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Light-Scattering Investigations on Dilute Nonionic Oil-in-Water Microemulsions

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Warangkana Warisnoicharoen, Alison B. Lansley, and M. Jayne Lawrence
Pharmacy Department, King's College London, University of London, Franklin Wilkins Building, 150 Stamford Street, London, United Kingdom

ABSTRACT Dilute 3-component nonionic oil-in-water microemulsions formulated with either a polyoxyethylene surfactant ($C_{18:1}E_{10}$ or $C_{12}E_{10}$) or the alkylamine-N-oxide surfactant, DDAO ($C_{12}AO$), and containing either a triglyceride or an ethyl ester oil have been examined using dynamic and static light-scattering techniques. Analysis of the results showed distinct differences in the tested oil's mode of incorporation into the microemulsion droplets, with both the molecular volume of the oil and the hydrophobic chain length of the surfactant being important. For example, microemulsions formulated by $C_{18:1}E_{10}$ and containing one of the larger molecular volume oils (that is, either a triglyceride, Miglyol 812, or soybean oil) or the ethyl ester of fatty acid oil, ethyl oleate, exhibited first a decrease and then an increase in hydrodynamic size and surfactant aggregation number, suggesting that the asymmetric $C_{18:1}E_{10}$ micelles became spherical upon the addition of a small amount of oil and grew thereafter because of further oil being incorporated into the core of the spherical microemulsion droplet. A similar conclusion of sphericity could not be drawn for microemulsions stabilized by $C_{18:1}E_{10}$ and containing one of the oils smaller in molecular volume (namely tributyrin, ethyl butyrate, or ethyl caprylate) where neither the aggregation number nor the hydrodynamic radius changed much upon the addition of oil. This result suggested that these oils were preferentially located in the interfacial surfactant monolayer, behaving in much the same way as a cosurfactant. A different trend of results, however, was seen for microemulsions prepared using $C_{12}E_{10}$ and $C_{12}AO$, most likely because these surfactants produced approximately spherical micelles. In this case, the microemulsions containing the oils larger in molecular volume tended to exhibit an increase in surfactant aggregation number and hydrodynamic size, suggesting the growth of spherical micelles, while the smaller oils (in particular ethyl butyrate) caused a significant decrease in surfactant aggregation number incompatible with their being incorporated into the centre of the droplet, suggesting that the oils were being located in the interfacial surfactant monolayer. These results suggest that the various oils are incorporated into the microemulsions in very different ways.

INTRODUCTION

The phase behavior of oil-in-water (o/w) microemulsions prepared using the same oils and surfactants as examined here, namely, the triglycerides (soybean oil, Miglyol 812, and tributyrin) and the ethyl esters (ethyl oleate, ethyl caprylate, and ethyl butyrate) and either a polyoxyethylene alkyl ether ($C_{18:1}E_{10}$ or $C_{12}E_{10}$) or alkylamine-N-oxide ($C_{12}AO$) surfactant, has been previously examined (1,2). These studies suggested that there were differences in the mode of incorporation of the various oils into the microemulsions and, furthermore, that these differences may have important implications in the drug-solubilizing capacity of the microemulsions (1,3). Of particular interest was the observation that the surfactant $C_{18:1}E_{10}$ incorporated the large-molecular-volume oils (ie, soybean oil, Miglyol 812, and ethyl oleate) to a much greater extent than the smaller molecular volume oils (tributyrin, ethyl caprylate, and ethyl butyrate), while $C_{12}E_{10}$ and $C_{12}AO$ incorporated the smaller oils to a much

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Corresponding author: M. Jayne Lawrence. Pharmacy Department, King's College London, University of London, Franklin Wilkins Building, 150 Stamford Street, London, SE1 8WA, United Kingdom; jayne.lawrence@kcl.ac.uk

greater extent. In this paper, we examine the microstructure of dilute o/w microemulsions by means of laser light-scattering studies in an attempt to understand the different ways in which the various oils are incorporated into the microemulsion droplets. However, because microemulsions are generally concentrated systems that may, because of interparticulate interactions and multiple scattering of the light beam, lead to an underestimation of the particle size and aggregation number (4,5), the microemulsions in the present study were diluted to surfactant concentrations within the range 0.1% to 1.0% w/w. This dilution was made possible because of the absence of a cosurfactant in the systems under study.

MATERIALS AND METHODS

Materials

The polyoxyethylene surfactants polyoxyethylene-10-oleyl ether ($C_{18:1}E_{10}$) and polyoxyethylene-10-dodecyl ether ($C_{12}E_{10}$), as well as ethyl butyrate and soybean oil, were supplied by Sigma Chemical Co. Ltd. (Dorset, UK). *N,N*-dimethyldodecylamine-*N*-oxide ($C_{12}AO$) (98% purity), ethyl caprylate, and tributyrin were purchased from Fluka Chemika Ltd. (Dorset, UK). Miglyol 812 was a gift from AG Hüls (Werk Witten, Germany), and ethyl oleate was supplied from Aldrich Chemical Co. Ltd. (Dorset, UK). All of the chemicals studied were commercially available and used as received, although before use the surfactants were well characterized and, in the case of $C_{12}AO$, purity was confirmed (2). Distilled water obtained from a well-seasoned glass apparatus was used for all experiments.

