



Effects of small ionic amphiphilic additives on reverse microemulsion morphology



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ARTICLE INFO

Article history:

Received 23 November 2013

Accepted 20 January 2014

Available online 25 January 2014

Keywords:

Microemulsions

Hydrotropes

Nanostructures

Phase behaviour

Small-angle neutron scattering

ABSTRACT

Hypothesis: Initial studies (Hopkins Hatzopoulos et al. (2013)) have shown that ionic hydrotropic additives can drive a sphere-to-cylinder (ellipsoid) transition in water-in-oil (w/o) microemulsions stabilized by the anionic surfactant Aerosol-OT; however the origins of this behaviour remained unclear. Here systematic effects of chemical structure are explored with a new set of hydrotropes, in terms of an aromatic versus a saturated cyclic hydrophobic group, and linear chain length of alkyl carboxylates. It is proposed that hydrotrope-induced microemulsion sphere-to-cylinder (ellipsoid) transitions are linked to additive hydrophobicity, and so a correlation between the bulk aqueous phase critical aggregation concentration (*cac*) and perturbation of microemulsion structure is expected.

Experiments: Water-in-oil microemulsions were formulated as a function of water content w ($= [\text{water}]/[\text{AOT}]$) and concentration of different hydrotropes, being either cyclic (sodium benzoate or sodium cyclohexanoate), or linear chain systems (sodium hexanoate, sodium heptanoate and sodium octanoate). Phase behaviour studies were performed as a function of w , additive type and temperature at total surfactant concentration $[S_T] = 0.10 \text{ M}$ and constant mole fraction $x = 0.10$ ($x = [\text{hydrotrope}]/[S_T]$). Microemulsion domain structures were investigated by small-angle neutron scattering (SANS), and these data were fitted by structural models to yield information on the shapes (spheres, ellipsoids or cylinders) and sizes of the nanodroplets.

Findings: Under the conditions of study hydrotrope chemical structure has a significant effect on microemulsion structure: sodium cyclohexanoate does not induce the formation of cylindrical/ellipsoidal nanodroplets, whereas the aromatic analogue sodium benzoate does. Furthermore, the short chain sodium hexanoate does not cause anisotropic microemulsions, but the more hydrophobic longer chain heptanoate and octanoate analogues do induce sphere-to-ellipsoid transitions. This study shows that underlying microemulsion structures can be tuned by hydrotropes, and that the strength of the effect can be identified with hydrotrope hydrophobicity in terms of the bulk aqueous phase *cac*.

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1. Introduction

Microemulsions are systems of significant interest in both academic studies and for industrial applications. Microemulsions comprise two or more immiscible or partially miscible fluids, stabilised by added surfactants. The surfactants must reduce interfacial tensions sufficiently for nanometre scale domains to form, which gives microemulsions their characteristic transparency (translucency), visually distinguishing them to other types of

emulsions. The visual appearance of microemulsions does not change with time, inferring thermodynamic stability, a further distinguishing feature to other emulsions. These properties and features lead to applications of microemulsions as nanoreactors in chemical [1] and nanoparticle synthesis [2], as nanoparticle recovery vehicles [4], in soil remediation processes, enhanced oil recovery [5], pharmaceutical delivery [6], and engine oil and fuel additives [7].

With such an array of applications, control over microemulsion properties becomes important. The phase behaviour with respect to composition, pressure and temperature are the most common property levers. The size of the microemulsion nanodomains can

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be varied by increasing the amounts of dispersed phase added. Size control in reverse microemulsions, for example, at constant water content can be attained by the choice of surfactant and (or) cosurfactant chemical structure.

Microemulsions are more than often reported as spherical [2–4]. Axial elongation of microemulsions or reverse hydrated micelles (in the cases of low water content reverse phases) in oil media and supercritical CO₂ is of interest for control over viscosity. To this end surfactant systems exhibiting axially elongated aggregation structures have been the topic of on-going research [8,9]. Such structures, commonly encountered in aqueous phases, are catanionic systems where the long chain ion is a cation and the ‘counter ion’ is a small molecule amphiphilic additive, commonly called a hydrotrope [8]. An example hydrotrope is sodium benzoate, which may be considered as a “primitive” short chain surfactant. The presence of a bulky hydrotrope is recognised as being critical for micellar elongation, with these systems shown to produce substantial increases in solution viscosities [10]. Close investigation by NMR and computer simulations revealed that the hydrotrope counterions adsorb at the micellar interfacial region [11]. In mixed solutions of surfactants and hydrotropes of the same charge only ellipsoidal structures have been observed [12]. The difference between the two systems is likely being the difference in the interfacially adsorbed amount of hydrotrope. In catanionic systems the two ions cannot separate or partition due to electrostatic attraction. In systems of mixed surfactants and hydrotropes of the same charge the electrostatic repulsion diminishes interfacial co-adsorption.

