

Accounts of Materials & Surface Research

Design criteria for rod-like reverse micelles as viscosifiers

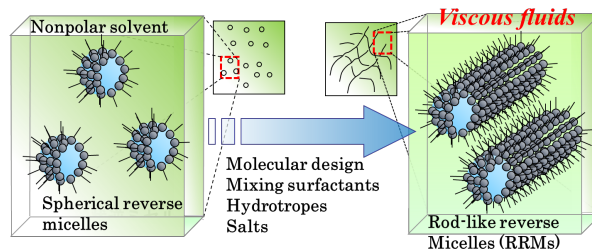
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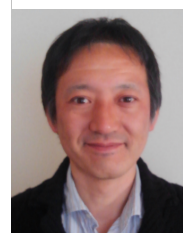
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The formation and growth of rod-like micelles are known to affect the viscosity of surfactant solutions. The rheological behavior of rod-like micelles plays an important role in fields, for example, enhanced oil recovery, drug delivery, cements, cosmetics, pressure-loss reduction agents. However, studies of rod-like reverse micelles (RRMs) are scarce compared with direct (non-reversed) rod-like micelle. Therefore, the design of surfactant molecules and mixed systems for the formation of RRM is a less well-developed field. This review covers previous reports of RRM and discusses how surfactants and mixed systems may be designed to generate RRM for practical applications.



Keywords: Reverse micelles, rod micelles, Supercritical CO₂, Viscosity, Hydrotropes

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1. Introduction

Certain lipophilic surfactants in nonpolar organic solvents can form reverse micelles (RMs) above a certain concentration (i.e. the critical reverse micelle concentration), and furthermore these micelles can solubilize water in their polar cores. RMs are surfactant molecular assemblies with hydrophilic head groups forming cores and shells of the hydrophobic tails in contact with the external continuous solvent. RMs have attracted much attention as “universal solvents” for dry-cleaning, enhanced oil recovery (EOR), dyeing, extraction and enzymatic reactions. Another promising application is in synthesis of nanomaterials using the RMs as nanoreactors. These nanoreactors allow for reactions between water-soluble components encapsulated in the closed polar nanospaces but also water-soluble and water-insoluble reactants, which can interact with each other across the water/nonpolar solvent interface. The size and shape of the nanoparticles produced depends on the dimensions of the RMs and the exchange rate between the aqueous cores¹⁻⁴.

For many surfactants water is considered an essential component in stabilization of RMs⁵. The sizes and shapes of RMs are generally affected by the water-to-surfactant molar ratio W_0 , composition and combinations of

surfactants, oil, pH, temperature, pressure and other additives like salts, hydrotropes, cosurfactants and cosolvents.¹⁻⁷

There are various possible micellar morphologies with shapes being not only spherical but also ellipsoidal, rod-like (thread-like or worm-like), ring-like and disk-like.⁷ Rod-like micelles can have significant effects on viscosity depending on the aspect ratio and rod length.⁸ The rheological behavior plays important roles in the fields of EOR, drug delivery systems, cements, cosmetics, pressure loss reduction agents, as typical examples. The rheological behavior of reversed rod-like micelle (RRM) solutions has been shown to be similar to that of aqueous rod-like micellar solutions⁹⁻¹¹. Although there are numerous studies dealing with aqueous rod-like micelles, RRM solutions are only occasionally reported. Therefore, the design of surfactant molecules and mixed systems for the formation of RRM solutions is a less well-developed field.

However, that said, RMs have been studied in supercritical CO₂ (scCO₂), which can be considered as an environmentally friendly, nonpolar solvent. One particular application of scCO₂ is in EOR (CO₂-EOR) from porous rocks^{12,13}. The main disadvantage of using CO₂ in EOR is the very low viscosity, which does not promote uniform flow of the CO₂

through oil-bearing reservoirs, but rather viscous fingering of the CO₂ via a pathway of least resistance through the porous media⁴. There is therefore a need to develop systems that can enhance CO₂ viscosity to a level comparable to that of the oil.