Micelle and Microemulsion Preparation

The concentrated micelles or microemulsion solutions were prepared as a 20% w/w surfactant solution, as previously reported (2). The only exception to this generalization was the microemulsions prepared with $C_{12}E_{10}$ and containing tributyrin where the intial surfactant concentration was 25% w/w; in this case it was not possible to make a microemulsion containing the required amount of oil at a surfactant concentration of 20% w/w. The diluted micelles and microemulsion samples were prepared by sequentially diluting freshly prepared concentrated samples with water to the required surfactant concentration. The compositions of the microemulsions studied are expressed in terms of the relative weights of oil and surfactant.

Photon Correlation Spectroscopy and Total Intensity Light-Scattering Measurements

Photon correlation spectroscopy (PCS) and total intensity light-scattering (TILS) measurements were performed simultaneously using a Malvern 4700c light-scattering instrument (Malvern Instruments Ltd., Malvern, Worcester, UK), as previously reported (6). In all the surfactant samples tested, the ratio of scattering intensities (for TILS) and of diffusion coefficients (for PCS) at angles of 45° and 135° were always in the range 1.00 ± 0.05, and so all further measurements were performed at 90°. For total intensity measurements, the instrument was calibrated with a dust-free sample of benzene (AnalaR) using an R_{90} for benzene at 488 nm and 298 K of 3.26×10^{-6} cm^{-1} (7). Specific refractive index measurements (dn/dc) required for analysis of the TILS data were determined at a wavelength of 589.6 nm (sodium lamp) using a high-precision Abbe (60 ED) refractometer (Bellingham and Stanley, Ltd, Sevenoaks, UK). For analysis of the PCS results, the autocorrelation function was analyzed using the cumulants assay of Koppel (8) assuming particle monodispersity. The diffusion coefficient of the particles thus obtained was converted to size using the Stokes-Einstein equation assuming spherical aggregates.

Analysis of TILS Results

Micelles

Assuming a spherical aggregate and using simple geometric considerations, it is possible to determine the radius of the micellar core (R_c) and the area occupied by the surfactant molecules at the core/mantle interface (a_o) using the volume of the hydrophobic core of the micelle (V) obtained from $V = vN_{agg}$, where v is the volume of the hydrophobic chain of the surfactant (ie, 352 Å^3 for $C_{12}AO$ and $C_{12}E_{10}$; 504 Å^3 for $C_{18:1}E_{10}$) (1) and N_{agg} is the aggregation number of the micelle (determined from TILS).

Microemulsions

By assuming the oil is evenly distributed between surfactant aggregates, and that each droplet contains f_o mole fraction of oil (ie, the moles of oil divided by the moles of oil plus surfactant present) and f_s mole fraction of surfactant (ie, the moles of surfactant divided by the moles of oil plus surfactant present), it is possible to obtain the number of oil (n_o) and surfactant (n_s) molecules associated with each droplet from a knowledge of the aggregate weight of the microemulsion obtained using TILS. Assuming that the oil forms a distinct core in the center of the spherical microemulsion droplet, the radius of the hydrophobic core (R_c) of the droplet and a_o (the area per surfactant at the core/mantle interface) can be calculated from:

$$(4/3)(\pi R\ ) = n_oV_o + n_sv \qquad \text{(Equation 1)}$$

and

$$R_c = 3\ (nV_o + v)/\ a_o \qquad \text{(Equation 2)}$$

where $n = n_o/n_s$ and V_o is the molecular volume of oil. V_o was calculated from summing the volume contributions of the various chemical groups comprising the structure of the oil molecule: 232 Å^3 for ethyl butyrate, 340 Å^3 for ethyl caprylate, 600 Å^3 for ethyl oleate, 520 Å^3 for tributyrin, 925 Å^3 for Miglyol 812, and 1563 Å^3 for soybean oil (1). From a knowledge of n_o and V_o, it is possible to estimate the radius of the oil core (R_o) of the microemulsion.

RESULTS AND DISCUSSION

To examine the influence of the oil on the microstructure of the microemulsion behavior, it is important to examine first the aggregation behavior of the micelles themselves.

Particle Size Characterization of Micellar Solutions

From Figure 1A, it can be seen that the hydrodynamic sizes of both the $C_{12}E_{10}$ and $C_{12}AO$ micelles remained approximately constant over a surfactant concentration range of 0.2% to 1.0% w/w, while the hydrodynamic size of the $C_{18:1}E_{10}$ micelles decreased in line with surfactant concentration, suggesting the presence of attractive micellar interactions in the latter system. Note that the surfactant concentrations in Figure 1A have been corrected for the cmc of the surfactants, as determined from the TILS experiments (data not shown). The hydrodynamic radii of the micelles at infinite dilution assuming spherical aggregates were found to be 3.40 nm, 6.15 nm, and 1.73 nm for $C_{12}E_{10}$, $C_{18:1}E_{10}$, and $C_{12}AO$, respectively (Table 1).