Elongated microemulsions were discovered by Petit et al. [13] and Eastoe et al. [14–16] who first observed cylindrical or ellipsoidal reverse microemulsions with the Aerosol-OT (AOT) anion coupled with Cobalt counterions (substituted for the normally found Sodium ion). This work was taken further to explore the effects of different metal counterions on AOT microemulsion morphology [14–16], and recently showing elongated self-assembly structures in supercritical CO₂ with related surfactants [17].

More recently, mixed AOT microemulsions containing anionic hydrotropes in the aqueous phase have been shown to stabilize cylindrical nanostructures that change to spherical micelles with increasing microemulsion water content ($w = [\text{water}]/[\text{surf}]$) [18]. Three structurally related homologous series of alkyl-hydrotropes were examined as additives in reverse AOT microemulsions with heptane as oil [18]. The additives ranged in size from short to medium chain length ‘alkyl-hydrotropes’. The effect of axial elongation was attributed to two features of the additives, (i) the hydrophobicity and plausibly strength of adsorption of the molecules at the water/oil interface and (ii) the position of the ring moieties in the molecules. Because hydrotropes do not partition strongly into oil (they are only weakly hydrophobic), at low water content the effective hydrotrope concentration in the water pools is high, and hence they might be expected to adsorb strongly at the interface. For a fixed mole fraction x of hydrotrope in the total microemulsion, increasing the water content w decreases the additive concentration in the water droplets, and eventually the micellar geometry change to spherical, as found for the native AOT (hydrotrope-free) systems [19]. However, the extent of axial elongation did not appear to directly correlate to additive architecture, with some less hydrophobic additives inducing longer cylinders as compared to the more hydrophobic homologues and analogues.

Here an attempt is made to isolate the two parameters, chemical structure and hydrophobicity, by comparing the effects of subtle structural changes in the hydrotropes (aromatic sodium benzoate and saturated sodium cyclohexanoate, and chain length with sodium hexanoate, heptanoate and octanoate) on the morphology of reverse AOT microemulsions.

2. Experimental

2.1. Materials

Sodium bis(2-ethylhexyl)sulfosuccinate (Aerosol-OT, AOT, 98%) was purchased from Aldrich. Purification of AOT was carried out by dissolving the surfactant in double distilled methanol. The solution was allowed to stand overnight, after which extraneous inorganic salts precipitated. The supernatant solution was removed and centrifuged at 600 rpm for 30 min to remove any suspended salt crystals. The solvent was then removed by rotary evaporation and the product was dried over phosphorous pentoxide in a vacuum over at 60 °C overnight. Sodium octanoate, sodium heptanoate, sodium hexanoate and sodium benzoate were purchased from Aldrich and used as received. Sodium cyclohexanoate was prepared from its parent acid (also purchased from Aldrich at the highest purity available) as described elsewhere [20]. Microemulsions were prepared at total surfactant concentration $[S_T] = 0.10$ M and $x = 0.10$ ($x = [\text{hydrotrope}]/[S_T]$), by mixing an appropriate AOT in *n*-heptane solution with a hydrotrope-D₂O solution (these solutions were not pH adjusted), adding D₂O and *n*-heptane to the required w values and total volume respectively and shaking until optically homogenous.

2.2. Phase behaviour

Temperature scans were carried out at 1 °C increments in a thermostated water bath with an error of 0.2 °C. The samples were allowed to thermally equilibrate for 20 min between temperature increments and examined visually.

2.3. SANS

Small-angle neutron scattering measurements were carried out on the LOQ instrument at ISIS at the Rutherford Appleton Laboratory with the exception of $w = 5$ AOT-benzoate, $w = 10$ for AOT-hexanoate and $w = 10$ and $w = 20$ for AOT-heptanoate and AOT-octanoate microemulsions, which were measured on D11 instrument at the Institut Laue Langevin, Grenoble France. Samples were contained in 1 mm path-length Hellma cells and thermostated at 20 ± 0.1 °C. On LOQ the incident wavelength $\lambda = 10$ Å, giving rise to a Q range of ~ 0.005 to 0.3 Å⁻¹. On D11 the incident wavelength was $\lambda = 10$ Å with detector distances at 1.2 m and 8 m and respective collimator distances at 5.3 m and 8 m, giving rise to a Q range of ~ 0.003 – 0.3 Å⁻¹.

The momentum transfer Q is defined as:

$$Q = \frac{4\pi \sin(\theta/2)}{\lambda} \quad (1)$$

where θ is the scattering angle and λ is the incident neutron wavelength.

The data were fitted using the least squares FISH program [21]. For colloidal particles the scattering profile curve is broadly described by:

$$I(Q) \propto P(Q)S(Q) \quad (2)$$

where $P(Q)$ is a form factor, which contains information about the size and shape of the aggregates, and $S(Q)$ is a structure factor reporting on interactions. In this case of non-interacting particles $S(Q)$ tends to unity. Trials with models various $P(Q)$ functions were carried out with parameters related to $S(Q)$ where absent. First approximation radii were derived by Guinier analysis and used as a starting point for model fitting. Scale factors (SF) were calculated using

$$SF = \Phi \Delta \rho^2 10^{-24} \quad (3)$$

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