STUDY OF EXTRACTANT MOLECULES AS COSURFACTANT AT THE WATER-OIL INTERFACE IN MICROEMULSIONS

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Abstract

In the present work specific adsorption phenomena of metal ions at the water –oil interface are studied. Bicontinuous microemulsions were chosen as a model system because of their high specific surface between water and oil phases. Mixing an extremely hydrophobic extractant considered here as the co-surfactant with an extremely hydrophilic sugar surfactant we succeed to formulate microemulsion that can be described with the classical Winsor formalism for multiphasic microemulsions. From the so-called “fish-cuts” inside the phase tetrahedron we observe the phase transition WI-WIII-WII by only increasing the extractant concentration. We were particularly interested in the WIII-type microemulsions and their two excess phases. Chemical analysis of these excess phases gives us the exact film composition. Neutron scattering experiments of the microemulsion inform about the microemulsion structure as well as characteristic length scales and specific area. Finally, highly precise analytical techniques like ICP-AES permit to determine adsorption isotherms for various ions of interest in nuclear industry, like Nd^{3+}, Eu^{3+}, Fe^{3+}, UO_2^{2+}, at this water oil interface. These results lead to a better understanding of interfacial effects taking place in liquid/liquid extraction processes used for the nuclear fuel reprocessing. Ultimately this paves the way for the design of new selective ion extraction processes.

Introduction

An effective strategy to co-solubilise water and oil is the addition of amphiphilic molecules. The use of a hydrophilic surfactant in combination with a hydrophobic co-surfactant, typically n-alcohols with $3<n<8$, permits to create microemulsions (µE) that are clear, isotropic and thermodynamically stable dispersions of water and oil separated by a mixed surfactant/co-surfactant film [17] [3] .In recent years microemulsions were designed more complex in terms of their composition, e.g. carrying polymers, biomolecules [2] complexing surfactants, nanoparticles and more recently ionic liquids [11] [22]

Moreover in the last 20 years substantial improvements of experimental characterisation techniques like small-angle neutron scattering permitted to get a better insight of the microemulsion structure at the Ǻ resolution [4].

Under certain conditions bicontinuous µE form in equilibrium with both water and oil excess phases (so-called Winsor III). This can be obtained around the phase inversion when the system changes from an oil-in-water µE with excess oil phase

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(Winsor I) to an water-in-oil µE with an excess aqueous phase (Winsor II) [19]. We will present that microemulsion systems are suitable systems in order to increase the interfacial area between oil and water for extractant molecules . In the field of ion separation science the main process used is based on liquid-liquid extraction where ions are selectively transferred from an aqueous phase to an organic phase containing a solvent and an extractant molecule. In the nuclear industry for instance tributyl phosphate (TBP, see figure 1) is a popular extractant used in the so-called PUREX process (Plutonium and Uranium Refining by EXtraction) where uranium and plutonium are extracted from an acidic aqueous solution [13] [12]. TBP and other classical extractants are hydrophobic, i.e. nearly insoluble in water, and have an amphiphilic structure composed of a complexing polar part and one or more alkyl chain(s) as apolar part. Hence extractants have all the properties required to play the role of a co-surfactant [21]. Incorporating extractants in µEs might permit to artificially functionalise the interfacial film by a complexing group.