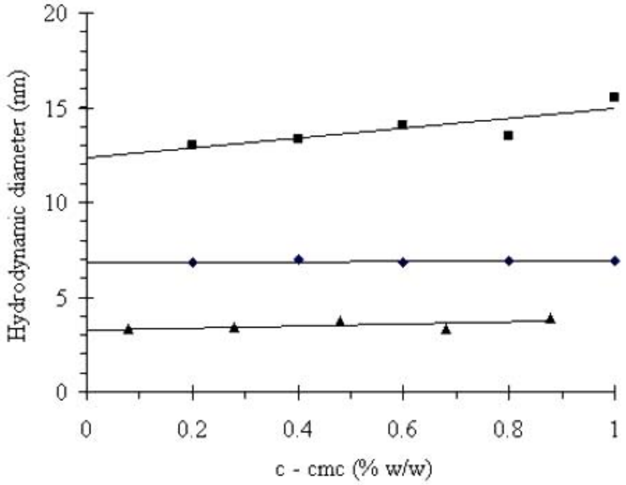

Figure 1A. Variation in micelle hydrodynamic diameter as a function of surfactant concentration (corrected for cmc) at 298 K. $C_{18:1}E_{10}$ micelles (solid square), $C_{12}E_{10}$ micelles (solid diamond), and $C_{12}AO$ micelles (solid triangle).

Figure 1B shows the variation in S_{90} against surfactant concentration (corrected for the cmc determined by TILS). S_{90} is the ratio of the scattering intensity of the micelles/microemulsions, corrected for that of the solvent to the scattering intensity of benzene at 90°. As can be seen from Figure 1B, the variation in the intensity of light scattered was linear over the surfactant concentration range studied, suggesting that the micelle size does not vary significantly over the concentration range studied, thereby allowing micelle size to be determined using the Debye equation.

Table 1. Micellar properties of nonionic surfactants at 298 K. N_{agg} is the surfactant aggregation number; R_h is the hydrodynamic radius obtained assuming spherical particles; R_c is the radius of the hydrophobic core of the aggregate obtained assuming spherical particles; and a_o is the surfactant molecular area at the core/mantle interface assuming spherical particles.

		Droplet radius (nm)		
Surfactant	N_{agg}	R_h	R_c	a_o (Å^2)
$C_{12}E_{10}$	59	3.40	1.70	62.0
$C_{18:1}E_{10}$	307	6.15	3.33	45.4
$C_{12}AO$	51	1.63	1.62	65.1

It can be seen in Table 1 that the aggregation number calculated for the $C_{18:1}E_{10}$ micelles was about 5 times higher than that obtained for $C_{12}E_{10}$ and $C_{12}AO$. This result is undoubtedly attributable to the long hydrophobic chain present in $C_{18:1}E_{10}$, which increased the driving force for aggregation. Because the aggregation numbers for the C12 surfactants are similar, the larger hydrodynamic size obtained using PCS for $C_{12}E_{10}$ compared to $C_{12}AO$ is obviously a consequence of the long hydrophilic polyoxyethylene chains present in the former surfactant.

To obtain an estimate of aggregate shape, the radius of the micellar core (R_c) calculated using the surfactant aggregation number and assuming spherical droplets can be compared to the extended length of the hydrophobic chain of the surfactant. As the fully extended alkyl chain lengths of C18:1 and C12, (ie, 2.16 nm and 1.67 nm, respectively) (9) are less than the radii calculated for the hydrophobic core of micelles of $C_{18:1}E_{10}$ and $C_{12}E_{10}$ and very close to that obtained for $C_{12}AO$ micelles (see Table 1), it is unlikely that these surfactants form spherical micelles, forming in preference asymmetric aggregates. It is worth noting, however, that because the extended chain length of a C12 moiety is not much different from R_c, the micelles formed by $C_{12}E_{10}$ and $C_{12}AO$ probably approximate to spheres. In support of this hypothesis, the areas per surfactant molecule obtained for $C_{12}E_{10}$ and $C_{12}AO$ at the core/mantle interface were fairly close to the (minimum) value seen (70.0 Å^2) in spherical micelles (10).

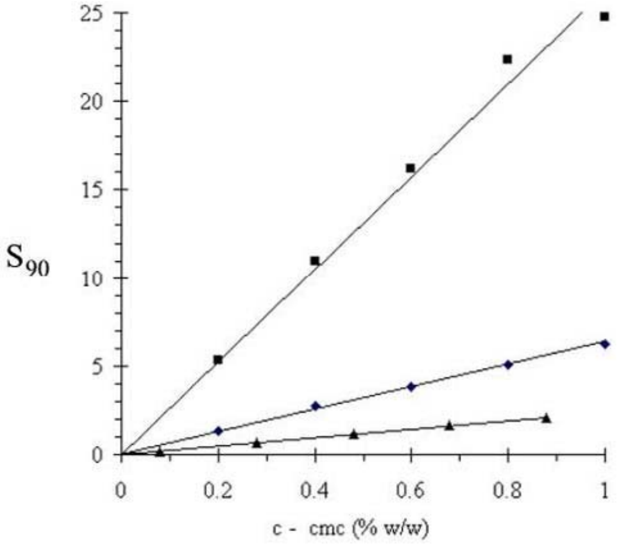

Figure 1B. Variation in relative scattering intensity (S_{90}) as a function of surfactant concentration (corrected for cmc) at 298 K. $C_{18:1}E_{10}$ micelles (solid square), $C_{12}E_{10}$ micelles (solid diamond), and $C_{12}AO$ micelles (solid triangle)

Particle Size Characterization of O/W Microemulsions

It should be noted that because neither the PCS nor the TILS data for the microemulsion systems gave any evidence of a change in aggregate shape or size over the concentration range studied (Figures 2A, 2B, 3A, 3B, 4A, 4B), there appears to be no problems with dilution of the microemulsion samples. It is also important to note that, in the present study, the different microemulsion samples are compared on the basis of weight of oil present, which is not considered unreasonable because the densities of the oils (within the same chemical class) are similar. The only exception to this was the triglyceride oil, tributyrin, which possessed a higher density than both Miglyol 812 and soybean oil.