Numerous hydrocarbon (HC)-based polymers, surfactants and cosolutes are known to generate viscous phases in organic media¹⁴⁻¹⁶, but due to the limited solvency of CO₂, they are unsuitable for use in this medium. Based on this background, a CO₂-soluble thickener has been required for over the last three decades. An efficient CO₂-EOR compatible CO₂-thickener would prolong the lifetime of crude oil reserves while simultaneously sequestering CO₂ and giving scientists time to develop other clean and sustainable energy producing technologies. This review introduces previous reports of RRM and discusses how surfactant molecules and mixed systems may be designed to generate RRM for such practical applications.

2. The main parameters to design RRM

Important parameters known to affect surfactant aggregate morphology are the critical packing parameter (CPP)¹⁷ and the hydrophilic-lipophilic balance (HLB)⁷. CPP is given by $V/(a_0 l_c)$, where V is the volume and l_c is the length of hydrophobic tail group, a_0 is the interfacial area of the hydrophilic group. When CPP is $<1/3$, indicating a conical shape of the surfactant molecule, normal water-soluble spherical micelles are formed. CPP values of $1/2-1/3$ and $1/2-1$ are suitable for water-soluble rod-like micelles and vesicles (or lamellar liquid crystals at $CPP=1$), respectively. Surfactants with CPP larger than

1 have the ability to form reversed micelles (spherical, rod-like).

According to the HLB approach, a hydrophilic surfactant with a high HLB tends to form water-soluble normal micelles, whereas a lipophilic surfactant, with a low HLB index, forms reversed oil-soluble micelles RMs. For typical nonionic surfactants, HLB decreases with increasing temperature and increasing salt concentration, as hydrogen bonding strength between polyoxyethylene (PEO) headgroups and water molecules decreases. The CPP also depends on temperature and the concentration of additives (salts, co-surfactants, cosolvents and hydrotropes) due to the headgroup area a_0 being affected by hydration and electrostatic and steric headgroup-headgroup repulsions.

The micellar surface curvature changes from positive to zero (e.g. spherical micelles \rightarrow rod-like micelles \rightarrow vesicles) and then to negative (lamellar LCs \rightarrow RRM \rightarrow spherical RMs) with increasing CPP and/or decreasing HLB. For example, spherical micelles in aqueous cetyltrimethylammonium chloride (CTAB) solutions turn into rod-like and worm-like micelles upon addition of sodium bromide or potassium bromide above certain salt concentrations¹⁸. HLB decreases and CPP increases due to a decrease in hydration caused by a salting out effect.

For a water/supercritical CO₂ (W/CO₂) system, the general CPP concept can also be applied. In terms of the HLB approach, the concept of "lipophilicity" can be replaced by "CO₂-philicity" giving the hydrophilic/CO₂-philic balance HCB (instead of HLB)¹⁹. In earlier studies of the phase behavior of emulsions in W/CO₂ mixtures, HCB was defined by equation (1):

$$1/\text{HCB} = (A_{\text{TC}} - A_{\text{TT}} - A_{\text{CC}})/(A_{\text{HW}} - A_{\text{HH}} - A_{\text{WW}}) \quad (1)$$

where A_{ij} is the energy for various interactions between CO_2 (C), surfactant tail (T), water (W), and surfactant head group (H)²⁰. As with HLB, HCB strongly links to phase behavior and dispersion stability and suggests the formation of W/CO_2 dispersions at $\text{HCB} < 1$ and CO_2/W dispersions at $\text{HCB} > 1$. Formation of RRM therefore requires $\text{CPP} > 1$ and low HLB (or low HCB).

3. Earlier studies of W/O and W/CO_2 RRM systems

The formation of RRM in W/O mixtures using various surfactants (e.g. lecithin) and additives has previously been studied.²¹⁻²⁵

The chemical structures of these surfactants and the additives are shown in **Figure 1**.

