# Effect of *n*-Octanol on the Structure at the Supramolecular Scale of Concentrated Dimethyldioctylhexylethoxymalonamide Extractant Solutions

B. Abécassis,[†] F. Testard,*,[†] Th. Zemb,[†] L. Berthon,[‡] and C. Madic[§]

*CEA, DSM/DRECAM/SCM/LIONS, CEA-Saclay, 91191 Gif-sur-Yvette, Cedex, France, CEA, DEN/VRH/DRCP/SCPS/LCSE, CEA-Valrhô (Marcoule), B.P. 171, 30207 Bagnols-sur-Ceze, Cedex, France, and DEN/SAC/DIR, CEA-Saclay, 91191 Gif sur Yvette, Cedex, France*

Using small-angle X-ray scattering (SAXS) and interfacial tension measurements, we show that concentrated solutions of dimethyldioctylhexylethoxymalonamide diluted in dodecane are organized in reverse aggregates that have many features in common with reverse micelles. The critical micellar concentration is determined from interfacial tension measurements using the pendant-drop technique, and the aggregation number is given by fitting SAXS data on the absolute scale. The effect of the addition of *n*-octanol, a modifier widely used in liquid/liquid extraction, is studied by SAXS. It is shown that, for small amounts of alcohol, the modifier acts as a cosurfactant; it swells the reverse micelles by adsorbing onto the aggregates and increases the surface per extractant polar head. When *n*-octanol is added in larger quantities, a new microstructure appears, and the amount of octanol required for this transition depends on the amount of diamide in solution (for example, octanol concentration ≥ 1 M for 0.7 M diamide). Therefore, a hydrogen-bond network is present in solution, and the presence of areas of high electronic density separated by a distance varying from 15 to 20 Å is found to explain the scattering patterns.

## Introduction

Hydrometallurgy is the preferred separation method used in nuclear fuel reprocessing. The so-called PUREX process, based on the use of tri-*n*-butyl phosphate diluted in an aliphatic solvent, is used worldwide in all existing reprocessing plants.[1] Uranium and plutonium are separated from the rest of the spent fuel to be reused.

New strategies of managing nuclear wastes coming from the PUREX process are under study in several countries. The final objective of this research is to separate selectively actinides and some long-lived fission products from the rest of the waste to make up specific strategies for each kind of waste (transmutation, storage in specific materials).[2]

The DIAMEX process[3] aims at separating lanthanides and actinides from the fission products downstream from the PUREX process. The extractant used in this hydrometallurgical process is a malonamide. One of the malonamides recently tested on active waste is the dimethyldioctylhexylethoxymalonamide (DMDOHEMA; Figure 1). The hydrometallurgical process consists of a liquid/liquid extraction: an organic phase containing the extractant is contacted with a water phase containing the ions to be extracted. The stability of the organic phase is crucial for industrial processes. Depending on the temperature, extractant, and solute concentration, the organic
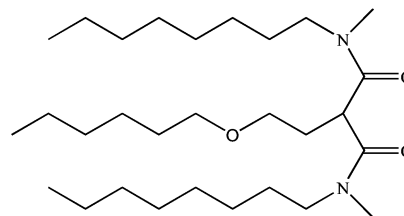


**Figure 1.** DMDOHEMA, the extractant used in the DIAMEX process.

phase can split into two layers; this phenomenon is known as third-phase formation.[4]

Previous studies[5] showed that concentrated organic solutions of another malonamide-type extractant, dimethyldibutyltetradecylmalonamide, or DMDBTDMA, are organized in reverse oligomeric aggregates that have many features in common with reverse micelles. Water pools containing dissolved ions are surrounded by the diamide and dispersed in the organic phase. This molecular organization is found to be at the origin of the "third-phase phenomenon" observed in numerous hydrometallurgic processes. An attractive interaction between those aggregates induces the separation of the organic phase into two phases.[5] The main difference with reverse micelles, such as the well-studied aerosol OT (AOT) system,[6] is that the polar volume of DMDBTDMA droplets dispersed in oil is smaller by typically 2 orders of magnitude.[5] However, when compared at the same water/surfactant ratio ($W \cong 1$), micelles formed by extractants exhibit no difference with model molecular systems such