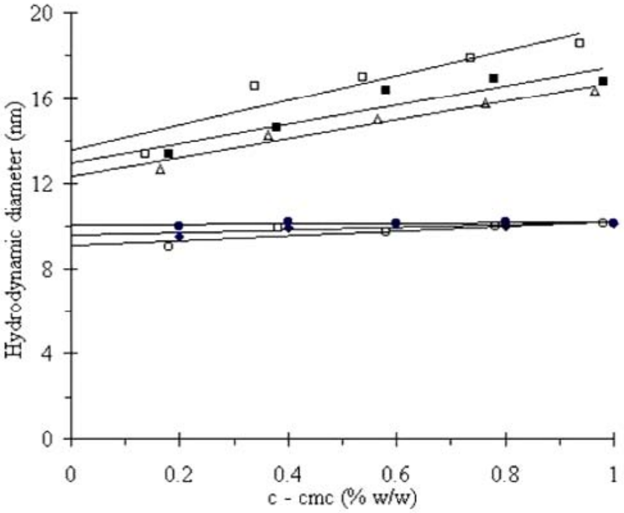

Figure 2A. Variation in hydrodynamic diameter for microemulsions prepared with $C_{18:1}E_{10}$ at a surfactant-to-oil weight ratio of 1:10 with surfactant concentration (corrected for cmc) at 298 K. Microemulsions containing tributyrin (solid square), Miglyol 812 (solid diamond), soybean oil (solid circle), ethyl butyrate (open triangle), ethyl caprylate (open square), and ethyl oleate (open circle).

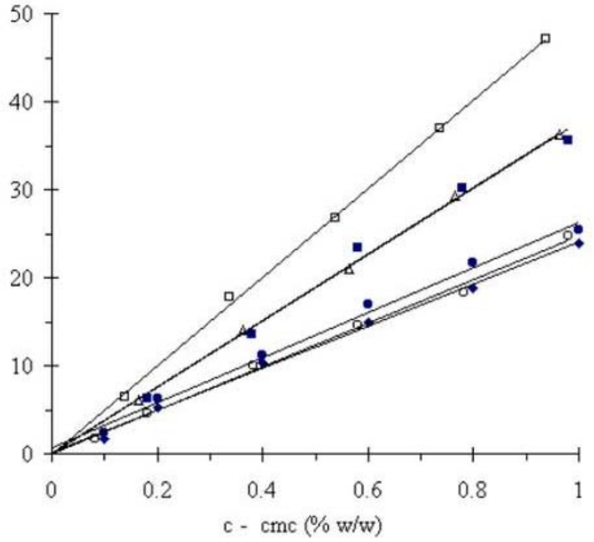

Figure 2B. Variation in relative scattering intensity (S_{90}) for microemulsions prepared with $C_{18:1}E_{10}$ at a surfactant-to-oil weight ratio of 1:10 as a function of surfactant concentration (corrected for the cmc) at 298 K. Microemulsions containing tributyrin (solid square), Miglyol 812 (solid diamond), soybean oil (solid circle), ethyl butyrate (open triangle), ethyl caprylate (open square), and ethyl oleate (open circle).

Microemulsions Formulated With $C_{18:1}E_{10}$

Figure 2A shows the variation in hydrodynamic size for microemulsions containing a weight ratio of oil:surfactant of 1:10, and Figure 2B shows the variation in the intensity of scattering for the same systems. Table 2 summarizes the results obtained for all the $C_{18:1}E_{10}$- stabilized microemulsions tested. The first noticeable thing about the results obtained with the $C_{18:1}E_{10}$ systems is that despite the very low level of oil incorporated, there is a distinct difference in the way in which the various oils affect the light-scattering behavior of the microemulsions, with the oils falling into two categories based broadly on their molecular volume. For example, when the larger molecular volume oils are present, there is a definite decrease in aggregate size when compared to the parent micelles (Table 2). In contrast, the addition of the smaller molecular volume oils (namely ethyl butyrate, ethyl caprylate, and tributyrin) into the $C_{18:1}E_{10}$ micelles caused relatively small changes in size (Table 2). Moreover, the surfactant aggregation numbers for microemulsions containing tributyrin, ethyl caprylate, and ethyl butyrate at a weight ratio of 1:10, and indeed the parent $C_{18:1}E_{10}$ micelles, were about twice the value (ie, 155) obtained for microemulsions containing Miglyol 812, soybean oil, or ethyl oleate (Table 2). Both the reduction in size and aggregation number observed in the presence of the oils large in molecular volume suggest that these oils cause a transformation of the asymmetric $C_{18:1}E_{10}$ micelles to spherical microemulsion droplets. In contrast, the absence of any large change in size or aggregation number for the microemulsions incorporating the smaller molecular volume oils implies that these oils do not effect such a transformation at this low concentration.

