<div align="center">**Electronic Supplementary Information (ESI)**</div>

Probing water mobility in confining channels of reverse wormlike micelles

Hilda C. N. Nogueira, Daniela A.V. F. da Rocha, Edvaldo Sabadini*

Institute of Chemistry, University of Campinas – UNICAMP, 13083-970, Campinas, Brazil.
*Corresponding author: sabadini@unicamp.br

I - Preparation of reverse wormlike micelles

<u>Materials</u>: Soybean lecithin (95% purity) was obtained from Avanti Polar Lipids. Heptane (anhydrous, 99%), octane (anhydrous, 99% purity), nonane (anhydrous, $\geq$ 99% purity), decane (anhydrous, $\geq$ 99% purity), undecane ($\geq$ 99% purity), dodecane (anhydrous, $\geq$ 99% purity), cyclooctane ($\geq$ 99% purity), and deuterium oxide (99.9 atom % D) was obtained from Sigma Aldrich.

<u>Sample preparation</u>: R-WLM was prepared according to the phase diagram proposed by Angelico et al.[1] The lecithin ($\approx$ 1.3x10^{-3} mols) was dissolved in organic solvents ($\approx$ 3.5x10^{-2} mols) at room temperature under stirring for approximately 3 hours. After the complete dissolution, a desirable amount of water (W_0) was added, and subsequently, the solution was gentle stirring for 12 hours until became homogeneous and transparent. All samples were equilibrated at room temperature for at least 36 hours before the measurements.

II – Measurements

II.I – TD-NMR

Samples were inserted into glass tubes with the auxiliary of a syringe. Tubes of 10 mm diameter were used and the volume completed was about 3 cm in height. It was also used a paraffin plastic film to minimize solvent evaporation. The experiments were performed on a Bruker Minispec mq 20 NMR analyzer (Bruker BioSpin, Rheinstetten, Germany) with a temperature probe at 25 °C. CPMG Sequence Pulse was used by measuring the T_2 relaxation time, in which the 90° and 180° proton pulses were 8.89 µs and 17.78 µs, respectively, and an echo time of 0.3 ms.

Data were acquired from 30,000 echoes with 16 scan repetitions and recycle delay of 15 s. The relaxation decays were evaluated by distributed exponential fit analysis using Peakfit software (version 4.0, Systat Software, Chicago, USA) by the Inverse Laplace Transform algorithm. The distinct populations' relaxation time (Tables S1, S2, and S4) was determined by cumulative integration using log-normal distribution.

Table S1. Values of relaxation time (T_2) for R-WLM formed by lecithin in cyclooctane at the $W_0 = 4 - 12$.

Sample	T$_2$ values (ms)		
	Group A	Group B	Group C
$W_0 = 4$	4.20	29.13	1358.20
$W_0 = 5$	4.81	30.04	1354.23
$W_0 = 6$	7.71	46.39	1356.37
$W_0 = 7$	12.27	85.44	1359.15
$W_0 = 8$	12.59	86.20	1363.07
$W_0 = 9$	17.43	167.42	1323.53
$W_0 = 10$	17.10	147.17	1362.69
$W_0 = 11$	14.91	126.47	1355.21
$W_0 = 12$	17.55	176.61	1354.35

Table S2. Values of relaxation time (T_2) for RWLM in the linear alkanes: heptane (7C), octane (8C), nonane (9C), decane (10C), undecane (11C), and dodecane (12C) with the same water content $W_0 = 3$.