* Author to whom correspondence should be addressed. E-mail: testard@drecam.saclay.cea.fr.
† CEA, DSM/DRECAM/SCM/LIONS, CEA-Saclay.
‡ CEA-Valrhô (Marcoule).
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as AOT. To avoid third-phase formation, modifier molecules with a hydrocarbon chain containing a polar atom[7−9] are often added to the organic phase. A well-known modifier is *n*-octanol;[10] it is used in several systems for the formulation of solvent.[7,11,12] The adjunction of a modifier changes the physicochemical properties of the extractant and has a direct influence on the maximum attainable actinide concentration in the organic phase. A review is available on this subject.[8] Octanol is a hydrogen-bonded liquid inducing specific thermodynamic properties (excess thermodynamic quantities) to the alkane/octanol mixtures. It was demonstrated by IR, Raman, or NMR studies[13−17] that this results from the formation of hydrogen-bonded octanol aggregates. These self-association properties of octanol must have an effect on the aggregates of diamide extractant. In the literature, several studies focused on the influence of added octanol on the distribution coefficient of metals in liquid/liquid extraction. Sinegribova and Muraviova[18] showed that, as the amount of octanol increases, the distribution ratio of zirconium goes through a maximum with organophosphorus extractants. Octanol behaves differently depending on its concentration in the organic phase, acting as a cosurfactant or a cosolvent. Bogacki[19] demonstrated that the association of a modifier (hydrophilic alcohols) and especially its coassociation with an extractant changes the optimum strength of the extractant (extraction equilibrium constant) for both the multistage countercurrent and cross-current extraction systems.

The present work focuses on the self-association properties of DMDOHEMA in dodecane and on the effect of octanol on the structure of diamide aggregates. In the first part, the aim is to determine the microstructure at the supramolecular scale of DMDOHEMA/dodecane solutions. Interfacial tension measurements and small-angle X-ray scattering (SAXS) are performed to quantify the self-assembling properties of DMDOHEMA [critical micelle concentration (cmc), surface per polar head, aggregation number]. In the second part, the structuralization of alkane/octanol mixture is evidenced by SAXS and the effect of the addition of *n*-octanol on the structure of the diamide aggregates in dodecane is studied. Depending on the concentrations, the octanol behaves as a cosurfactant and then as a cosolvent. The structuralization of the solvent can be compared to the behavior of hydrotrope molecules in water.

## Experimental Section

**Chemicals.** The extractant DMDOHEMA (99% pure) is supplied by Panchim (Evry, France) and used without further purification. *n*-Dodecane (99% pure) is from Sigma, and *n*-octanol (96% pure) is from Merck. Millipore water is used throughout the study.

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**Table 1. Sample Compositions**

| [DMDOHEMA] (M) | solvent | [H₂O] (M) | [octanol] (M) |
|---|---|---|---|
| 0 | octanol | 2.36 | 6.36 |
| 0.3 | octanol | 2.10 | 5.16 |
| 0.7 | octanol | 1.95 | 3.87 |
| 1.1 | octanol | 1.51 | 2.88 |
| 0 | d/o 50:50 | 0.72 | 3.18 |
| 0.3 | d/o 50:50 | 0.55 | 2.65 |
| 0.7 | d/o 50:50 | 0.98 | 1.97 |
| 1.1 | d/o 50:50 | 1.02 | 1.29 |
| 0.7 | dodecane | 0.22 | 0 |
| 0.7 | d/o 82:18 | 0.43 | 0.65 |
| 0.7 | d/o 24:76 | 1.38 | 2.89 |

**Techniques.** *Preparation of the samples.* A total of 1.5 mL of the organic phase containing the extractant at a given concentration in the organic solvent (dodecane/octanol, d/o, at different volume fractions) and 5 mL of the aqueous phase (water or nitric acid) are thoroughly mixed for 5 min using a Vortex mixer.[20] The mixture is then centrifuged with a thermostated Sigma 3K30 centrifuge for 15 min at 4500 min⁻¹.

*Densities of the Organic Phases.* The densities of the organic phases are measured on a DMA 500 densimeter (Antoon-Paar, Graz, Austria). The molecular volume of the diamide ($V_2$) is measured from the densities of the diamide solutions at different concentrations using eq 1:

$$\frac{\rho}{\rho_0} = C\left(\frac{M}{\rho_0} - V_2\right) + 1 \qquad (1)$$

where $\rho$ is the density of the diamide solution of concentration $C$, $\rho_0$ is the density of the solvent (dodecane), and $M$ is the molar mass of the diamide. The slope of the straight line representing $\rho/\rho_0$ versus $C$ gives $V_2 = 876.5$ Å³·molecule⁻¹. The molar mass is 482 g·mol⁻¹; therefore, the apparent density of a 0.0108 M diamide solution in dodecane is 0.747. The apparent density is lower than that for water; this is important when phases coexist.

*Karl Fischer Method.* The Karl Fischer method is used to determine the amount of water in the organic phase. The apparatus is a Metrohm 684KF coulometer. It can detect between 10 and 1000 µg of water. The exact compositions of the samples (organic phase) are presented in Table 1.

*Interfacial Tension Measurements.* Interfacial tensions are measured by the pendant-drop technique. A drop of the organic phase containing the extractant at a given concentration is injected into the aqueous phase (water) through a curved needle (popper Chrome 18G-6). The series of five drops are weighed with a Mettler AE 200 balance. The average mass value of one drop is calculated from five series of five drops. Then, the interfacial tension is given by

$$\gamma = \frac{(\rho_{aq} - \rho_{org})mg}{2\pi\rho_{org}rf} \qquad (2)$$

where $\gamma$ is the interfacial tension at the oil/water interface (mN/m), $\rho_{org}$ and $\rho_{aq}$ are the densities of the organic and aqueous phases (g·cm⁻³), $r$ is the internal radius of the needle (cm), $m$ is the mass of a drop, $g$ is the acceleration due to gravity, and $f$ is the Harkins and Brown correction factor.[21]

The radius of the needle ($r = 0.43$ mm) is found by calibration with pure *n*-dodecane.