For the $C_{18:1}E_{10}$ -stabilized microemulsions containing the larger molecular volume oils, it was possible to increase the level of oil incorporation. Increasing the oil-to-surfactant weight ratio from 1:10 to 2:10 and 3:10 increased the droplet size of the microemulsions (Table 2). For example, the hydrodynamic radius of microemulsions containing Miglyol 812 at oil-to-surfactant weight ratios of 2:10 and 3:10 were 5.70 nm and 6.65 nm, respectively, compared to 4.76 nm at an oil-to-surfactant weight ratio of 1:10.

Table 2. Properties of $C_{18:1}E_{10}$ microemulsions at 298 K. R_h is the hydrodynamic radius obtained assuming spherical particles; n_s and n_o are the numbers of surfactant and oil molecules per microemulsion droplet, respectively; a_o is the surfactant molecular area at the core/mantle interface assuming spherical particles; R_c is the radius of the hydrophobic core of the aggregate obtained assuming spherical particles; R_o is the radius of the oil core of the microemulsion obtained assuming spherical particles.

	Ratio of oil to surfactant				Radius (nm)			
Oils	Weight ratio	Molar ratio	n_o	n_s	R_h	R_o	R_c	a_o (Å^2)
$C_{18:1}E_{10}$	0	0	0	307	6.15	0	3.33	N/A
Tributyrin	1:10	1:4.3	62	264	6.49	1.97	3.41	55.1
Miglyol 812	1:10	1:7.1	21	155	4.76	1.68	2.86	66.3
	1:5	1:3.6	54	196	5.70	2.30	3.30	69.3
	1:3.3	1:2.4	99	238	6.65	2.80	3.70	72.1
Soybean oil	1:10	1:12.5	12	155	5.05	1.68	2.85	66.4
	1:5	1:6.3	35	218	5.90	2.37	3.41	67.0
	1:3.3	1:4.2	66	272	6.50	2.92	3.86	69.0
Ethyl butyrate	1:10	1:1.6	157	258	6.17	2.06	3.41	56.7
Ethyl caprylate	1:10	1:2.3	150	365	6.60	2.30	3.83	50.4
Ethyl oleate	1:10	1:4.3	36	159	4.54	1.73	2.90	66.3
	1:5	1:2.2	90	198	5.30	2.35	3.33	70.1
	1:3.3	1:1.5	148	217	5.50	2.77	3.62	76.0

The variation in surfactant aggregation number with increasing oil concentration for the microemulsions at a constant surfactant concentration when incorporating the larger molecular volume oils was distinctive in that there was an initial drop in scattering intensity and surfactant aggregation number followed by an increase up to the level of oil saturation, mirroring the variation in hydrodynamic radius with oil concentration (Table 2). The initial drop in scattering intensity is characteristic of a change in aggregate shape from asymmetric to spherical, while the subsequent increase in scattering suggests the growth of the now-spherical micoremulsion droplets (11). This effect can be clearly seen by considering the number of surfactant molecules associated with the droplet. For example, the surfactant aggregation number of the Miglyol 812-containing microemulsions increased from 155 at an oil-to-surfactant weight ratio of 1:10 to 196 and 238 molecules at oil-to-surfactant weight ratios of 2:10 and 3:10, respectively. A similar trend in results was seen for the microemulsions containing soybean oil and ethyl oleate.

It is clear that there are differences in the mode of oil incorporation into the $C_{18:1}E_{10}$-stabilized microemulsions and that these differences can be equated with the molecular volume of the oil, although it should be noted that these differences may also be correlated with the differences in polarity of the oils, with the more polar oils being solubilized to a greater extent. However, previous work has suggested that, for the particular oils studied, the molecular volume is the dominant factor in deciding the nature of the oil incorporation (1). From our results, we propose that the larger molecular volume oils form a distinct core in the $C_{18:1}E_{10}$-stabilized microemulsions, thereby promoting the formation of a spherical microemulsion droplet. This conclusion is supported by simple geometric modelling, performed assuming that the oil forms a distinct core, which shows that for the larger molecular volume oils, the calculated area for a surfactant molecule at the core-mantle interface is close to the minimum value required for a spherical droplet (70.0 Å^2). In contrast, for the smaller molecular volume oils, the area per surfactant molecule was no greater than 60.0 Å^2, suggesting that these oils penetrate, at least partially, the interfacial surfactant monolayer, thereby maintaining the asymmetric behavior of the aggregates. In support of our hypothesis, the proposed mode of oil incorporation is in agreement with the results of cloud point/phase inversion temperature studies reported by Warisnoicharoen et al (2).

Microemulsions Formulated with $C_{12}E_{10}$

Figure 3A shows the variation in the hydrodynamic size of microemulsions as a function of surfactant concentration for $C_{12}E_{10}$-stabilized microemulsions containing the various oils at an oil-to-surfactant weight ratio of 1:10.