Sample $W_0 = 3$	T$_2$ values (ms)		
	Group A	Group B	Group C
Heptane	5.04	31.18	1947.66
Octane	4.07	25.9	1669.22
Nonane	2.48	20.24	1521.64
Decane	2.13	19.03	1344.96
Undecane	2.13	13.97	1152.68
Dodecane	1.58	11.77	1051.17

To corroborate the attribution of the bands, we calculated, by integration, the area corresponding to each peak for groups A, B, and C. The percent of area values were correlated to the quantity of hydrogen in each group. Figure S1 shows these values as a function of W_0.
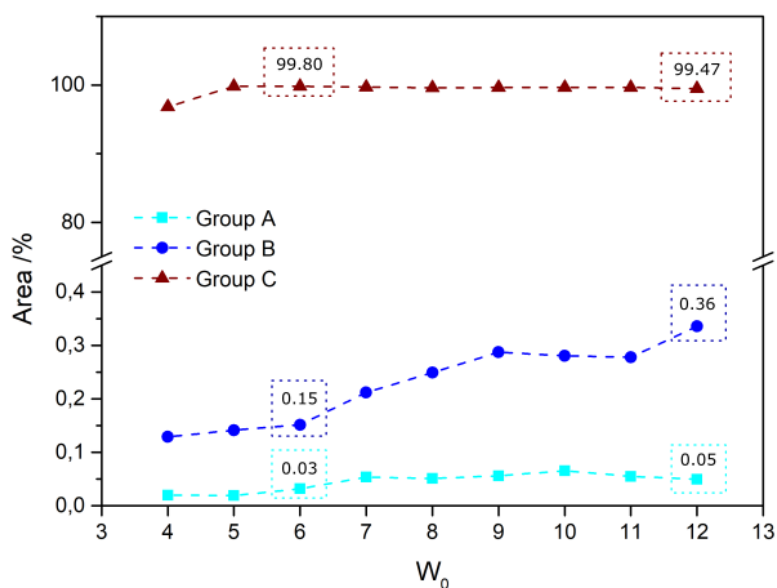
Figure S1. Percent of the total area for the peaks of groups A, B, and C as a function of the increase of water content for R-WLM in cyclooctane.

In this regard, it is possible to observe that groups A and B are more sensible to the addition of water, while group C is pretty much not affected. Furthermore, the upward trend of area values shows correspondence with W_0; eg, for $W_0 = 6$ and $W_0 = 12$, the peaks present 0.03 % and 0.05 % for the less mobile group, A. Therefore, the area changes around 1.7 times when the water content is doubled. The same trend is observed for group B: the values change from 0.15 % to 0.36 % indicating a change of 2.4 times. Group C, on the other hand, presents an insignificant variation in the area which goes from 99.80 % to 99.47 % when doubling W_0.

Therefore, these values confirm that groups A and B, related to the less mobile protons (shorter T_2) are sensitive to the addition of water, which agrees with the attribution of groups A and B to the aqueous channels formed in the reverse wormlike systems. The independence of group C to the water content also supports the attribution to the more mobile protons (relaxing in long T_2) of the headgroup and chains of lecithin and the solvents.

Also, ^{1}H TD-NMR was performed in R-WLM formed in undecane with D_2O (considering $W_0 = 3$). The spectrum is presented in Figure S2 and Table S4 contains the correspondent T_2 values. As for the R-WLM in cyclooctane, the percent of area values from the three groups was calculated and presented in Table S3.
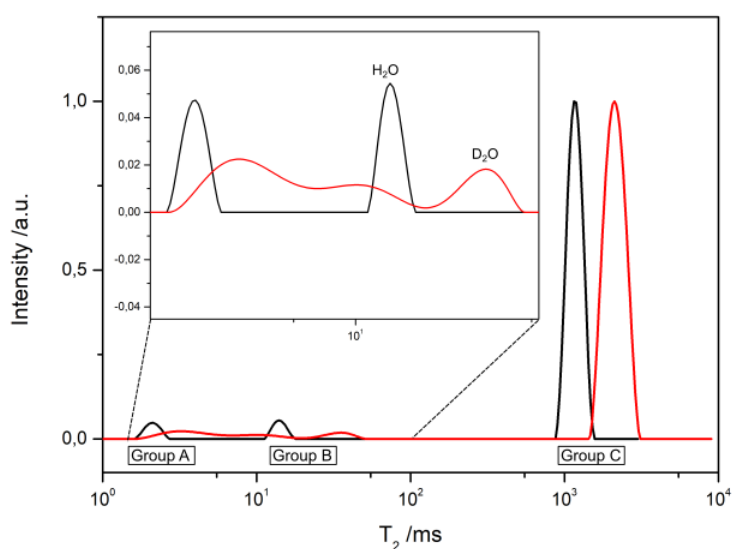
Table S3. Percent of area values for peaks of groups A, B, and C of R-WLM formed in undecane with water and with deuterium oxide at the $W_0 = 3$.