In these studies, low viscosity solutions of cyclohexane, *n*-decane and *n*-hexadecane containing spherical (globular) RMs were transformed into viscoelastic organogels containing long worm-like RRM through the addition bile acids and/or salts.²¹ The efficiency of formation of these RRM on addition of bile salts followed the order (Sodium cholate SC and Sodium deoxycholate SDC) > taurine salts (Sodium taurocholate STC and Sodium taurodeoxycholate STDC) > bile acids (Cholic acid CA and Deoxycholic acid DCA)²¹. This suggests that these additives alter the surfactant CPP making the formation of RRM more favorable. From these results, the hydrogen bonding of the additives to lecithin and AOT was identified as a key to generating a larger headgroup area and, therefore reducing CPP, leading to the formation of RRM as shown in **Figure 2**.

Compared with bile salts SC and SDC, a large molecular size of taurine-based bile salts (STC and STDC) was indicated to be less effective at RRM formation.

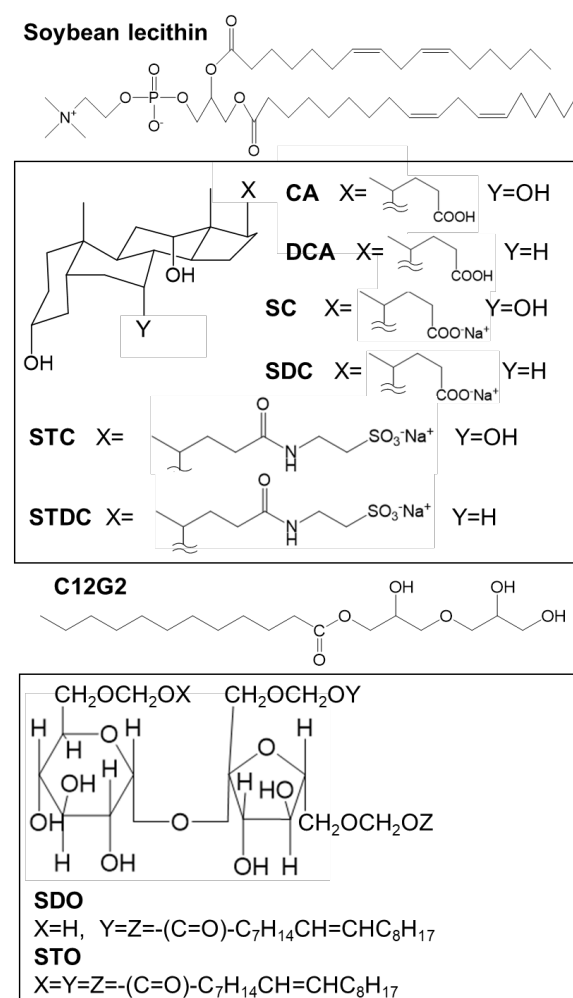


Figure 1. Chemical structures of surfactants and additives examined for W/O-type RRM.

The formation of RMs in hexadecane through the mixing two kinds of surfactants with different CPPs and HLBs was also examined. The triple-tail surfactant STO (**Figure 1**), having high lipophilicity, formed globular RMs but these could be transformed into RRM by the addition of the less lipophilic double-tail surfactant SDO²¹.

