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### **Electronic Supplementary Information**

## The impact of the structuring of hydrotropes in water on the mesoscale solubilisation of a third hydrophobic component

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### **SANS-Measurements**



**Figure S1:** SANS spectra of the binary  $D_2O/TBA$  mixture and the ternary  $D_2O/TBA/BA$  mixture. Symbols indicate the different mass ratios of  $D_2O$  water and BA in percentage.

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Already the binary mixture  $D_2O/TBA$  provides a strong scattering signal indicating the presence of a structured binary system. The substitution of TBA by BA leads to a strong increase of the scattered intensity. The correlation length obtained by fitting the curves with the Ornstein-Zernike formalism increases from 0.8 nm for the binary  $D_2O/TBA$  mixture to 2.1 nm for the ternary  $D_2O/TBA/benzyl$  alcohol mixture. This increase can be interpreted as a swelling of the aliphatic rich bulk phase formed by strong TBA aggregation.

Taking into account conductivity measurements for the binary and ternary mixtures  $D_2O/TBA(/benzyl alcohol)$ , where it was found that the structure induced by TBA does not change upon benzyl alcohol addition, SANS measurements support our hypothesis: The structuring of the ternary system  $D_2O/TBA/benzyl$  alcohol is induced by the binary mixture  $D_2O/TBA$  and benzyl alcohol intercalates into the given structuring.



### Second-order derivative of Figure 4c

**Figure S2:** Fourth order polynomial/exponential fit function (Eq. 1 and 2) of data gained from OD measurements of DR-13 in (a) TBA/H<sub>2</sub>O and (b) EtOH/H<sub>2</sub>O mixtures with water (red curve) and their corresponding second derivative (blue curve). Black squares denote the experimentally determined data.

Calculations of the fit functions and the corresponding second-order derivative were done using Origin 9.0 software. A second-order differentiation of the fitted curves reveals huge differences in the solvent character of the hydrotrope (see Figure S2). In case of EtOH the curvature of the curve stays always positive over the whole miscibility range whereas a negative curvature is observed in the case of TBA in the range of approximately 0.23 < x(TBA) < 0.6. This second order differentiation shows that EtOH possesses a more co-solvent character, whereas TBA shows a hydrotropic behaviour when DR-13 is dissolved. The proposed interfacial solubilisation mechanism is further supported by the fact that DR-13 has a very poor solubility both in pure dodecane and pure water which both do not provide an interface at all. As a consequence, DR-13 is also scarcely soluble in poorly structured mixtures, such as EtOH/H2O.<u>Functions used for data fitting:</u>

Values for OD/OD<sub>max</sub> of TBA were fitted according to a fourth order polynomial function as follows:

$$y = A_0 + A_1 X + A_2 X^2 + A_3 X^3 + A_4 X^4$$
(1)

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Values for  $OD/OD_{max}$  of EtOH were fitted according to an exponential function as follows:

$$y = B_0 + B_1 \cdot exp^{(n)}(B_2 \cdot x) \tag{2}$$

All fit parameters are summarized in table Table S3.

 Table S3: Fit parameters used for the fourth order polynomial/exponential fit function (Eq. 1 and 2) of data gained from OD measurements of EtOH/TBA mixtures with water.

Parameter	$A_0$	$A_1$	$A_2$	$A_3$	$A_4$	$B_0$	$B_1$	B <sub>2</sub>
	0.00984	-0.40876	6.76631	-13.56793	8.19464	0	0.01339	4.32016