*SAXS.* SAXS experiments are performed on the Huxley-Holmes High Flux camera[22,23] in the Service de Chimie Moléculaire, CEA-Saclay (France). The X-ray source is a copper rotating anode operating at 15 kW. Kα₁ radiation ($\lambda = 1.54$ Å) is selected by a combination of a nickel-covered mirror and a bent, asymmetrically cut germanium ⟨111⟩ monochromator. With

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a sample-to-detector distance of 2.15 m, a $q$ range from 0.01 to 0.4 Å$^{-1}$ is usually covered with this instrument using a two-dimensional gas-filled chamber of 0.3 m in diameter. The exposure time for each sample is 4 h.

For access to a larger $q$ range, additional spectra are obtained with a hard X-ray Guinier-Mering Camera in the same laboratory.[24] The source is a molybdenum tube with an X-ray energy of 17 keV and a flux of $3 \times 10^6$ photons/s. A $q$ range from 0.03 to 2 Å$^{-1}$ is usually covered with this instrument using a two-dimensional image plate detector.[25] The exposure time for each sample is 8 h.

For both cameras, the isotropic two-dimensional spectra after exposure are radially averaged, and the intensity of the scattered X-rays is expressed as a function of the momentum transfer $q$. The scattering cross sections $(1/V)(d\Sigma/d\Omega)$ on the absolute scale (cm$^{-1}$) are determined by a calibrated internal monitor proportional to the number of unscattered X-ray photons. Then, absolute data are corrected for the detector background.[25-27] The overlap of data obtained from the Huxley-Holmes camera and the Guinier-Meering camera is acceptable, with a precision of 10% on the intensity scale.

## Methods Section

**SAXS Modeling.** To obtain the aggregation number of malonamine in dodecane, we calculate the intensity with the following procedure:

The scattered intensity is given by[26]

$$I(q) = nP(q)\, S(q) \tag{3}$$

where $n$ is the number of scattering objects per unit volume (in objects/cm$^3$); $P(q)$, the form factor, depends on the geometrical form of the scattering object; and $S(q)$ is the structure factor that accounts for interparticle interactions. At the concentration used, the scattering objects are considered as polar monodisperse spheres without interaction.[5] In this case, $S(q) = 1$, and the form factor is given by[28]
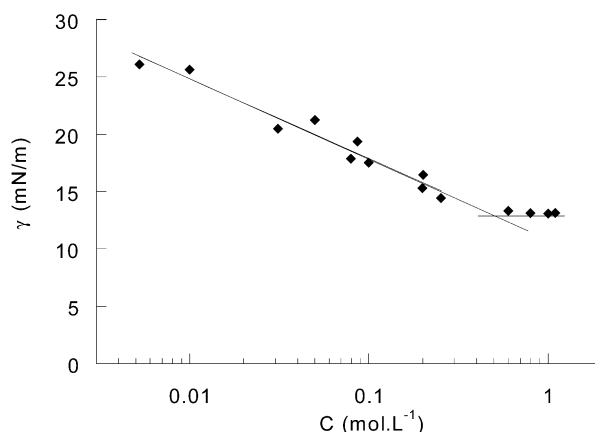
$$P(q) = V(R)^2 \Delta\rho^2 f^2(q, R) \tag{4}$$

where $R$ is the radius of the polar core of the reverse micelle (Å), $V(R)$ is the volume (cm$^3$) of the scattering particles (the core of the reverse micelles), $\Delta\rho$ is the difference in scattering length between the polar aggregate and the solvent (in cm$^{-2}$). The expression of $f(q, R)$ for a sphere is given by eq 5:

$$f(q, R) = \frac{3[\sin(qR) - qR\cos(qR)]}{(qR)^3} \tag{5}$$

The number of scattering objects is equal to $(c - \text{cmc})/N$ where $c$ is the diamide concentration, cmc is the critical micelle concentration, and $N$ is the number of molecules participating in one aggregate. A two-level model is chosen: (1) the core of the micelle consists of water and the polar head of the diamide, and (2) the solvent consists of dodecane, the apolar part of the diamide in the aggregate, and the diamide as free monomers in solution. The radius $R$ of the aggregate is obtained from eq 6:

$$V(R) = \frac{4}{3}\pi R^3 = \frac{(c - \text{cmc})v_{\text{polar}} + V_{\text{water}}}{(c - \text{cmc})/N} \tag{6}$$

where $v_{\text{polar}}$ is the polar volume of the malonamide and

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**Figure 2.** Interfacial tensions at the dodecane/water interface versus DMDOHEMA concentration in the organic phase at 23 °C.

