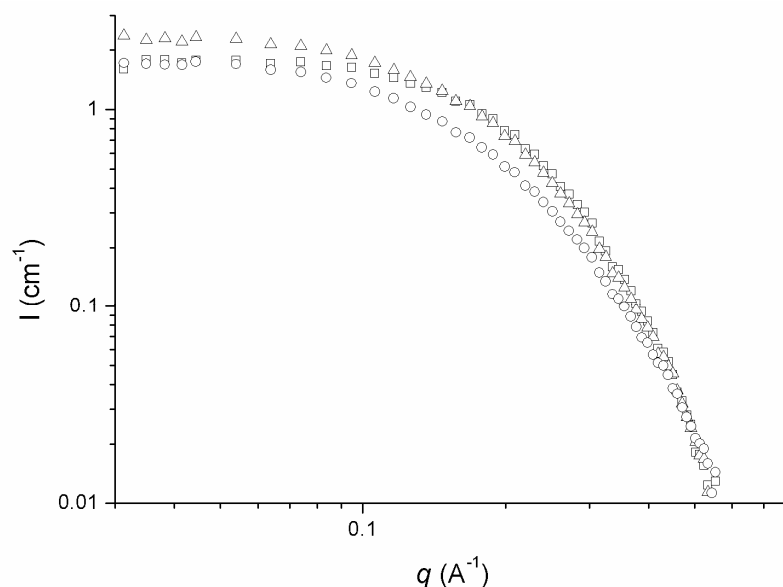


### DMDBTDMA/dodecane mixtures: SANS spectra

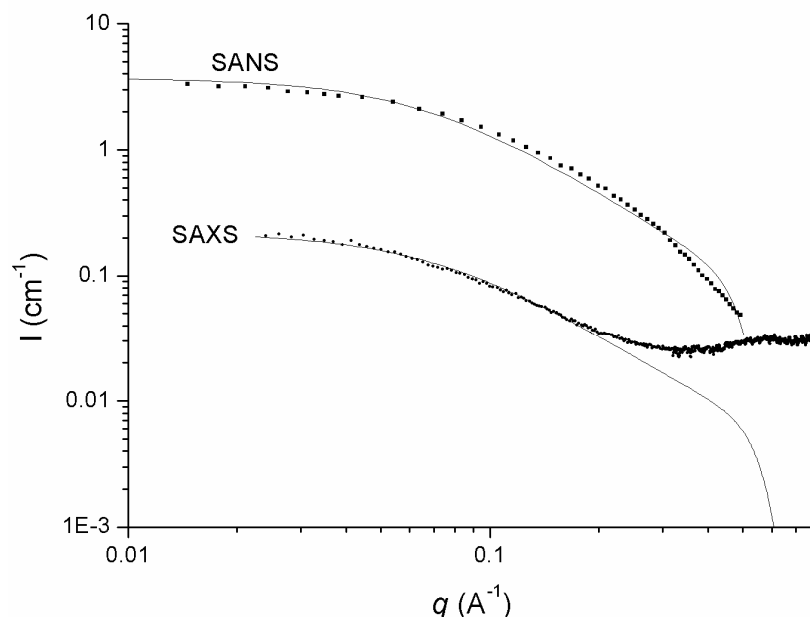


**Fig.S1:** SANS spectra of C14/dodecane-D solutions [ $\text{C14}$ ] = 0.4; 0.7 and 1M.

In the SANS spectra (Fig.S1), the SANS spectra of C14 in deuterated dodecane is shown at concentrations 0.4; 0.7 and 1M. The incoherent scattering due to hydrogens atoms is subtracted as background signal from the spectra. At 0.4 and 0.7M the spectra show the typical signature of reverse spherical micelles: maximum constant intensity at low  $q$  is followed by a decay in  $I$  at higher  $q$  values. From the Baxter's fitting procedure described in the Experimental Section an aggregation number ( $N_{agg}$ ) of around 4 and a polar radius of 7.5  $\text{\AA}$  are determined, as in agreement with the literature.<sup>2,3</sup> When the extractant concentration goes from 0.7 to 1M a small decrease in the intensity in the low  $q$  regime is observed. This is interpreted by an increase in the repulsive potential between micelles due to the high concentrations. The Baxter's fitting procedure can not be applied in that case, see Text.

### Combined SAXS and SANS spectra for DMDBPMA

The experimental scattered intensities modeled for the sample at 0.54M for both SAXS and SANS data are given as an example in Fig.S2. At this concentration, the solution contains small spherical reverse micelles interacting through an attractive potential.