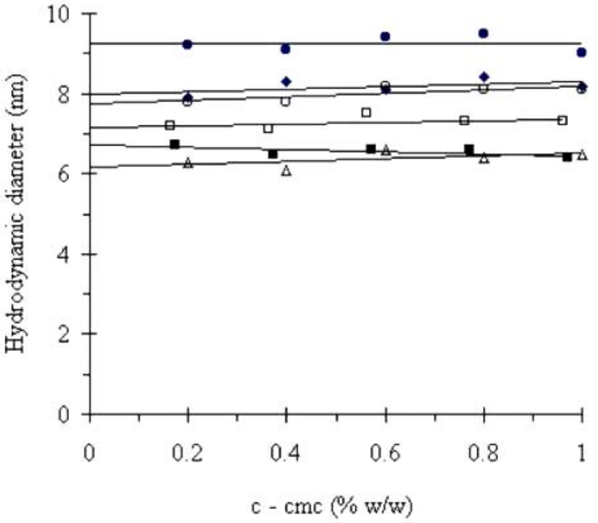

Figure 3A. Variation in hydrodynamic diameter for microemulsions prepared with $C_{12}E_{10}$ at a surfactant-to-oil weight ratio of 1:10 with surfactant concentration (corrected for cmc) at 298 K. Microemulsions containing tributyrin (solid square), Miglyol 812 (solid diamond), soybean oil (solid circle), ethyl butyrate (open triangle), ethyl caprylate (open square), and ethyl oleate (open circle).

For the microemulsions prepared by $C_{12}E_{10}$, the larger molecular volume oils produced the larger droplet sizes and the smaller molecular volume oils gave the smallest droplet sizes (Table 3), with the largest hydrodynamic radius (4.62 nm) being seen for the microemulsion containing soybean oil and the smallest (3.08 nm) for the ethyl butyrate-containing systems.

It should be noted that because tributyrin was solubilized in the microemulsion at an oil-to-$C_{12}E_{10}$ weight ratio of 1:12.5 and not 1:10 as with all other oils, care should be taken in comparing the results obtained with this oil. It is clear from Figure 3A that although the increase in size follows the increase in oil molecular volume, the differences between the oils of differing molecular volume were less pronounced than in the case of $C_{18:1}E_{10}$-stabilized microemulsions, with no clear distinctions being observed between the "large" and "small" molecular volume oils.

The scattering intensities of the microemulsions containing the various oils at an oil:surfactant weight ratio of 1:10 are shown in Figure 3B.

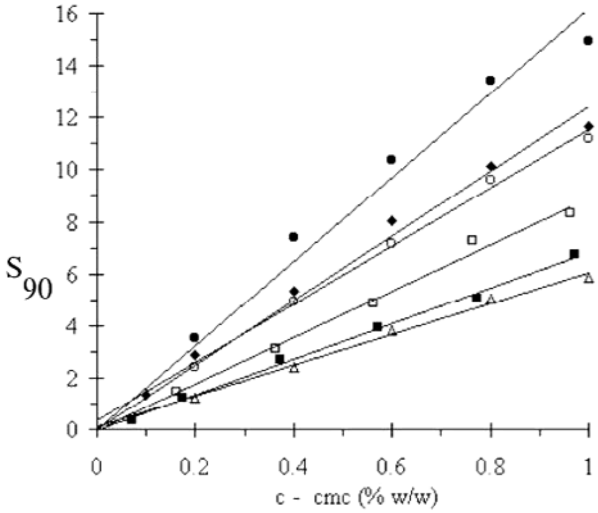

Figure 3B. Variation in relative scattering intensity (S_{90}) for microemulsions prepared with $C_{12}E_{10}$ at a surfactant-to-oil weight ratio of 1:10 as a function of surfactant concentration (corrected for cmc) at 298 K. Microemulsions containing tributyrin (solid square), Miglyol 812 (solid diamond), soybean oil (solid circle), ethyl butyrate (open triangle), ethyl caprylate (open square), and ethyl oleate (open circle).

As with the trend in the PCS results, the larger molecular volume oils exhibited the greatest level of scattering intensity. It is interesting that, although differences in scattering intensity were not pronounced, there are clear differences between the surfactant aggregation numbers obtained with the different molecular volume oils where a distinction between oils with large and small molecular volumes is clear (Table 3).

Table 3. Properties of $C_{12}E_{10}$ microemulsions at 298 K. R_h is the hydrodynamic radius obtained assuming spherical particles; n_s and n_o are the numbers of surfactant and oil molecules per microemulsion droplet, respectively; a_o is the surfactant molecular area at the core/mantle interface assuming spherical particles; R_c is the radius of the hydrophobic core of the aggregate obtained assuming spherical particles; R_o is the radius of the oil core of the microemulsion obtained assuming spherical particles.

	Ratio of oil to surfactant				Radius (nm)			
Oils	Weight ratio	Molar ratio	n_o	n_s	R_h	R_o	R_c	a_o (Å ^{2})
$C_{12}E_{10}$	0	0	0	59	3.40	0	1.70	62.0
Tributyrin	1:12.5	1:5.9	9	55	3.35	1.04	1.80	73.4
Miglyol 812	1:10	1:8.3	13	103	3.98	1.41	2.25	62.0
Soybean oil	1:10	1:14.3	10	139	4.62	1.55	2.50	56.0
Ethyl butyrate	1:10	1:1.85	31	58	3.08	1.20	1.87	76.3
	1:5	1:0.93	49	46	3.08	1.40	1.87	96.5
	1:1.33	1:0.62	56	35	3.15	1.46	1.82	119.6
	1:1.25	1:0.47	66	31	2.92	1.54	1.84	138.7
	1:2	1:0.37	76	28	2.86	1.61	1.87	156.6
Ethyl caprylate	1:10	1:2.8	27	74	3.58	1.30	2.03	70.1
	1:6.7	1:1.8	43	79	3.29	1.52	2.16	74.5
	1:5	1:1.4	53	73	3.34	1.62	2.18	82.4
Ethyl oleate	1:10	1:5.0	20	101	3.86	1.43	2.25	63.0