Samples ($W_0 = 3$)	Area (%)		
	Group A	Group B	Group C
With H_2O	< 0.01	0.06	99.93
With D_2O	< 0.01	0.03	99.96

Figure S2. ^{1}H TD-NMR spectrum for R-WLM formed by lecithin, undecane, and D_2O (red line); and H_2O (black line) at the $W_0 = 3$. In the inset is highlighted the peaks of groups A and B.

The decrease of intensity for groups A and B combined with the downward trend of area values (Table S3), from 0.0084 % to 0.0040 % in A and from 0.0506 % to 0.0303 % in B, support the trend observed for R-WLM in cyclooctane, once, in this case, the decrease of quantity of H is expected as the aqueous domain isn't formed by water. In addition, the low area values for the system with D_2O are related to traces of water strongly associated with lecithin, as indicated by Schurtenberger et al[2].

Already for group C, although the peak was a shift for high T_2-values, it is possible to observe again an independence concerning the component of confined channel, once the change of area is almost negligible: 99.93 % with H_2O and 99.96 % with D_2O, as shown in the Table S3. The shift of the peak C to longer T_2 values remains a topic to be investigated.

Table S4. Values of relaxation time (T_2) for R-WLM formed by lecithin, undecane, and deuterium oxide at the $W_0 = 3$.

| Sample	T_2 values (ms)		
$W_0 = 3$	Group A	Group B	Group C
D₂O	3.29	35.04	2112.91

II.II – Rheology

Steady and dynamic rheology experiments were performed on a Haake MARS III rheometer using a parallel-plate geometry with Peltier-based temperature control at 25 ºC. A solvent trap was used to minimize solvent evaporation. The samples were equilibrated for at least 5 min before measurements. Frequency spectra were recorded in the linear viscoelastic region, as determined from dynamic strain sweep tests, from 10^{-2} to 10^2 Hz. The flow curves were obtained over a shear rate from 10^{-3} to 10^3 s^{-1} (constant stress equal to 0.5 Pa).