$V_{\text{water}}$ is the total amount of water solubilized in 1 L of the organic phase (reverse micelles solution). $V_{\text{water}}$ is obtained by titration of the organic phase.

The molecular volumes of the alkyl chains are calculated from the Tanford formula.[29]

Therefore, two parameters are taken into account in the fitting procedure: the aggregation number ($N$) and the cmc.

## Results and Discussion

**Surfactant Properties of DMDOHEMA in Oil.** *Surface Tension Measurements.* To study the surfactant properties of DMDOHEMA, the interfacial tension was measured at the dodecane/water interface at different diamide concentrations. The results are presented in Figure 2. The general pattern of the experimental plot is that of a classical surfactant. The decrease in interfacial tension with increasing DMDOHEMA concentration shows that the diamide has amphiphilic character. The molecule is adsorbed at the dodecane/water interface, and, thus, the interfacial tension decreases. At a concentration of $0.43 \pm 0.15$ M, there is a change in the slope, showing that an aggregation phenomenon starts in one of the two liquids in contact, in this case in the oil. In standard textbooks of physical chemistry, this is called the cmc, that is, the concentration at which surfactant monomers self-assemble into aggregates.[21] It can also be interpreted as the concentration of "monomers" not included in the surfactant aggregates. In the present case, because the cmc value is very high, the aggregation of DMDOHEMA is not a sudden phenomenon with a well-defined concentration.[30] The diamide is thought to form progressively dimers, trimers, and possibly bigger assemblies, and all those species are coexisting in the organic phase. As a result, aggregates can be found at concentrations below the cmc, as it is observed with short-chain surfactants or surfactants with a high cmc value.[30]

The slope of the first straight line represents the interfacial excess of diamide ($\Gamma$ in mol·m$^{-2}$).[31] Then, the surface per polar head of extractant ($a_0$ in m$^2$·mol$^{-1}$) may be calculated from eq 7, which is derived from the Gibbs adsorption equation. From eq 7, we obtained $a_0 = 129$

$$a_0 = 1/\Gamma \tag{7}$$

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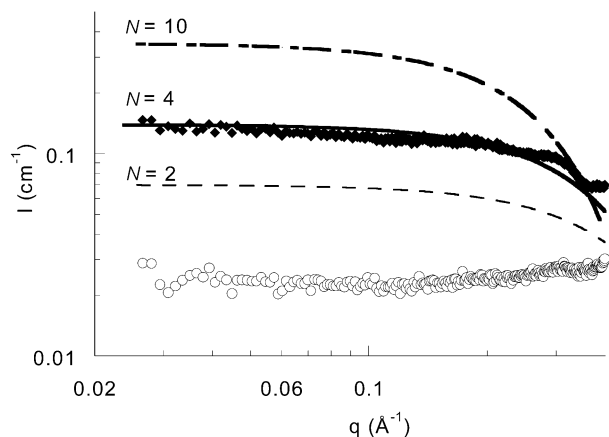(29) Tanford, C. T. *J. Phys. Chem.* **1972**, *76*, 3020.
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**Table 2. Numerical Values Used for the Fitting of the Scattered Intensity**

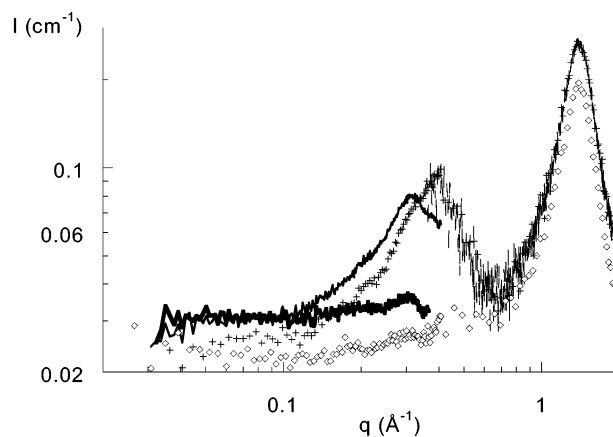| | water | polar head of DMDOHEMA | apolar part of DMDOHEMA | DMDOHEMA | dodecane |
|---|---|---|---|---|---|
| molecular volume (Å$^3$/molecule) | 30 | 95.6 | 780.9 | 876.5 | 373.5 |
| scattering length density ($10^{10}$ cm$^{-2}$) | $9.4 \times 10^{10}$ | $2.6 \times 10^{11}$ | $6.4 \times 10^{10}$ | $8.69 \times 10^{10}$ | $7.25 \times 10^{10}$ |



**Figure 3.** SAXS spectra of two organic solutions contacted with water. The curves represent the absolute intensity $I$ (cm$^{-1}$) versus $q$ (Å$^{-1}$). (◆) DMDOHEMA concentration = 0.7 M in dodecane; (○) dodecane alone. The full line represents the best fit obtained for spherical water droplets surrounded by diamide with an aggregation number of $N = 4$ ($R = 4.8$ Å) and cmc = 0.38 M. The scattered intensity produced by dimers only ($R = 3.8$ Å) or by larger aggregates of 10 molecules ($R = 6.5$ Å) are shown on the log scale for comparison.