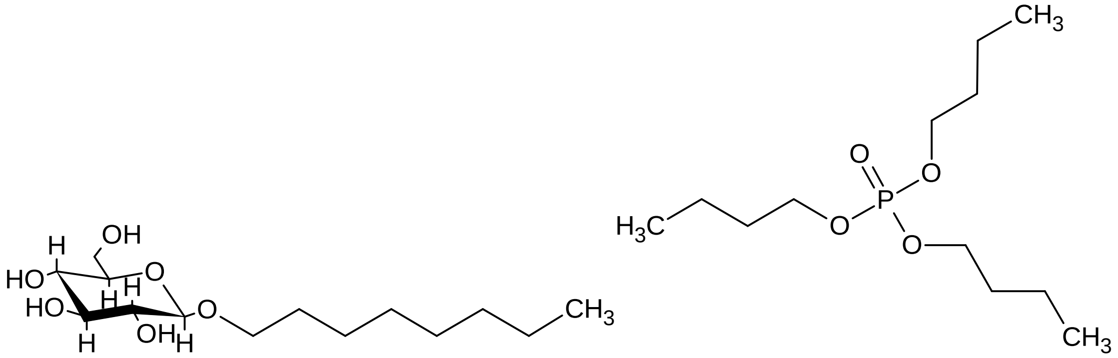
Here we demonstrate that TBP acts as an efficient co-surfactant to form microemulsions. We focus on WIII-type microemulsions because the bicontinuous structure provides large accessible oil-water interface that could promote both ion adsorption/depletion and ion transfer from the aqueous- to the oil-phase. The evaluation of the co-surfactant behaviour of TBP is done by comparison to the more standard n-alcohols systems. n-Octyl-β-glucoside (C8G1, see figure 1) was chosen because of its high hydrophilicity that enables to counterbalance the hydrophobicity of TBP or chosen n-alcohols. First phase behaviour was studied by realising the so-called “fish-cuts” that shows the region of existence of Winsor type systems. Secondly the film composition which consists only of surfactant and co surfactant was determined by chemical analysis of the excess phases since surfactant and cosurfactant are distributed between excess and microemulsion phases. In addition the microstructures were investigated by Small Angle Neutron Scattering (SANS) that gives access to the characteristic length scales and to specific area. Consequently a precise description of the µEs at the molecular and sub-molecular scales is obtained in the bulk µEs and at the water/oil interface.

Experimental

Materials

The surfactant n-octyl-β-glucopyranoside (C8G1, C14H28O6, purity >97%) was purchased from Anatrace (Ohio, USA). The hydrocarbon dodecane (C12H26, purity 99+%) was provides by Fluka, the alcohols n-pentanol (C5H12O, purity 99+%), n-hexanol (C6H15O purity +98%), n-octanol (C8H18O, purity +99%) were purchased from Sigma Aldrich. Tributylphosphate ((C4H9O)3PO, TBP, purity +98%) was purchased from Prolabo. Salts were dissolved in distilled water (MilliQ) or in D2O obtained from Sigma Aldrich with a degree of deuteration > 99.9%, respectively. The following salts were used: Lithium chloride (LiCl), Lithium nitrate (LiNO3) and Neodymium (III) nitrate hexahydrate (Nd(NO3)3). The purity of all salts which were provided by Sigma-Aldrich was >99%. All chemicals were used as delivered.

Figure 1 Molecular structures of the surfactant n-octyl-b-glucoside (C8G1) on the left side and the cosurfactant tributylphosphate (TBP) on the right side



Sample preparation and Phase diagram determination

To study phase behaviour samples were prepared by contacting 2 mL of aqueous solution, containing C8G1 and salt, and 2 mL of dodecane into sealed tubes. Aliquots of co-surfactant, 25 µL to 50 µL of either n-alcohols or TBP, were added stepwise to reach a given molar ratio γ of co-surfactant/surfactant:

$$\gamma = \frac{n_{co-surf}}{n_{surf}} \quad (1)$$

The samples were shaken using a vortex for 2 minutes, centrifuged to enhance phase separation and thermostated in a water bath at 25.0℃ ±0.1℃ for 24 hours. Visual observation enables the determination of the phase diagram by determining the phase transition from Winsor I to Winsor III to Winsor II systems. The phase diagrams studied show the regions of existence of the Winsor systems.

Two types of phase diagrams were determined. First the so-called “fish-cut” phase diagram, see Figure 2, were realised for different co-surfactants: pentanol, hexanol, octanol and TBP. Second the influence of salt on the phase transitions from Winsor I to III and from Winsor III to II was studied for hexanol and TBP systems. The surfactant concentration was fixed at 0.3M in water and the salt concentration was varied from 0 to 0.3M in water. The salts studied are: LiCl, $LiNO_3$ or $Nd(NO_3)_3$. The resulting phase diagrams are given in Figure a and b respectively for hexanol and TBP systems.