In this RM system, the oil-insoluble SDO molecules were solubilized in STO RMs

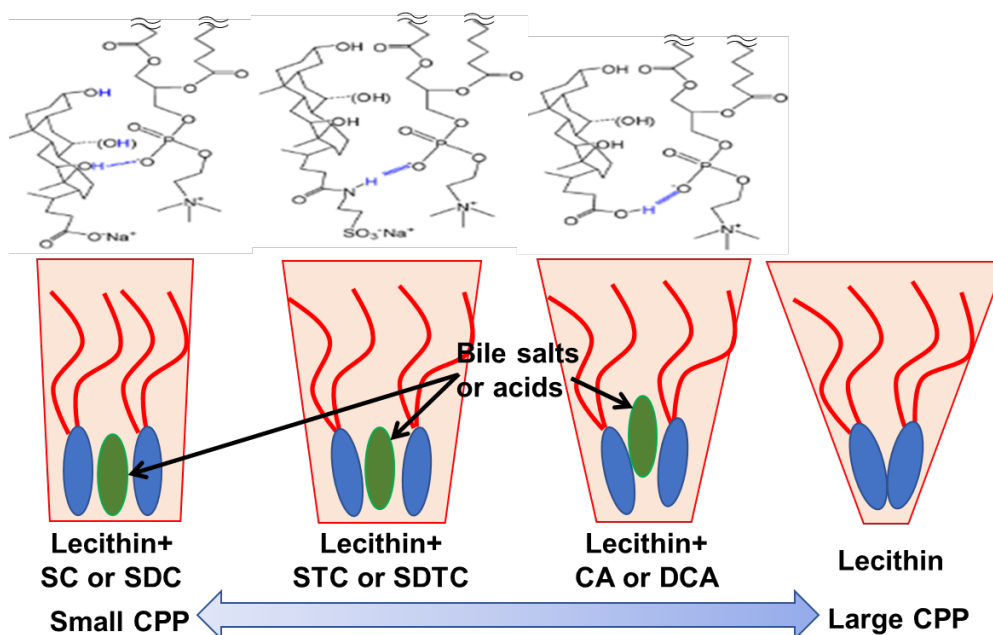


Figure 2. Steric structures of lecithin with bile acids or bile salts hydrogen bonded to the glycerol ester. The position of additive molecules to lecithin depends on the arrangement of the hydrogen bonding groups on the additive structures.

resulting in mixed STO/SDO micelles with hydrogen bonding between mutual sucrose groups. Therefore, the large CPP and low HLB of STO, usually favorable of globular RM formation, was altered by mixing with the lower CPP/higher HLB of SDO thus causing RRM formation.

As another example, the surfactant C12G2 (**Figure1**) formed longer RRM at higher surfactant concentration in cyclohexane and *n*-octane²². Elevating temperature and increasing the HC length of the surfactant caused a transition from RRM to globular micelles. In this case, the increase in HC length should hardly affect CPP, however, HLB is lowered with increasing HC length and therefore spherical RM morphology becomes preferred. For a nonionic surfactant, elevating temperature also increases HLB and drives RRM to be spherical as found for C12G2^{19,22}. An equi-molar mixture of cationic Gemini surfactant, C,C'-bis(sodium dodecyldimethylammonium bromide)-p-

benzenedimethylene (12-Ph-12), and anionic surfactant, sodium laurate (SL) in cyclohexane was found to form long RRM²³. The maximum zero-shear viscosity of this system was 1858 Pa s at a water to total surfactant molecule molar ratio, W_0 , of 14 and 0.2 M 12-Ph-12. As the 12-Ph-12 concentration increased to 0.3 M, the viscosity increased to 2200 Pa s. The dynamic rheology showed the typical viscoelastic response for thread-like or worm-like micelles at 0.2M 12-Ph-12 and $W_0 = 10$, with a relaxation time of 0.11 s.

In other studies, dynamic control over the viscosity of RRM solutions by UV-vis light irradiation was investigated. One successful example was achieved in lecithin/SDC/cyclohexane solutions by incorporating spiropyran (SP)²⁴. After exposure to UV light, a structural transition from SP to merocyanin (MC) (**Figure 3**) is induced and the long, viscosity enhancing, RRM in the system transform into shorter

RRMs leading to a significant reduction in viscosity. This long-RRM-to-short-RRM transition is reversible and the viscosity could be recovered by irradiation with visible light or by standing for several minutes to reform the worm-like RMs. The mechanism relies on different effects of the SP and MC photoisomers on RMs (**Figure 3**). The hydrophobic SP molecules locate in the hydrophobic regions of the micelles composed of the solvent and the hydrophobic tails of lecithin. After UV irradiation, the SP converts into the hydrophilic MC and strongly interacts with the lecithin headgroup leading to a concomitant decrease in the competing SDC-lecithin interaction. The headgroup area is thus reduced resulting in a molecular geometry closer to a cone and hence causing the formation of shorter RRM.