**Figure 4.** SAXS spectra of different mixtures of dodecane and octanol contacted with water. (◇) dodecane; (thick line) $\phi_{\text{dodecane}}/\phi_{\text{octanol}} = 82{:}18$; (thin line) $\phi_{\text{dodecane}}/\phi_{\text{octanol}} = 23{:}77$; (+) octanol. $\phi$ is the volume fraction of dodecane or octanol in the solvent.

Å$^2$/molecule, giving a value for the spontaneous chain length at a flat interface of $876.5/129 = 6.8$ Å. It is a remarkably low value.

Those interfacial tension measurements demonstrate that for concentrations higher than 0.43 M, the DMDOHEMA organizes into water-in-oil reverse aggregates. To quantify more precisely the structure of the organic phase, SAXS experiments are performed on an organic phase containing 0.7 M diamide in dodecane equilibrated with a water phase. The SAXS spectrum is presented in Figure 3.

SAXS is sensitive to spatial fluctuations of electronic densities in the sample.[32] The fact that the X-ray scattered intensity is higher in the DMDOHEMA solution than that in pure dodecane proves that electronic density heterogeneities are present in the sample. Furthermore, a well-defined amount of water ($\phi = 0.004$, where $\phi$ is the volume fraction of water in the organic phase) is molecularly solubilized in the organic phase. This does not occur for pure dodecane contacted with water ($\phi = 0.000$). Therefore, at this particular diamide concentration (0.7 M), polar aggregates are present in the organic phase. To deduce quantitative information about these aggregates, experimental X-ray scattered intensities are fitted using the theoretical model described in the Methods section. The numerical values used for the modelization are given in Table 2.

Three curves obtained for three different values of the aggregation number are shown in Figure 3. The best fit between the experimental scattered intensity and the theoretically calculated curve is obtained for $N = 4$ and cmc = 0.38 M. This value of the cmc is in good agreement with that obtained from the interfacial tension measure-

ments (cmc = 0.43 M). Because two parameters are needed to calculate the theoritical intensity, a more precise determination of the aggregate's structure (apolar/polar limit) could only be obtained by fitting both the SAXS and the small-angle neutron scattering spectra of the same solution.[33]

Therefore, DMDOHEMA and DMDBTDMA[5] display similar self-assembling properties.

**Addition of Octanol to a Reverse Micelle.** *Structure of the Solvent.* Although thermodynamical properties of alkane/alcohol mixtures have been studied,[13−15,17,34] the structure of such solutions at the molecular scale is not clearly established to our knowledge.

Different mixtures of dodecane/$n$-octanol at various octanol compositions are studied by SAXS. The experimental scattering patterns are presented in Figure 4. The X-ray scattered intensity of the dodecane sample is constant in a $q$ range of $0.01-0.6$ Å$^{-1}$. The limit at zero $q$ value can theoretically be calculated from the isotherm compressibility of pure dodecane[35] ($9.8 \times 10^{-11}$ Pa$^{-1}$). The broad peak at 1.4 Å$^{-1}$ corresponding to a distance (given by $2\pi/q_{\text{max}}$) in real space of 4.5 Å is due to an average distance between CH$_2$ groups in liquid dodecane. Figure 4 shows that, as the amount of octanol increases, a broad peak appears between 0.32 and 0.40 Å$^{-1}$. This peak corresponds to a distance ranging from 19.6 to 15.7 Å. The presence of a broad peak in the SAXS pattern reveals the apparition of electronic density heterogeneities, in agreement with the literature data on octanol/alkane mixtures.

Liquid alcohols are characterized by their ability to form intermolecular hydrogen bonds. Previous studies[15,16,36,37] using Raman and IR spectroscopies showed that polymeric

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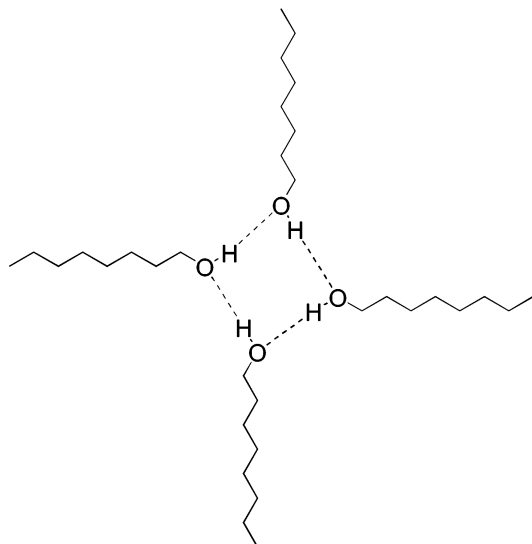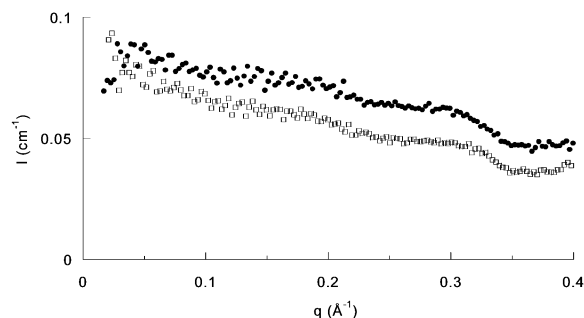
**Figure 5.** Example of a small cyclic cluster of four octanol molecules linked together by hydrogen bonding.