For neutron scattering experiments and chemical analysis water was replaced by D_2O. The molar ratio γ of co-surfactant/surfactant was fixed at around 1.1; 1.9 and 2.6 in order to be located inside the three-phasic region. The compositions of the samples used for the SANS experiments are listed in Table 1. Their representations are given in the phase diagrams with the corresponding sample name, Figure 3 (circles). Once the phase equilibrium was reached the three phases were separated with a micro-syringe and stored in glass vials.

Table 1 Composition of the Winsor III type microemulsions prepared for neutron scattering experiments and chemical analysis

system	sample name	n C8G1 [mol]	n Cosurf [mol]	c salt [mol/L]	γ see (1)
C8G1/hexanol	A1	0.00079	0.0009	0	1.14
C8G1/hexanol/LiCl	A2	0.00079	0.0009	0.3	1.14
C8G1/hexanol/LiNO3	A3	0.00078	0.0009	0.3	1.15
C8G1/hexanol/Nd(NO3)3	A4	0.00075	0.0009	0.3	1.20
C8G1/hexanol	B1	0.00082	0.00151	0	1.84
C8G1/hexanol/LiCl	B2	0.00081	0.00151	0.3	1.86
C8G1/hexanol/LiNO3	B3	0.00081	0.00151	0.3	1.86
C8G1/hexanol/Nd(NO3)3	B4	0.00078	0.00151	0.3	1.94
C8G1/hexanol	C1	0.00081	0.0021	0	2.59
C8G1/hexanol/LiCl	C2	0.00081	0.0021	0.3	2.59
C8G1/hexanol/LiNO3	C3	0.00080	0.0021	0.3	2.62
C8G1/hexanol/Nd(NO3)3	C4	0.00076	0.0021	0.3	2.76
C8G1/TBP/LiCl	D2	0.00061	0.0012	0.3	1.97
C8G1/TBP/LiNO3	D3	0.00064	0.0012	0.3	1.88
C8G1/TBP/Nd(NO3)3	D4	0.00060	0.0012	0.3	2.00

Methods

SANS

Neutron scattering experiments were carried out at the Hahn-Meitner-Institute (HMI) in Berlin, Germany on the instrument V4 [9]. Two wavelengths were selected, 4.5 Å and 6 Å. To access a Q-range of 0.03 – 4 nm^{-1} the sample to detector distances of 1, 2, 4, 8, and 16 m were applied. Data were registered on a 64 x 64 two-dimensional detector, radially averaged and converted into absolute units according to a standard procedure. The data treatment was done by the software BerSANS available at HMI [8].

Density measurements of the excess oil phases

Since the three macrophases are in thermodynamic equilibrium the distribution of cosurfactant between the µE and the excess oil phase can be investigated. The determination of the co-surfactant concentration in dodecane excess phase is made by density measurement. Therefore after phase separation the density of the oil excess phase was measured at 25℃ using a precise vibrating tube densimeter, DSA 5000 Anton Paar. We assume that only cosurfactant is dissolved in the excess oil phase. The residual cosurfactant in the excess oil phase is determined using a calibration curve.