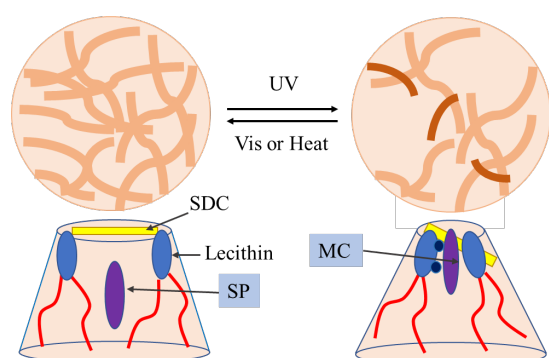


Figure 3. Mechanism of elongating/shortening of lecithin/SDC/SP-based RRM.²⁴

Another dynamic viscosity control study of RRM employed an equally-charged mixture of an anionic Gemini surfactant, O,O' - bis(sodium 2-tetradecylcarboxylate)-p-azodiphenol (G14-azo), and a cationic surfactant, cetyltrimethylammonium bromide (CTAB) in cyclohexane²⁵. The low shear viscosity of this system reached 4370 Pa s at $W_0 = 13$ and 0.2 M G14-azo. Under UV-light

irradiation, the transparent 0.3 M G14-azo /0.6M CTAB solution at $W_0 = 40$ became turbid and the viscosity decreased from 285 Pa s to 0.3 Pa s, consistent with a transition from worm-like RMs into spherical ones. The spherical micellar solution returned to its original homogeneous state with a viscosity of ~290 Pa s under visible light irradiation. Formation of RRM in scCO₂ has been examined to develop an efficient and effective CO₂-EOR technology for the last three decades.²⁶ Some double fluorocarbon (FC)-tail surfactants and hybrid surfactants having both fluorocarbon (FC) and HC tails were often found to form not only globular RMs but also RRM. **Figure 4** shows chemical structures of the surfactants studied in those papers.

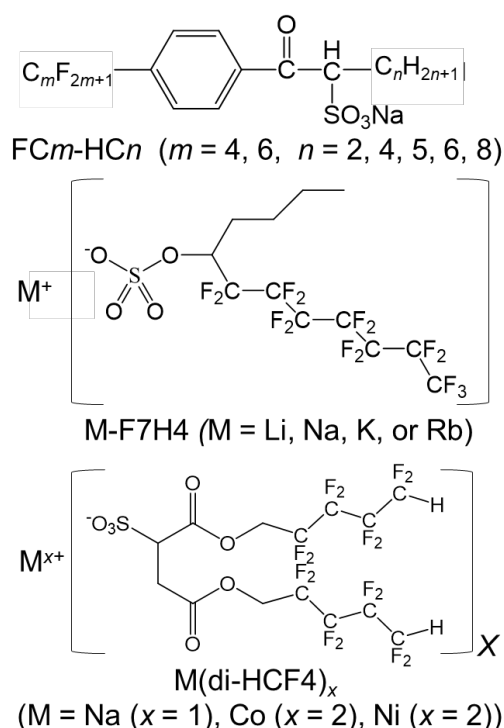


Figure 4. Chemical structure of the CO₂-philic surfactants for W/CO₂-type RRM²⁷

One example of RRM in scCO₂ was found using the hybrid surfactant series M-F7H4²⁷

(where the counter ion, $M = \text{Li}^+, \text{Na}^+, \text{K}^+, \text{or Rb}^+$). RRM appeared when $M = \text{Na}^+$, but ellipsoidal or spherical RMs were seen for systems with Li^+, K^+ or Rb^+ . The length and aspect ratio of Na-F7H4 RRM reached 525 Å and 10.5 respectively at a surfactant concentration of 4.4 wt% (75 mM), $W_0 = 12.5$, 400 bar and 40 °C.

Intrinsic viscosity $[\eta]$ at infinite dilution is very sensitive to particle shape, for hard spheres $[\eta] = 2.5$, whereas for one-dimensional, anisotropic particles $[\eta]$ is greater than this and can be approximated using equation (2)^{28,29},

$$[\eta] = 2.5 + 0.4075 (X_{\text{micelle}} - 1)^{1.508} \quad (2)$$

where X_{micelle} is the aspect ratio of the RM. The value of $[\eta]$ can be used to estimate the specific viscosity η_{sp} ($\eta_{\text{sp}} = (\eta/\eta_0) - 1$ where η and η_0 are viscosities of solution and pure solvent, respectively). As such, equation (3) details an approximate formula which is valid for the dilute regime of micelle volume fraction $\phi_p < 0.2$, and the calculated viscosity has been confirmed to be coincident with the experimental data³⁰.