Figure S3 presents comparatives curves of the zero-shear viscosity, η_0, as a function of W_0 for octane and cyclooctane.
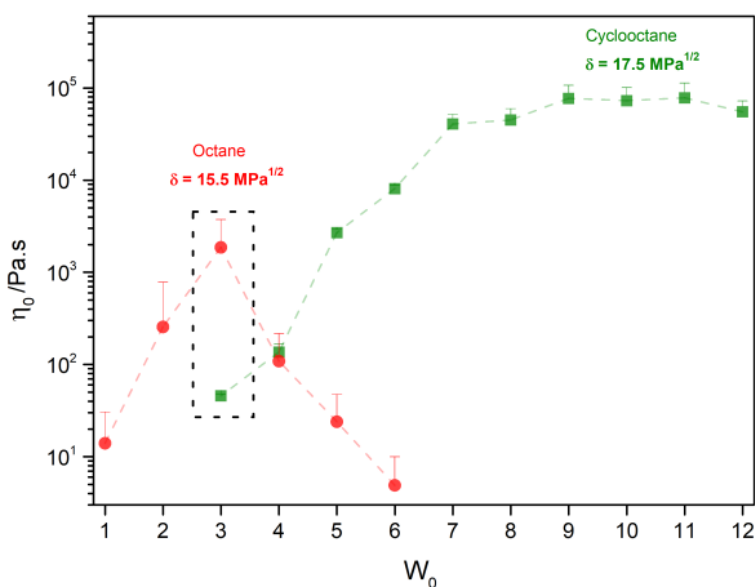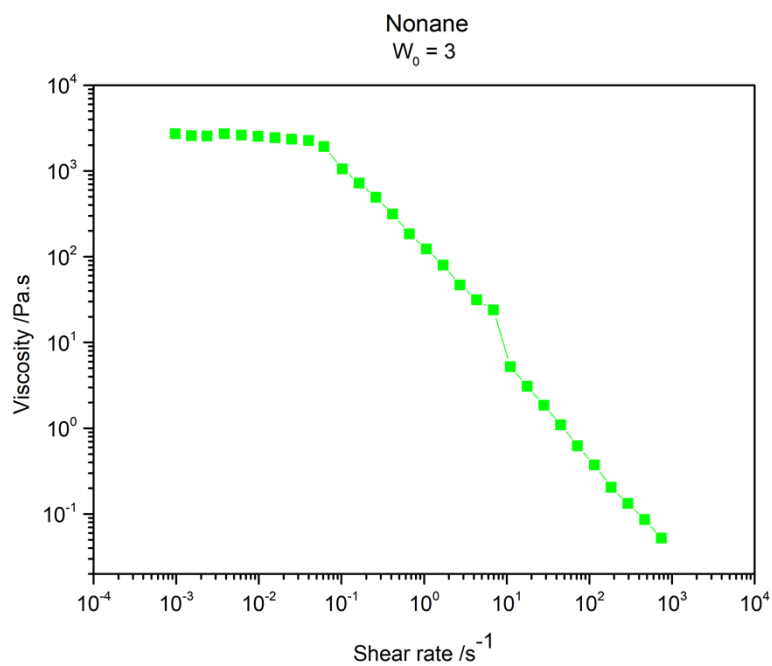