Results and discussion

Fish cut

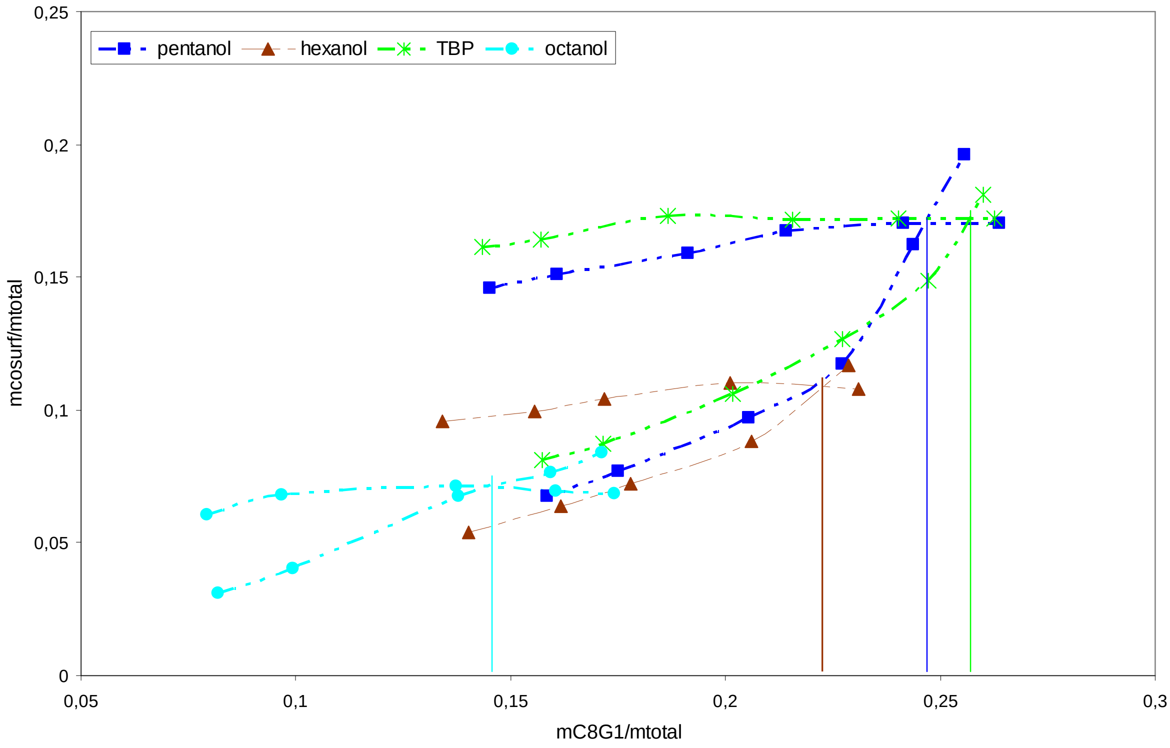
The studied system contains four components: water (or brine), oil, hydrophilic surfactant and hydrophobic co-surfactant [6] [14]. By adding co-surfactant stepwise to a surfactant-water-oil mixture two phases are observed at first. A surfactant rich phase, being an oil-in-water microemulsion, is then in equilibrium with an excess oil phase (Winsor I, $\underline{2}$). By increasing the cosurfactant content the well-known three phase body occurs. A microemulsion coexists then with excess water and oil (Winsor III, 3). At higher co-surfactant content the system is driven into a two-phase region where a water-in-oil microemulsion and excess water phase coexists (Winsor II, $\overline{2}$). At sufficiently high surfactant concentrations a one-phase microemulsion can be obtained (Winsor IV, 1). By fixing the water-to-oil volume ratio at 1:1 the schematic phase boundaries in the resulting two-dimensional section of the tetrahedron have the shape of a fish. The head of the fish represents the $\underline{2}$-3-$\overline{2}$ phase transitions whereas the tail situated at high surfactant concentrations corresponds to the $\underline{2}$-1-$\overline{2}$ phase transitions.

We studied the co-surfactant behaviour of a highly hydrophobic extractant molecule, here tri-n-butylphosphate (TBP), in comparison to classical n-alcohols cosurfactants. Hence fish-cuts were realised with a hydrophilic surfactant C8G1, water and dodecane by varying the co-surfactant: n-pentanol, n-hexanol, n-octanol and TBP, see Figure 2. For the n-alcohol series, by increasing the chain length the fish is shifted both to (i) lower surfactant concentrations and to (ii) lower co-surfactant to surfactant ratios. This can be interpreted respectively as (i) an increase in the solubilisation efficiency [3b] i.e. less surfactant is needed to co-solubilize water and dodecane, and as (ii) an increase in the hydrophobicity of the co-surfactant, i.e. less co-surfactant is required to reverse the system from direct to reverse microemulsions. Such an evolution as a function of the alcohol chain length is usually observed in microemulsions [3b]. Note also that the head of the fish becomes thinner as the length of the n-alcohol increases. This is usually interpreted by an increase in the interfacial film rigidity [5] [1] [7] which becomes too stiff to accommodate water and oil i.e. to form a soft bicontinuous structure usually observed in Winsor III microemulsions.

In the case of TBP the fish diagram is observed and is comparable to the one obtained with n-pentanol but only very slightly shifted to higher surfactant concentrations. Hence TBP is an efficient co-surfactant to form microemulsions and is just a little less efficient in terms of solubilisation power compared to n-pentanol.