**Fig. S2: Combined SAXS and SANS spectra for DMDBPMA (C5) at 0.54M. Lines represent fits using the Baxter's model for spherical shape particles interacting through a sticky potential. Parameters are the same for both SAXS and SANS fits:  $N_{agg.} = 4$  and  $U/kT = -1.92$ .**

**Porod's treatment: molecular area of extractant.** Molecular area of extractant  $\sigma$  ( $\text{\AA}^2$ ) at the polar/apolar interface can be obtained from the SAXS spectra in the large  $q$ -range where the intensity follows a  $q^{-4}$  behavior, it is the so-called Porod regime described by the Eq. S1.<sup>30</sup>, where  $\Sigma$  ( $\text{cm}^{-1}$ ) is total interface per unit volume. This regime is only obtained if a thin interface separates two media of different scattering length densities<sup>31</sup>. Such an hypothesis is verified by evaluating the so-called experimental invariant ( $Q_{Exp.}$ , Eq. S2) which is a general property of scattering spectra and is calculated from scattering intensity. In our case the Porod regime is observed only after subtraction of the background and  $Q_{Exp.}$  is then calculated after this subtraction in a  $q$ -range from 0.02 to 0.8  $\text{\AA}^{-1}$ . In order to use Eq. S1 with confidence  $Q_{Exp.}$  must be equal to the theoretical invariant ( $Q_{Theo.}$ , Eq. S3) calculated with volumic fraction and scattering length density contrast.

The total interface per unit volume,  $\Sigma$ , is related to the average concentration of extractant participating to the aggregates and to the specific surface per extractant molecule,  $\sigma$ , through:  $\Sigma = [\text{Extractant}]_{agg.} \times \sigma$ . The results of the Porod's treatment are presented for C14 in the table S1.

$$\lim_{q \rightarrow \infty} (I \cdot q^4) = 2\pi^2 \Delta \rho^2 \Sigma \quad \text{Eq(S1)}$$

$$\int_0^{\infty} i(q) q^2 dq = Q_{exp} \quad \text{Eq(S2)}$$

$$Q_{theo} = 2\pi \Delta \rho^2 \Phi (1 - \Phi) \quad \text{Eq(S3)}$$

**Table S1** Parameters for the Porod's law treatment of the SAXS spectra in Fig.5 for C14.  $\Phi$ ,  $\sigma$ ,  $\Sigma$  and  $Q$  are respectively the volume fraction of the polar part of extractant molecules, the specific surface per molecule, the total surface and the invariant.  $\sigma$  ( $\text{\AA}^2$ ) from dilution laws are obtained from the one dimensional dilution law obtained in Fig.5 (see text).

C(mol/L)	$\Phi$	$\Phi$ - cm $\epsilon$	Porod	$\sigma$ ( $\text{\AA}^2$ ) from Porod	$\sigma$ ( $\text{\AA}^2$ ) from dilution laws	$\Sigma \cdot 10^{-6}$ ( $\text{cm}^2/\text{cm}^3$ )	Q exp.	Q theo.
0.8	0.19	0.13	1.8 10 <sup>-4</sup>	126±6		5.92	0.00095	0.0011
1.2	0.28	0.22	2.5 10 <sup>-4</sup>	116±3	98.7	8.22	0.0012	0.0016
1.45	0.35	0.29	3.6 10 <sup>-4</sup>	132±2	98.7	11.84	0.0015	0.002
1.73	0.4	0.34	3.9 10 <sup>-4</sup>	126±2	98.7	12.82	0.00146	0.0021
2.0	0.47	0.41	4.8 10 <sup>-4</sup>	132±2	97.5	15.78	0.00139	0.0023

Treatments of the spectra shown in Fig.5 SAXS C14 were done according to the Porod's law<sup>1,2</sup>. A good agreement between  $Q_{Exp.}$  and  $Q_{Theo.}$  is obtained (see Table S1), this validates the method used. The molecular area occupied by the polar head at the aggregate/solvent interface,  $\sigma$  ( $\text{\AA}^2$ ), can thus be determined with confidence. The molecular area values are calculated to be of around  $130\text{\AA}^2$ . This is reasonable and in good agreement with the value determined from Langmuir isotherms (around  $120\text{\AA}^2$ ) during the formation of a C14 monolayer at the water/air interface (unpublished results). This point is important since both methods are not always in agreement.<sup>3,4</sup>

1 G. Porod In *Small Angle X-ray Scattering*, Ed. O. Glatter, O. Kratky, Academic Press, London, 1982, chap. 2.

2 O. Spalla In *Neutrons, X-ray and light: Scattering methods applied to soft condensed matter*, Ed. P. Lindner, T. Zemb, North Holland, Amsterdam, 2002, chap. 3, 49-71.

3 G.G. Warr, Th. Zemb, M. Drifford *J. Phys. Chem.*, 1990, **94**, 3086-3092.

4 S. Hyde, S. Andersson, K. Larsson, Z. Blum, T. Landh, S. Lidin, B.W. Ninham, in *The language of shape*, Elsevier, Amsterdam, 1996.

## Modelling of interaction potentials between aggregates

The results of this modeling (see the main text) are shown in the following figures, respectively for spheres, cylinders and lamellae. The attraction/repulsion potentials and the total interaction potentials are plotted for C5 and C14. For the three types of structures the curves representing the total interaction potentials show a similar shape. A strong decrease in the total interaction potential is observed at short distances ( $6.5 < D < 6.9\text{\AA}$ ) and an energy barrier whose value depends both on the extractant molecule and on the type of aggregate is situated at a distance of around  $7.3\text{\AA}$ . For all cases the energy barriers are listed in Table 3. Such an energy barrier determines whether the system is kinetically stabilized. Usually a system showing an energy barrier above  $30 kT$  is considered as to be kinetically stabilized.