$$\eta_{\text{sp}} = [\eta] \phi_p + K_H [\eta]^2 \phi_p^2 \quad (3)$$

where the K_H is the Huggins coefficient for rods (in this case ~ 0.4)²⁹, calculated from the estimated shear rate and rotational diffusion coefficient D_{rot} ; shear rate being obtained by analytical solution of the Navier–Stokes equation and D_{rot} being calculated using the SANS structural parameters and neat solution viscosity. The equations (2) and (3) estimated a relative viscosity of ~ 2 for the Na-F7H4 RRM²⁷.

The effect of counter ion on RM morphology in scCO₂ was also examined for a double FC-tail surfactant $M(\text{di-HCF})_x$ series (where $M = \text{Na}^+$ with $x = 1$, Co^{2+} with $x = 2$, and Ni^{2+} with

$x = 2$). The Na(di-HCF₄) formed only spherical RMs and increased CO₂ viscosity by only 10% even at the surfactant concentration of 10 wt%. In contrast with Na(di-HCF₄), Co(di-HCF₄)₂ and Ni(di-HCF₄)₂ generated RRM. The rod lengths were 300 Å for Co(di-HCF₄)₂ and 700 Å for Ni(di-HCF₄)₂ at surfactant concentration of 50 mM, $W_0 = 10$ at 25 °C and 400 bar, and the RMs increased CO₂ viscosity by 20-90 % at 6-10 wt%³¹. Thus, employing divalent transition metal ions as counterions for CO₂-philic surfactants is a very effective approach for RRM formation and increasing viscosity. The counterion effect probably originates from a decrease in CPP due to an increase in hydrophilic group volume containing a large counter ion.

There are some studies investigating the effect of hydrophobic chain lengths on RM morphology. For the hybrid surfactant series FC m -HC n (where m and n are FC and HC lengths, $m=4$ or 6 , $n = 2, 4, 5, 6$, or 8 as shown in **Figure 3**) RRM morphology was investigated at different FC and HC chain lengths^{32,33}. SANS studies revealed FC6-HC n RMs to be ellipsoidal for $n = 4$, cylindrical for $n = 5$ or 6 , spherical for $n = 8$. The aqueous core length and the aspect ratio of the FC6-HC5 RRM at 35 mM were estimated to be about 880 Å and 36, respectively. The length was 5.3 times longer than that of FC6-HC6 and identified to be the longest of the W/CO₂ systems studied. The intrinsic viscosity was calculated as $[\eta] = 30.9$ and specific viscosity $\eta_{\text{sp}} = 2.07$ for the FC6-HC5 RRM. When compared with the largest viscosity effect of $\eta_{\text{sp}} = 1.0$ for the 75 mM Na-F7H4/W/CO₂ systems with $W_0 = 12.5$, the η_{sp} value of the FC6-HC5/W/CO₂ system achieves an even

greater viscosity enhancement.