The influence of the presence of salt on the fish cut was also studied for TBP by using $Nd(NO_3)_3$ at 0.3M instead of pure water, but is not shown here. Neodymium salt was chosen because it is supposed to have the greatest effect due to (i) its three charges and (ii) its strong interaction with TBP i.e. which is known to form a complex with Nd^{3+} [16] [10]. A slight shift in the solubilisation power to lower surfactant concentration is observed in presence of Nd^{3+}. Moreover the phase transition appears slightly at higher co-surfactant to surfactant ratios. This is likely to be related to a salting-in effect, subsequent to ion adsorption at the TBP functionalized interface, increasing therefore the hydrophilicity of organic molecules i.e. it increases the film curvature towards water. Nevertheless addition of salt on the studied system affects only slightly the phase transitions. This is not surprising because salt addition is well known to have large effects on Winsor type system based on ionic surfactants and only slight effects on non-ionic ones [15] [20]. Hence this observation is confirmed here when TBP, a non-ionic extractant, is used as co-surfactant with a non-ionic surfactant. Using TBP in the presence Nd^{3+} does not affect much the phase transitions. We will now go further by studying the microemulsion structure for alcohols and TBP.

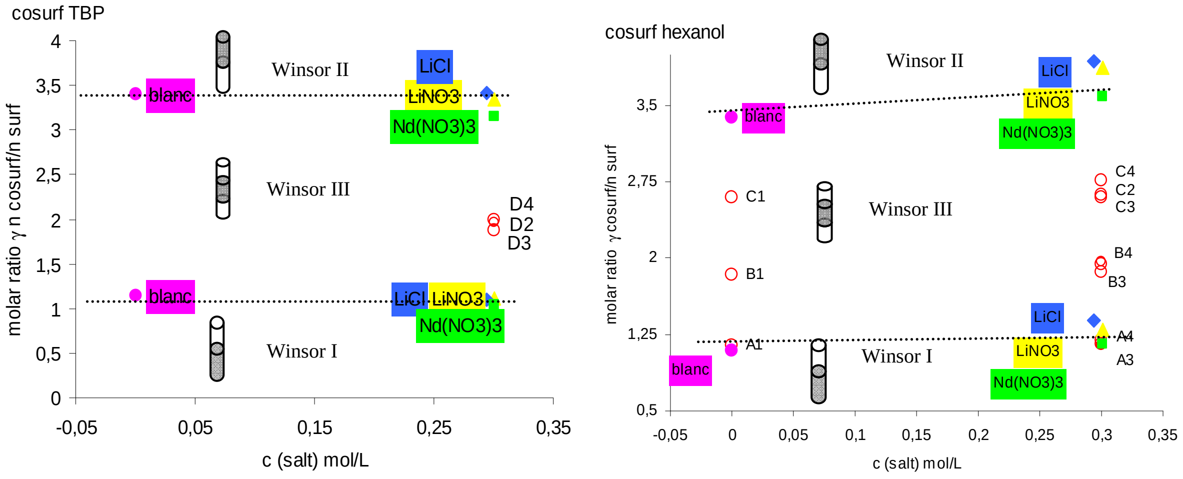
Figure 2 Fish cuts for the different cosurfactants used to form threephasic microemulsions: pentanol (blue rectangles), hexanol (brown, triangles), octanol (turquois circles) and TBP (green stars)



Microemulsion microstructure and the effect of salt

After investigating the co-surfactant behaviour of TBP with the help of pseudo-binary fish-cut like phase diagrams we will go now one step further and consider the effect of salts on Winsor III systems. We chose to compare TBP and hexanol at low surfactant mass fraction because the $\underline{2}$ - 3 and 3 – $\overline{2}$ phase transitions appears at similar γ with both co-surfactants. LiCl, $LiNO_3$ and $Nd(NO_3)_3$ were used in order to study the salt specificity. The salt concentration was fixed at 0.3M. The compositions of the samples, see Table 1, were chosen so as to lie in the three phasic region located between the dashed lines in Figure 3. The empty symbols correspond to the composition of the samples studied. Hence these phase diagrams represent cuts in the fish plot in Figure 2 at constant surfactant mass fraction. In order to access the microemulsion structure from large distance scale to a molecular description, i.e. the interfacial composition, SANS experiments and chemical analysis were performed.