Figure S3. Zero shear viscosity (η_0) as a function of the water content of the R-WLM samples in octane (red circles) and cyclooctane (green squares). The correspondent values of δ for the two solvents are indicated.
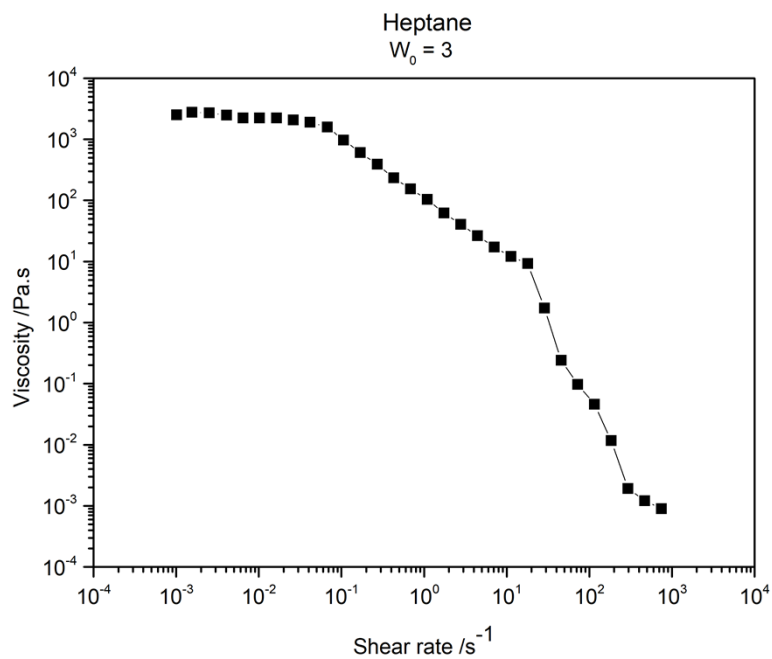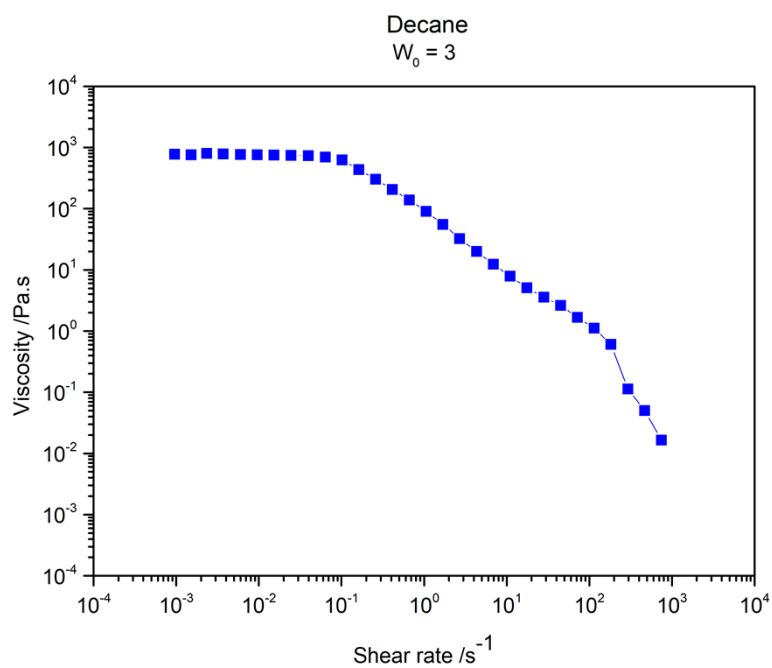
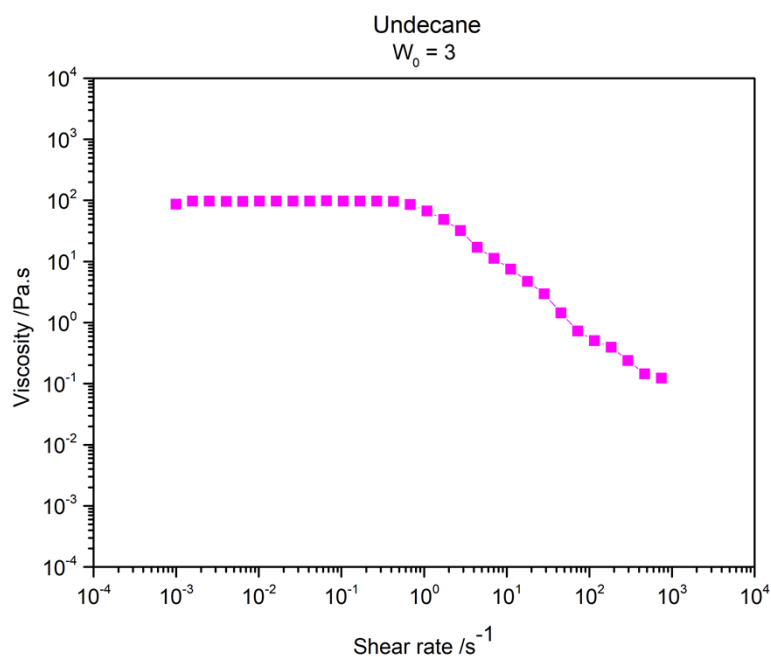**Figure S4.** Flow curves of the R-WLM in heptane at $W_0 = 3$.
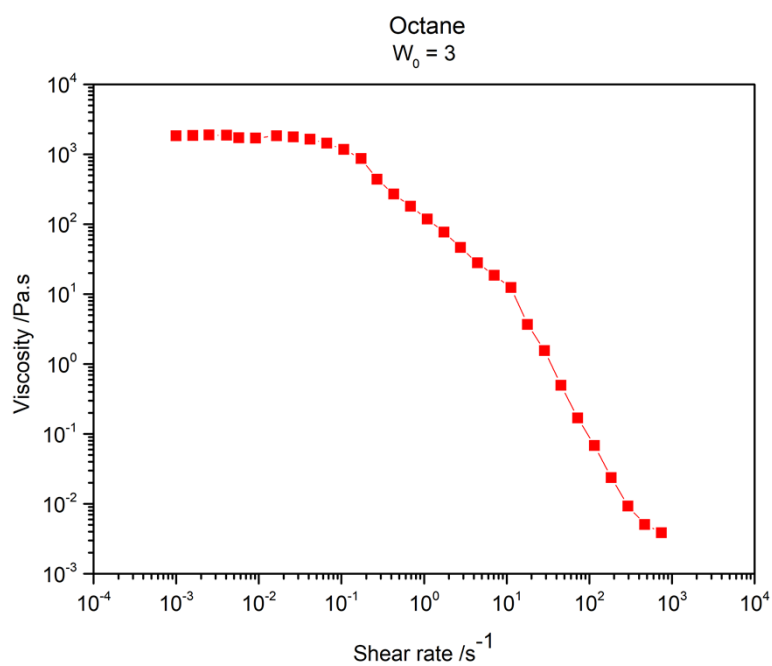
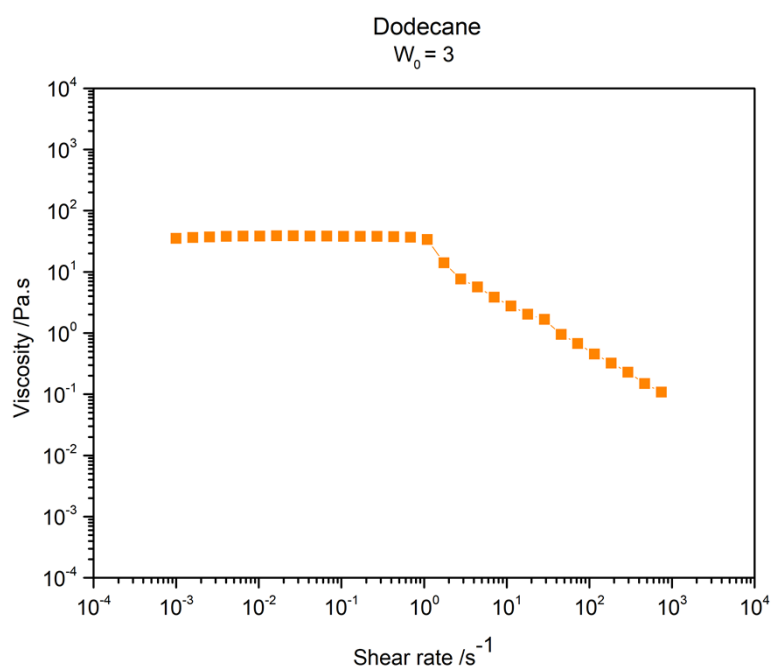**Figure S5.** Flow curves of the R-WLM in octane at $W_0 = 3$.

Figure S6. Flow curves of the R-WLM in nonane at $W_0 = 3$.

Figure S7. Flow curves of the R-WLM in decane at $W_0 = 3$.

Figure S8. Flow curves of the R-WLM in undecane at $W_0 = 3$.

Figure S9. Flow curves of the R-WLM in dodecane at $W_0 = 3$.

III-References

1. Angelico, R., Ceglie, A., Olsson, U. & Palazzo, G. Phase diagram and phase properties of the system lecithin-water-cyclohexane. *Langmuir* **16**, 2124–2132 (2000).

2. Schurtenberger, P., Scartazziniv, R., Magid, L. J., Leser, M. E. & Luisif, P. L. Structural and Dynamic Properties of Polymer-like Reverse Micelles. *J. Phys. Chem* **94**, 3695–3701 (1990).

3. Hansen, C. M. Methods of characterization - surfaces. *Hansen Solubility Parameters A Users*

Handbook, Second Ed. 113–123 (2007) doi:10.1201/9781420006834.

4. Scartazzini, R. & Luisi, P. L. Organogels from lecithins. *J. Phys. Chem.* **92**, 829–833 (1988).