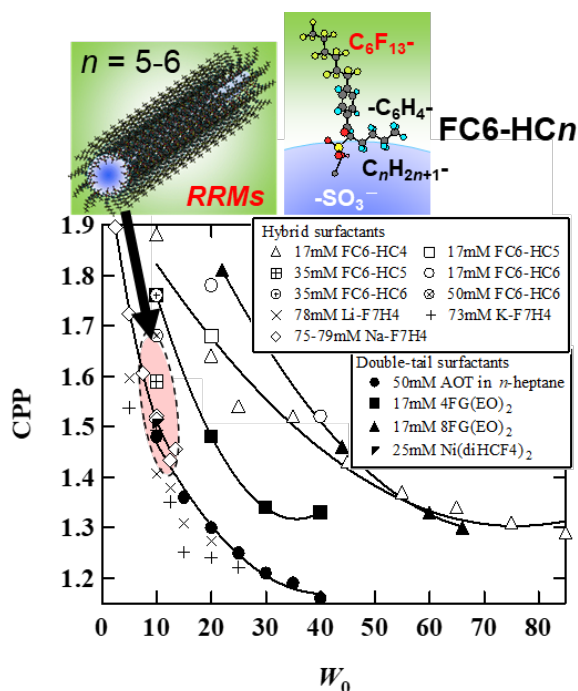


Figure 5. Change in CPP as a function of W_0 for W/CO₂ RMs with hybrid and double-tail surfactants or W/n-heptane RMs with AOT. Experimental conditions were 45 °C and 350 bar for 17mM FC6-HC n ($n = 4-6$) and 17mM n FG(EO)₂ ($n = 4, 8$), 23-40 °C and 380-400 bar for 78 mM Li-F7H4 and 73 mM K-F7H4, 75-79 mM Na-F7H4, 25 °C and 350-400 bar for 25 mM Ni(di-HCF4)₂ in W/CO₂ RMs, and 25 °C and 1 bar for 50 mM AOT in W/n-heptane RMs.³²

To find the optimum condition for RRM formation, a relationship between CPP and W_0 of RMs was investigated as shown in **Figure 5**.³² RRMs having rod lengths exceeding 250 Å could be obtained with the optimum conditions being $W_0 = \sim 10$, at surfactant concentrations ≥ 25 mM, and CPP of 1.4 ~1.7. In the case of FC6-HC n , the longer HC length gave the larger headgroup area and a smaller CPP. Therefore, FC6-HC5 is considered to have the optimum HC chain length giving the most appropriate CPP for

RRMs.

To tune the CPP and HCB of a CO₂-philic surfactant, additives with known effects in W/O RMs were also examined in W/CO₂ RMs.^{34,35} One of the additives is a hydrotrope well-known to affect RM morphology in a W/O system.³⁴ **Figure 6** shows chemical structures of hydrotropes sodium *p*-ethylbenzoate (C2benz) and sodium *p*-octylbenzoate (C8benz) and the CO₂-philic surfactants tested in W/CO₂ systems. Mixing hydrotropes C2benz and C8benz to a CO₂-philic surfactant DCF2 (the Na(di-HCF4) analogue having double C₂F₅CH₂CH₂-tails) induced ellipsoidal RMs. Change in HC length of the hydrotrope did not show a clear difference in RM morphology in scCO₂.³⁴ A mixture of the non-fluorinated co-surfactant DIGSS and the low F-content hybrid surfactant Hybrid CF2:SIS1 also generate ellipsoidal RMs at low CO₂ pressures (low CO₂ density)³⁴. Here, the addition of DIGSS probably changed the CPP of CF2:SIS1 and then curvature of the RMs.

Furthermore, the addition of DIGSS to the double fluorinated tail surfactant n FG(EO)₂ ($n = 6, 8$) showed remarkable effects on elongation of RMs and stabilization of W/CO₂ microemulsions. The effects could be given by the interaction between ethoxy groups of DIGSS and the surfactant headgroups, and short and branched HC tails of DIGSS keeping an appropriate HCB and CPP for RM system. As such hydrotropes can be applied to modify RM morphology of other fluorinated surfactants. Unfortunately, the mixing effect of hydrotropes on RM morphology in fluorine-free W/CO₂ systems is not as pronounced as in W/O systems³⁵.

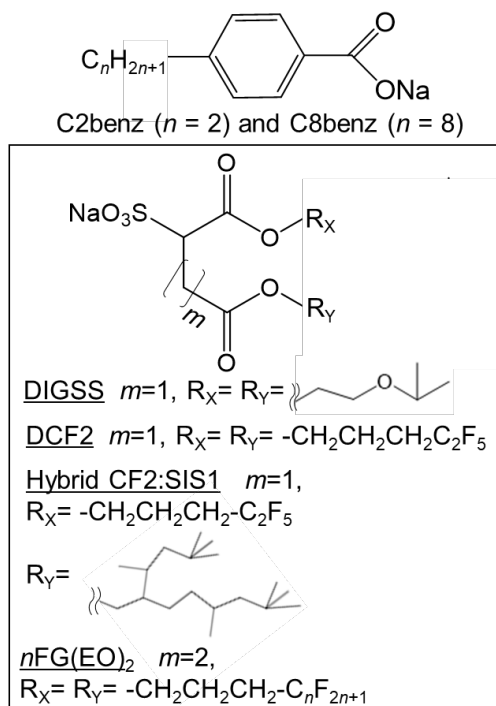


Figure 6. Chemical structure of hydrotropes and CO₂-philic surfactants for W/CO₂-type RRMs.