Figure 3 Cut in the phase diagram of C8G1/TBP - brine – oil and C8G1/hexanol - brine – oil, respectively; with increasing molar ratio γ cosurf/surf the following phase transition was observed $\underline{2}$ – 3 – $\overline{2}$; the points shown in this graph represent the limit of these phase transition without salt (dots) or for different salts LiCl (rhombi), LiNO3 (triangles) and Nd(NO3)3 (rectangles)



SANS: The scattering pattern of classical and modified microemulsions

In order to study the microstructure of the microemulsions and to have access to their length scales, SANS experiments were carried out. The goal here is to highlight *(i)* the effect of the molar ratio γ on the structure of microemulsions and *(ii)* the effect of TBP and hexanol as co-surfactant. To do so we compare first the Winsor III samples A1, B1 and C1 and A2, B2 and C2. Figure 4a and b show then the bulk contrast scattering curves for samples with salt (LiCl 0.3M) or without salt for γ 1.1 to 2.6 plotted in a double logarithmic representation. We find for microemulsions at low γ scattering pattern that could be well fitted to elongated particles, like ellipses, rods or disks. By increasing γ the scattering curve changes and the characteristic interaction peak appears which is related to the bicontinuous internal structure. Here Teubner Strey model [18] is useful in order to obtain characteristic length scales like the periodicity D* of repeating water or oil domains and their persistence length ζ. At higher γ the scattering peaks disappears and we obtain by fitting the scattering curves a spherical structure. All these different structures could be obtained within the threephasic region of the fish like diagrams. Under exactly the same composition this structural sequence is found when salt is added or not. This means that the microemulsions structure does not depend on salinity. It will be an important point when we interpret ion adsorption phenomena in the future. Knowing that the internal structure is not affected by the addition of salt will permit to use these microemulsions as suitable model systems.

Figure 4 a Scattering curves for microemulsions containing no salt with increasing molar ratio γ, from low γ= 1.1 (rectangles) over intermediate γ= 2.0 (triangles) to high γ= 2.6 (rhombi)

