observed. Probably, the capillary surface guides a linear growth of the gel fibers which in turn serve as a soft template for the $N_c$ phase, as shown in (b) the schematic drawing of the gelled $N_c$ phase.

An overview of the 2D SAXS diffractograms of the gelator-free $N_c$ and $N_d$ phase, as well as the $N_c$ and $N_d$ phase gelled with DBS and DBC is shown in **Figure S8.** In all cases, a magnetic field is applied in the direction shown in the diffractograms of the gelator-free nematic phases (left). However, for the nematic gels the magnetic field effect is superimposed by the soft-templating of the gel fibers, which guides the nematic orientation. A uniform alignment of the nematic gels is easier achieved for nematic phases gelled with DBC than with DBS.
In the 2D SAXS diffractograms a second broad diffraction maximum is visible at $q_2 \approx 2q_1$, which is (for the gelator-free nematic phases) oriented in the same direction as the first peak. In the direction of the director $\mathbf{n}$ (for the $N_c$ phase, perpendicular to $\mathbf{n}$ for the $N_d$ phase respectively) no weak peak for the long micelle to micelle distance is present. This features make the obtained 2D SAXS diffractograms of the system $H_2O - n$-decanol – SDS highly unusual for nematic phases. The occurrence of a second order reflection indicates the formation of clusters in the nematic phase, in which short-range translational order is present. A previous study on the nematic phases of the same system reports a local pseudo-lamellar arrangement of the micelles.\cite{10} Additionally, a similar pseudo-lamellar structure was found for the $N_d$, $N_c$ and $N_{bx}$ (biaxial nematic) phases of two further lyotropic systems.\cite{11} Such smectic clusters are also known to appear in nematic phases of thermotropic LCs when approaching the nematic-smectic phase transition.\cite{12-14} As the diffraction maxima exhibit a
Lorentzian shape, the intensity vs $q$ profiles (see Figure S9) obtained from the 2D SAXS diffractograms are analyzed with a cumulative fit of two Lorentz fits according to

$$I(q) = \frac{2A}{\pi} \frac{FWHM}{4(q - q_0)^2 + FWHM^2}. \quad (1)$$

$q_0$ is the position of the pseudo-Bragg peak, FWHM is the full width at half maximum and $A$ is the area of the peak. As shown by the Lorentzian shape of the diffraction maxima the positional correlation function decays exponentially, with $\xi$ being the correlation length obtained from the width of the peak ($\xi = \frac{2}{FWHM}$). The mean micelle to micelle distance $d_c$ is obtained from the center of the diffraction maximum using the Bragg relation $d_c = 2\pi/q_c$.

The corresponding fit parameters are listed in Table S3.

While the peak positions of the DBS gelled nematic phases are almost identical to the peak position in the gelator-free nematic phases, the diffraction profiles of the DBC nematic gels show a shift of the peak position to lower $q$ values. An explanation for the enlargement of the intermicellar distance due to gelation with DBC might be the thickness of the formed gel fibers. While the diameter of the DBS fibers received by FFEM is with $\sim$ 6.5 nm in the range of the intermicellar distance (6.1 nm and 5.9 nm for the gelator-free $N_d$ and $N_c$ phases, respectively), the diameter of the DBC gel fibers ($\sim$ 10 nm) exceeds the intermicellar distance.

To incorporate the thick gel fibers into the micellar nematic structure a local widening of micellar arrangement is necessary. However, it is questionable whether the fraction of gel fibers formed by the addition of only 2 wt% DBC is sufficient to explain the observed increase in the intermicellar distance ($d_c$ is 20 Å and 32 Å larger than in the corresponding gelator-free $N_d$ and $N_c$ phase, respectively).

The correlation length of the local lamellar arrangements in the nematic phase is larger for the $N_d$ than for the $N_c$ phase, as can be seen by the narrower diffraction maxima. With the exception of the $N_c$ phase gelled with 2 wt% DBC, the correlation length in the nematic gels is in the same range although slightly smaller than in the gelator-free nematic phases.
**Figure S9.** Intensity vs q profiles obtained from radial averaging of the 2D X-ray diffractograms shown in Figure S8 for (left) the gelator-free, (middle) the DBS gelled and (right) the DBC gelled Nd (above) and Nc (below) phases. All experimental data is fitted by a cumulative fit of two Lorentz fits.

**Table S3.** The mean intermicellar distance $d_c$ and the positional correlation length $\xi$ obtained from the analyses of the first order diffuse scattering maxima of the SAXS data shown in Figure S9 for the studied gelator-free nematic phases and the nematic gels.

| Sample            | $d_c$ [Å] | $\xi$ [Å] |
|-------------------|-----------|-----------|
| Gelator-free Nd   | 60.8      | 156.6     |
| Nd, 1 wt% DBS     | 59.4      | 142.5     |
| Nd, 2 wt% DBC     | 80.6      | 154.5     |
| Gelator-free Nc   | 59.0      | 57.8      |
| Nc, 1 wt% DBS     | 57.7      | 51.3      |
| Nc, 2 wt% DBC     | 90.9      | 94.9      |
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