4. Surfactant and mixed system designs for RRMs

As described in previous sections, the most important parameters for forming RRMs are the CPP, and the affinity of the surfactant for nonpolar solvents (namely the HLB or HCB). CPP values of 1/3-1/2 are known to form rod-like micelles in water and appropriate CPP values for RRMs in nonpolar solvents are expected to be in a range of the inverse of these numbers (i.e. 2-3). However, long RRMs were found to appear at CPPs of 1.4-1.7 as shown in **Figure 5**. Obtaining the smaller CPP values needed for RRMs can be achieved by decreasing V at the same chain length l_c (i.e. increasing the number of tail groups triple-tail \rightarrow double-tail \rightarrow single-tail) or increasing l_c at constant V (branched tail \rightarrow less-branched tail, like iso-stearyl \rightarrow n -stearyl). Unfortunately, this affects not only CPP but also the affinity toward solvents,

though the HLB or HCB. Therefore, this often dominates and destabilizes the RRMs, showing the delicate balance in molecular architecture needed to generate RRMs. A few successful examples of W/CO₂ RRMs have been demonstrated with the hybrid surfactant series FC m -HC n ²⁴ and the double-FC tail surfactant series M(di-HCF n) $_x$ ²³. In the case of FC m -HC n , RRMs did not form with FC length $m = 4$ and/or HC length $n=2$, but did with $m = 6$ and $n = 4-8$, depending on CO₂ affinity of the FCs or HCB of the surfactants. When HC length increased with the constant FC length of $n = 6$, RM morphology changed in the sequence of spherical ($n = 4$), rod-like ($n = 5$ and 6), returning to spherical at $n = 8$. As another example of M(di-HCF n) $_x$, longer RRMs tend to form with the longer FC length of ≥ 4 . These are successful examples showing how it is necessary to balance up HCB and CPP by carefully designing the hydrophobic group to achieve RRM formation. Reasons why the FC surfactant, and especially the hybrid surfactant, are effective at forming the W/CO₂-type RRMs, could be: FC surfactants can achieve a stable RM system with high solubility; and hybrid surfactants can develop micro-segregation between the HC and FC chains, helping with the necessary uniaxial micellar growth. Another advantage of using a hybrid surfactant is the hydrophilic group area a_0 can be adjusted by varying the HC-chain length and enlarging the molecular distance (**Figure 4**). This is identified as a good way to tune CPP to induce RRM formation. The orientation of HC chains along the W/CO₂ interface is likely to occur due to the hydrophobicity, CO₂-phobicity and FC-phobicity. Tuning hydrophilic group area a_0 to

obtain RRM can also be achieved by changing spacer length in Gemini surfactants. As introduced in the previous section, adding hydrophilic additives (bile salts, hydrotropes, and transition metal ions) to the typical spherical RMs is another approach to control a_0 and favour RRM.

5. Conclusion

This review details previous studies involving various approaches for RRM formation in oil as well as in supercritical CO₂ solvents. Design criteria for surfactant molecules and mixed surfactant/additive systems for RRM and thickening ability were discussed in detail. As shown in this review, long RRM can be readily generated to control rheological behavior in W/O systems, and addition of additives and temperature as well as concentration can be used as a control parameter. On the other hand, RRM are much more difficult to obtain in W/CO₂ systems, and are only found with a few specialized FC-surfactants. Unfortunately, the W/CO₂-type RRM generated so far were not long enough to show significant thickening, and the use of FCs should be avoided for economic and environmental issues. Hopefully, the information described here will be beneficial in the advancement of RRM systems for CO₂-EOR, drug delivery systems and nanomaterial synthesis as well as in numerous other applications.

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