hydrogen-bonded aggregates are present in pure octanol. Those molecules can link together to form long polymeric chains, or self-assemble into small cyclic clusters of a few molecules. Even though some authors[15,37] consider that *n*-octanol forms only tetramers, DeBolt and Kollman[17] showed by numerical simulations and comparison with experimental results that all those species could be present together in solution, though at ambient temperature, octanol preferentially forms four-, five-, and six-membered cyclic aggregates. An example of such cyclic aggregates is shown in Figure 5.

This supramolecular organization includes polar areas consisting of hydroxyl groups more densely packed than the rest of the solution. Those aggregates can be linked together by long polymeric chains resulting in a wide hydrogen-bond network in the whole solution with the presence of regions containing higher or lower concentrations of polar groups. In addition, when octanol is saturated with water (as in the present study), the water molecules tend to locate preferentially in the polar areas described previously, forming larger and more distinct hydrophilic regions than those in pure octanol. The broad peak visible on the scattering spectrum corresponds to an average distance between these polar zones. For octanol contacted with water, the experimental value of 15.7 Å (at 25 °C) is of the same order as the distance of 21 Å predicted by ab initio calculations (at 40 °C) by DeBolt and Kollman.[17]

*Influence of Octanol on the Structure of Diamide Reverse Micelles. Cosurfactant Effect.* To evaluate the effect of adding a small amount of octanol in DMDOHEMA/dodecane solutions, a 0.3 M DMDOHEMA solution in dodecane containing 0.3 M octanol is studied by SAXS.

Figure 6 shows the X-ray intensity scattered by this solution in comparison to the scattered intensity of a solution without octanol. We observe a small increase in the intensity when octanol is present in the solution. As the X-ray scattered intensity is proportional to the number of scattering objects, we can deduce that the presence of octanol in the solution increases the number of aggregates. In small quantities, *n*-octanol has a cosurfactant effect.[38,39] Octanol molecules adsorb at the surface of small micelles and, consequently, increase the surface *per* polar head.

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**Figure 6.** SAXS spectra of solutions of DMDOHEMA concentration = 0.3 M in different solvents: (□) dodecane; (●) 0.3 M octanol in dodecane. The solutions are contacted with water.
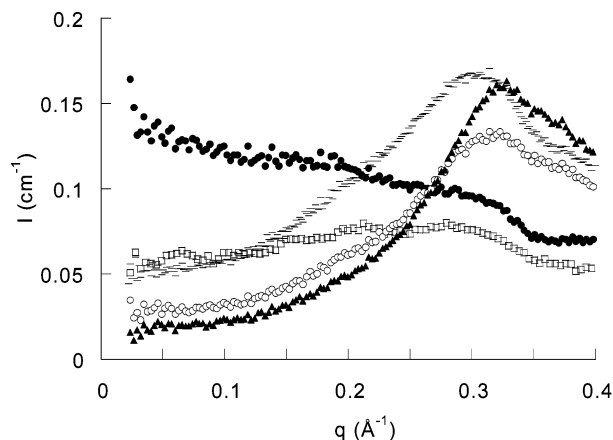


**Figure 7.** SAXS spectra of solutions of DMDOHEMA concentration = 0.7 M in different solvents: (●) dodecane; (□) $\phi_{dodecane}/\phi_{octanol}$ = 82:12; (−) $\phi_{dodecane}/\phi_{octanol}$ = 50:50; (○) $\phi_{dodecane}/\phi_{octanol}$ = 24:76; (▲) octanol. The solutions are contacted with water.

The specific surface of the dodecane/water interface as well as the number of micelles are increased by this phenomenon, and as a result, the intensity on the SAXS pattern increases at small *q*.

*Cosolvent Effect.* Because alkane/octanol mixtures are structured in the absence of diamide (presence of a broad peak on the SAXS pattern), we studied the effect of a larger amount of octanol in the diamide organic phases.