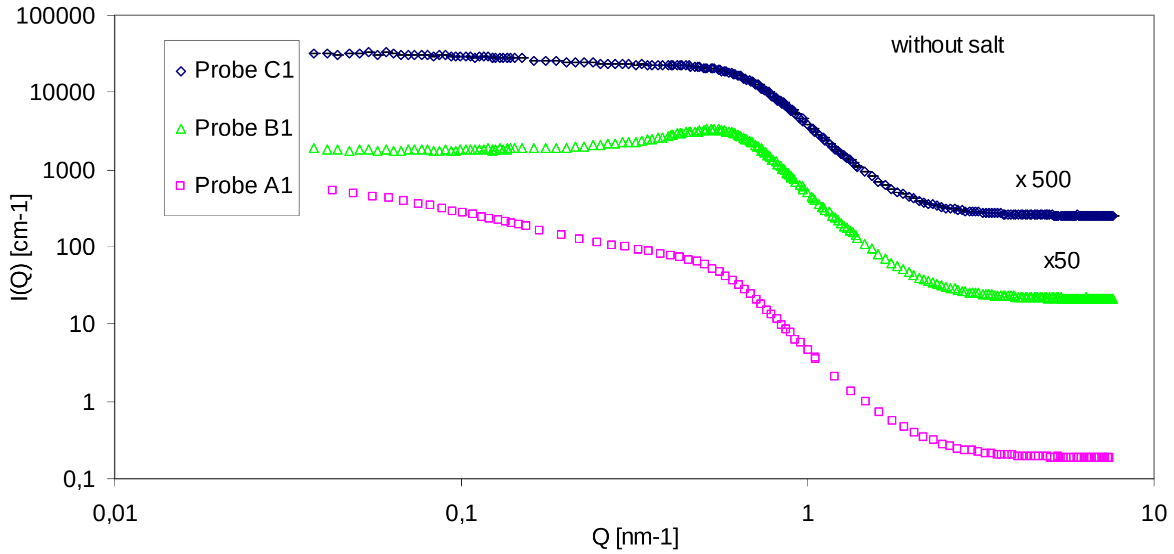
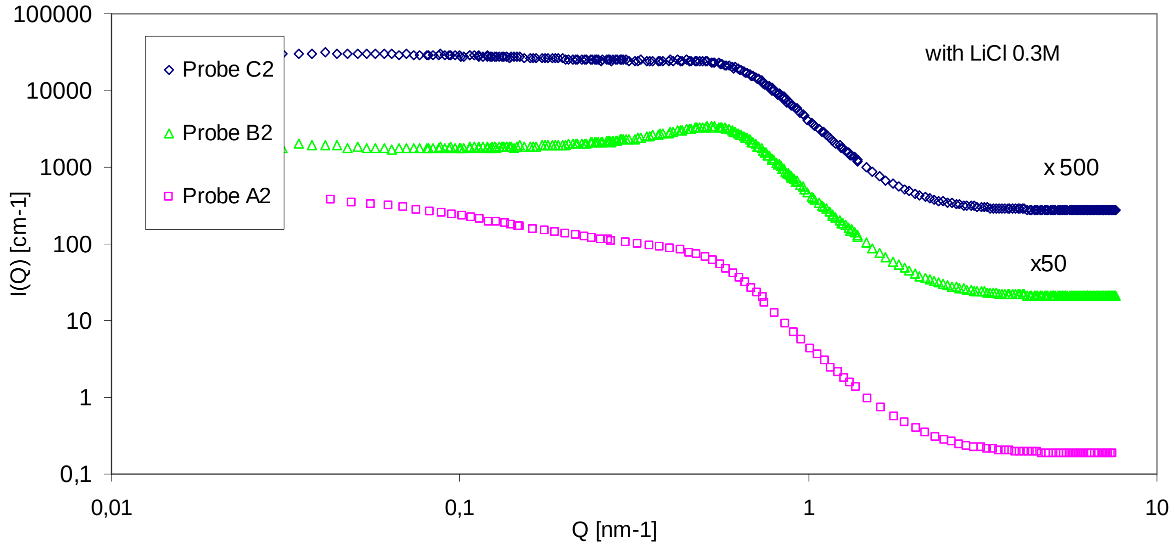
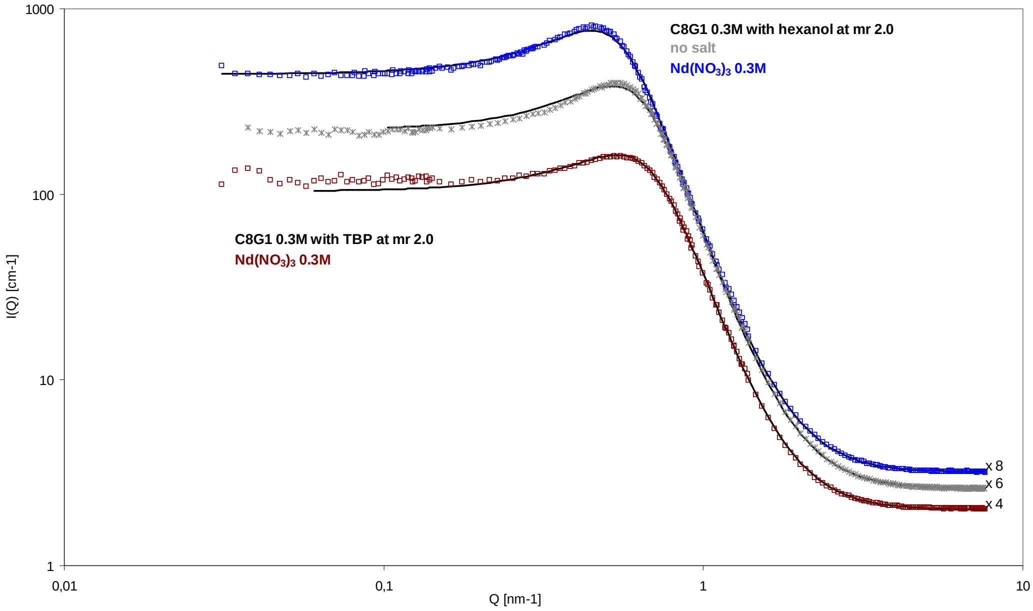