In contrast to the results obtained with $C_{18:1}E_{10,}$ it was the smaller molecular volume oils that could be incorporated to the largest extent in the $C_{12}E_{10}$ microemulsions. Table 3 gives the variation in size and aggregation number with oil content. It is surprising that the hydrodynamic radius of microemulsion droplets containing ethyl butyrate remained largely unchanged upon increasing the weight ratio of oil to surfactant from 1:10 to 2:10, 3:10, 4:10, and 5:10, respectively. A similar effect was seen in microemulsions containing ethyl caprylate at oil-to-surfactant weight ratios of 1:10, 1.5:10, and 2:10.

In agreement with the PCS results, the TILS results obtained for the microemulsions incorporating an increasing concentration of ethyl butyrate exhibited a very similar level of scattering, and the systems containing ethyl caprylate showed a nonregular variation in the scattering intensity at the various weight ratios of oil to surfactant studied (data not shown). Calculation of the surfactant and oil aggregation numbers of the ethyl butyrate-containing microemulsions showed that the number of surfactant molecules associated with the droplet decreased as the oil-to-surfactant weight ratio increased; for example, the number of surfactant molecules associated with the aggregate decreased from 58 at an oil:surfactant weight ratio of 1:10 to 28 at a ratio of 5:10 (Table 3). For microemulsions solubilizing ethyl caprylate, the number of surfactant molecules associated with the aggregate seemed to vary slightly in that surfactant aggregation numbers of 74, 79, and 73 were found upon increasing the oil-to-surfactant weight ratios of 1:10 to 1.5:10 and 2:10, respectively. These results obtained with both oils are clearly incompatible with the formation of spherical microemulsion droplets containing a central oil core.

Indeed, the calculated interfacial area per surfactant molecule at the core/mantle boundary of the systems containing the smaller molecular volume oils tributyrin, ethyl butyrate, and ethyl caprylate was large and increased considerably with increasing oil. The extremely large areas per molecule calculated for the small-molecular-volume oils are incompatible with the relatively small E10 head group and with the added oil forming the central core of the microemulsion droplet, suggesting that these oils are also located, at least in part, in the interfacial surfactant monolayer and that the extent of this penetration is increased with increasing oil concentration. In contrast, the area per molecule calculated for the larger molecular volume oils at an oil-to-surfactant weight ratio of 1:10 were similar to the molecular area calculated for the $C_{12}E_{10}$ micelle (Table 3), supporting the idea that the aggregates were spherical in nature. This result is not unexpected, as it would be unlikely that the large-molecular-volume oils penetrate the hydrophobic chains of the interfacial $C_{12}E_{10}$ layer to any significant extent. It was noteworthy that, in terms of changes in surfactant molecular area, these findings were opposite to the trends found with the microemulsions prepared using $C_{18:1}E_{10}$. However, it must be remembered that the micelles formed by $C_{18:1}E_{10}$ were asymmetric, whereas those formed by $C_{12}E_{10}$ were spherical. Again, the conclusion of this part of the study is in agreement with our earlier cloud point/phase inversion temperature studies (2).

Microemulsions Formulated with $C_{12}AO$

The variation in hydrodynamic size of the $C_{12}AO$ microemulsion droplets containing the various oils at an oil-to-surfactant weight ratio of 1:10 can be seen in Figure 4A, and the scattering intensities of the same microemulsions are given in Figure 4B. It should be noted that soybean oil could not be solubilized by $C_{12}AO$ micelles. As with the $C_{12}E_{10}$ systems, the trend was that the largest molecular volume oils produced the largest aggregates with the highest surfactant aggregation number (Table 4), although, as with $C_{12}E_{10}$, there was no distinct difference between the "large" and "small" molecular volume oils.

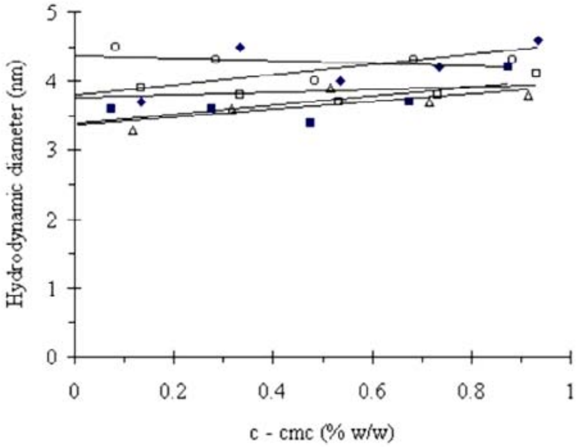

Figure 4A. Variation in hydrodynamic diameter for microemulsions prepared with $C_{12}AO$ at a surfactant-to-oil weight ratio of 1:10 with surfactant concentration (corrected for cmc) at 298 K. Microemulsions containing tributyrin (solid square), Miglyol 812 (solid diamond), soybean oil (solid circle), ethyl butyrate (open triangle), ethyl caprylate (open square), and ethyl oleate (open circle).