Figure 7 shows the X-ray scattering spectra of 0.7 M DMDOHEMA solutions in mixtures of dodecane and octanol at different volume fractions. Clearly, the X-ray intensity scattered at small angles decreases when the amount of octanol in the solvent increases. In addition, a broad peak appears at around 0.3 Å$^{-1}$ as the volume fraction of octanol increases in the organic phase. This peak corresponds in real space to the distance between regions of different electronic density. This distance varies from 21 to 19 Å as the volume fraction of octanol in the solvent increases. Such a peak was already observed in pure d/o mixtures, but at a higher *q* position. Thus, it is assumed that a hydrogen-bond network appears whenever a sufficient quantity of octanol is present in solution. The presence of this peak corresponds to the fact that regions of higher electronic density are present in the solution and that the average distance between those regions ranges from 21 to 19 Å depending on the amount of octanol in the solvent. There is a small difference in the mesh size of the hydrogen network for the d/o mixture with (21−19 Å) or without diamide (19.6−15.7 Å).
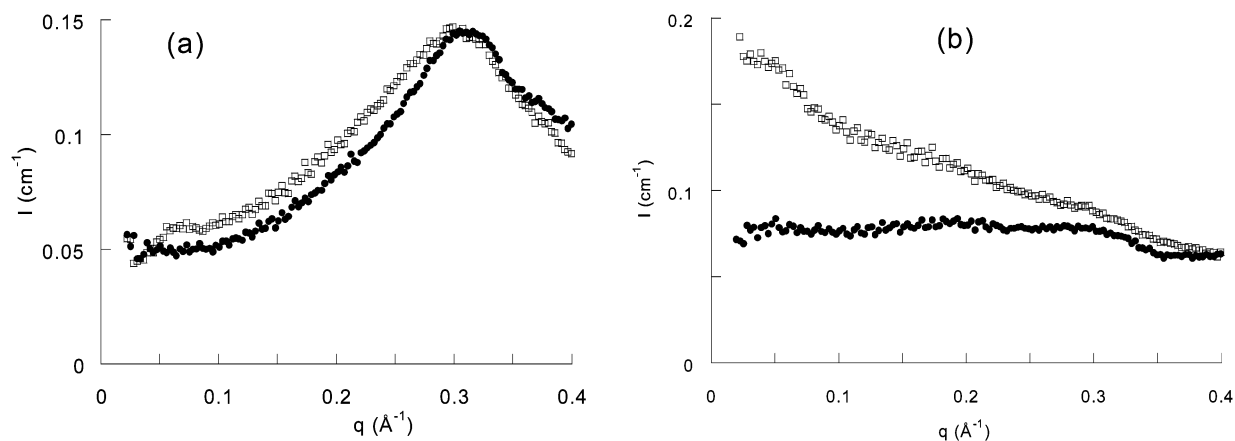
Figure 8a shows the scattering spectra of DMDOHEMA solutions of different concentrations in d/o (85:15) mixtures. The broad peak appears with increasing diamide
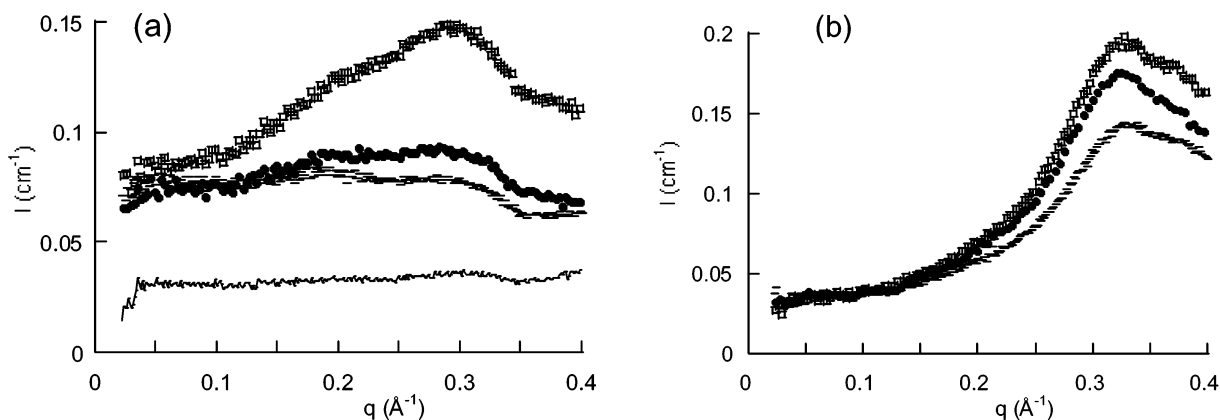
**Figure 8.** (a) Scattered intensity versus momentum transfer $q$ of solutions of DMDOHEMA in d/o (85:15), contacted with water. DMDOHEMA concentration = (−) 0.3; (●) 0.7; (□) 1.1 M. The full line is for the solvent. (b) Scattered intensity versus momentum transfer $q$ of solutions of DMDOHEMA in octanol contacted with water. DMDOHEMA concentration = (−) 0.3; (●) 0.7; (□) 1.1 M.