Figure 4 b Scattering curves for microemulsions containing LiCl 0.3 M mit increasing molar ratio γ, from low γ=1.1 (rectangles) over intermediate γ= 2.0 (triangles) to high γ=2.6 (rhombi)



Then we compare bicontinuous microemulsions containing hexanol as cosurfactant to microemulsions with TBP at a given molar ration γ (2.0) and with $Nd(NO_3)_3$ at 0.3M. The scattering curves are represented in figure 5. Interestingly a structure peak is obtained with TBP as cosurfactant indicating that it forms microemulsions like it is the case with hexanol. We obtain for both, TBP and hexanol a periodicity D* of about 10nm and a persistence length ζ of about 2.8nm-4nm. We furthermore could extract from the Porod regime at large q-range of the curves the internal specific surface Σ , which is highly elevated for bicontinuous microemulsions. We find values about $2 \cdot 10^6$ to $3 \cdot 10^6$ cm^{-1} that are in good accordance with values found in the literature.

Figure 5 Bulk contrast curves for microemulsions obtained at a molar ratio γ of 2.0 containing either TBP as cosurfactant or hexanol. The nature and concentration of the salt was kept constant for both samples



The interfacial film composition

From mass balance the composition of the interfacial film, i.e. the molar ratio of cosurfactant over surfactant at the interface, is calculated (see Table 2). This was obtained by density measurements of the excess oil phase which is in equilibrium with the microemulsion phase. With the help of a calibration curve and the known initial mass fraction of cosurfactant we can have access to the interfacial surfactant-to-cosurfactant composition. Parts of the results are listed in table 2 which are representative and could be interpreted as follows. We find for the microemulsions prepared with hexanol as cosurfactant values between 0.92 and 1 and for microemulsions containing TBP values between 0.32 and 0.37. Microemulsions containing TBP as cosurfactant have less cosurfactant at the water oil interface than microemulsions containing hexanol. We are able to compare the two systems since the initial conditions, like the surfactant, nature of the oil, salinity are exactly the same and we observe for the two co surfactants the same phase behaviour. Tentatively this difference can be explained in terms of size and solubility of the cosurfactant. TBP is expected to have a greater cross sectional area than hexanol. More bulky means more effective than hexanol in its ability to change the curvature of the film.

Table 2 Overview over initial molar ratio of cosurfactant-to-surfactant and molar ratio at the interface for the case of hexanol and TBP taking into account the cosurfactant or surfactant concentrations in the bulk excess phases

sample description	sample name	initial molar ratio cosurf/surf	mole of cosurf in excess oil [mol]	mole of cosurf initial [mol]	mole of surf at interface [mol]	molar ratio cosurf/surf at interface
C8G1 without salt hexanol	B1	1.8	0,0009	0,0016	0,0008	0,9280
C8G1 LiCl hexanol	B2	1.9	0,0008	0,0015	0,0007	0,9820
C8G1 $LiNO_3$ hexanol	B3	1.9	0,0008	0,0016	0,0008	1,0200
C8G1 $Nd(NO_3)_3$ hexanol	B4	1.9	0,0009	0,0016	0,0008	0,9800
C8G1 LiCl TBP	D2	2.0	0,0010	0,0012	0,0006	0,3730
C8G1 $LiNO_3$ TBP	D3	1.9	0,0010	0,0012	0,0006	0,3830
C8G1 $Nd(NO_3)_3$ TBP	D4	2.0	0,0010	0,0012	0,0006	0,3140

Conclusion

In order to conclude we could say that the investigated extractant TBP can play the role of a cosurfactant in microemulsion systems. We furthermore were able to determine exactly the film composition. We find that the interfacial film is composed of three times more cosurfactant than surfactant when we use a classical cosurfactant such as hexanol. Under similar conditions and replacing hexanol by tributylphosphate the interfacial film is composed of equal amounts of cosurfactant and surfactant. The efficiency of TBP in changing the film curvature is directly related to its bulky structure composed of three alkyl chains compared to classical single chain cosurfactants.

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