**Figure 9.** (a) Absolute scattered intensity versus momentum transfer $q$ of 0.3 M DMDOHEMA solution in d/o ($\phi_{dodecane}/\phi_{octanol}$ = 25:75) contacted with (●) $H_2O$; (□) 4 M $HNO_3$. (b) Absolute scattered intensity versus momentum transfer $q$ of 0.3 M DMDOHEMA solution in d/o ($\phi_{dodecane}/\phi_{octanol}$ = 85:15) contacted with (●) $H_2O$; (□) 4 M $HNO_3$.

concentration because there is no broad peak for the solvent without diamide. Figure 8b shows the scattering spectra of DMDOHEMA solutions of different concentrations in pure octanol. In both cases, the intensity of the peak increases with the extractant concentration in the solution. According to these observations, it is clear that the diamide molecules participate in the structuralization of the organic phase by means of its electron donor oxygen atoms. As the DMDOHEMA extractant concentration increases, the solution becomes organized over a longer length scale.

The main point to be mentioned in the scattering patterns is the difference between the scattering of dispersed droplets, with a maximum intensity at zero $q$ followed by a decay in $I(q)$, as is expected from the form factor of a nanometric sphere, and the system where polar residues are distributed along a tridimensional network of typical mesh size 1−2 nm, which gives a broad peak at high $q$. SAXS is a powerful direct technique to distinguish between micelles incorporating surfactant and cosurfactant[40] and the structured solvent.[41,42] When the solvent is water, hydrotrope is the general class of molecules allowing substantial solubilization of insoluble molecules in water without the formation of micellar aggregates or microemulsion.[43] By analogy and with this terminology,

octanol can be considered a reverse hydrotrope or a cosolvent.

Figure 9a,b shows X-ray scattering spectra of 0.3 M DMDOHEMA organic solutions in d/o mixtures of two different compositions. Both solutions were equilibrated with 4 M nitric acid or water. For the d/o composition of 25:75 (Figure 9a), the X-ray scattered intensity remains essentially the same whenever the solution is contacted with water or nitric acid at 4 M. For a d/o composition of 85:15 (Figure 9b), the X-ray intensity scattered at small angles is much higher when the organic solution is contacted with acid than it is when contacted with water. This increase in intensity is explained by an increase of van der Waals attractive interactions between the water core of the reverse aggregates,[4] whose presence was shown in dodecane. The dispersion forces dominate the interactions between the polar cores, as it was demonstrated for the DMDBTDMA/dodecane system by Erlinger et al.[5] Therefore, the presence of polarizable $HNO_3$ in the water core of the reverse aggregates induces an increase of the attractive interaction. This phenomenon is not visible in the "octanol-rich" solution (d/o = 25:75), where a hydrogen-bond network is present in solution.

All those results are coherent with the fact that a structural transition, between swollen reverse micelles and a polar network with octanol as a cosolvent, occurs when large quantities of *n*-octanol are added in the extractant organic solution. The molar ratio of octanol for this transition to occur depends on the diamide concen-

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tration. For example, at 0.7 M diamide the transition from swollen reverse micelles to a structured solvent is observed for an octanol concentration higher than 1 M. In pure dodecane, small reverse aggregates are present in solution, and DMDOHEMA acts as a "classical" surfactant. When the amount of octanol is small (typically ≤0.3 M), the alcohol plays a cosurfactant role, increasing the number of aggregates in solution. When octanol becomes a cosolvent, the previous microstructure modeled by droplets disappears and a new microstructure modeled by a network of mesh size $2\pi/q_{max}$ takes place, with $q_{max}$ being the position of the scattering peak. A hydrogen-bond network appears, and regions of high electronic densities separated by a mesh size ranging from 15 to 20 Å are present in the organic phase, as is shown by the broad peak corresponding to those distances in the scattering patterns. Clearly, the extractant molecules are included in this network and micelles do not form. Important variations in the extraction properties are expected in parallel to this micelle-to-cosolvent microstructural transition. The dodecane solution is more finely divided than the "octanol-rich" one. In the first system, clear polar microdomains are separated from the apolar solvent by an interface, whereas in the second system, the transition between polar and apolar areas is spatially more extended, probably open, and the difference in the electronic densities between the two regions is smaller.

## Conclusion

SAXS and interfacial tension measurements showed that above a certain DMDOHEMA concentration, the extractant self-organizes into small reverse water-in-oil aggregates. Those aggregates consist on average of four DMDOHEMA molecules for a concentration of 0.7 M. A good correlation between the SAXS results and the fitted X-ray scattered intensities is obtained on the absolute scale. The effect of a modifier (*n*-octanol) on the solution structures at the supramolecular scale was studied. For small amounts of octanol, the modifier has a cosurfactant effect and does not perturb the previous organization. In a larger amount, when octanol is used as a cosolvent, a structural transition in the molecular organization of the solution occurs. A less divided structure appears organized by a hydrogen-bond network that contains the diamide. A similar structure was observed with pure octanol. Thus, the transition in solvent structure must have a great impact on the extraction mechanism and the extraction rate should, in the future, be linked to the supramolecular structure of the organic solution. This correlation could bring a predictive character to the formulation of novel extracting systems.