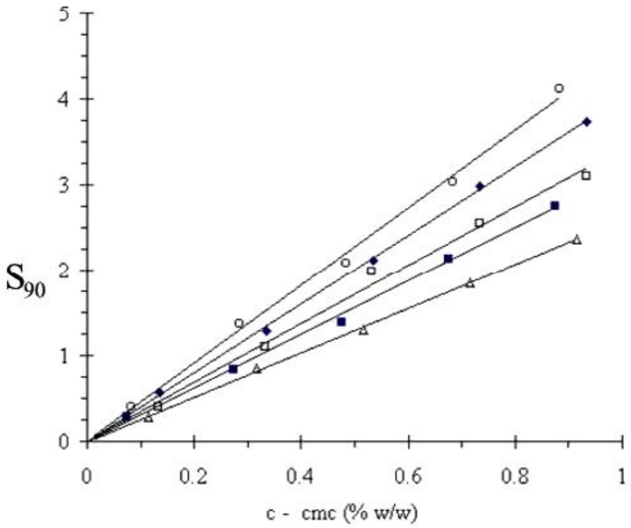

Figure 4B. Variation in relative scattering intensity (S_{90}) for microemulsions prepared with $C_{12}AO$ at a surfactant-to-oil weight ratio of 1:10 as a function of surfactant concentration (corrected for cmc) at 298 K. Microemulsions containing tributyrin (solid square), Miglyol 812 (solid diamond), soybean oil (solid circle), ethyl butyrate (open triangle), ethyl caprylate (open square), and ethyl oleate (open circle).

In line with the $C_{12}E_{10}$ systems, the smaller molecular volume oils could be incorporated to the largest extent. As with the ethyl butyrate-containing $C_{12}E_{10}$ microemulsions, the hydrodynamic radius of the C_{12}AO-stabilized ethyl butyrate microemulsions remained fairly constant, despite a large relative increase in the amount of oil present (Table 4). Similarly, the surfactant aggregation numbers for the C_{12}AO microemulsions incorporating ethyl butyrate followed the same trend as the corresponding $C_{12}E_{10}$ microemulsions in that the number of the surfactant molecules per microemulsion droplet decreased upon increasing the amount of oil added (Table 4). For example, the number of surfactant molecules per droplet at oil-to-surfactant weight ratios of 1:10 and 11:10 were approximately 55 and 15 molecules, respectively. For this surfactant, similar findings were found for microemulsions incorporating ethyl oleate at various oil-to-surfactant weight ratios examined (namely, 1:10, 1.5:10, and 2:10), in that the number of surfactant molecules decreased upon increasing the amount of oil added. Note in contrast that ethyl oleate could not be incorporated to any significant extent in the $C_{12}E_{10}$- stabilized microemulsions. Again in common with the $C_{12}E_{10}$ microemulsions, the variation in surfactant aggregation numbers for the ethyl caprylate systems did not follow a clear trend.

Table 4. Properties of C_{12}AO microemulsions at 298 K. R_h is the hydrodynamic radius obtained assuming spherical particles; n_s and n_o are the numbers of surfactant and oil molecules per microemulsion droplet, respectively; a_o is the surfactant molecular area at the core/mantle interface assuming spherical particles; R_c is the radius of the hydrophobic core of the aggregate obtained assuming spherical particles; R_o is the radius of the oil core of the microemulsion obtained assuming spherical particles.

	Ratio of oil to surfactant				Radius (nm)			
Oils	Weight ratio	Molar ratio	n_o	n_s	R_h	R_o	R_c	a_o (Å^2)
C_{12}AO	0	0	0	51	1.63	0	1.62	65.1
Tributyrin	1:10	1:12.5	4	51	1.70	0.78	1.68	69.8
Miglyol 812	1:10	1:25	3	65	1.90	0.86	1.83	64.6
Ethyl butyrate	1:10	1:5	11	55	1.69	0.84	1.73	68.5
	1:3.3	1:1.7	23	38	1.74	1.08	1.64	89.4
	1:2	1:1	24	24	1.94	1.09	1.50	117.1
	1:1.4	1:0.72	26	19	1.82	1.13	1.45	139.3
	1:1.1	1:0.56	30	17	1.90	1.18	1.45	157.7
	1:0.9	1:0.46	32	15	1.80	1.21	1.44	177.8
Ethyl caprylate	1:10	1:7.7	9	65	1.88	0.90	1.83	64.8
	1:5	1:3.7	12	46	1.86	1.00	1.70	78.6
	1:3.3	1:2.5	20	49	1.81	1.17	1.80	81.6
	1:2.5	1:1.9	24	45	1.65	1.25	1.80	89.6
	1:2	1:1.5	33	50	1.28	1.40	1.90	91.1
Ethyl oleate	1:10	1:14.3	6	77	2.19	0.93	1.94	61.4
	1:6.7	1:9.0	8	69	2.10	1.03	1.90	65.9
	1:5	1:6.7	10	65	1.91	1.11	1.89	69.6

It is interesting that for all oils tested, there was not much change in the area per molecule when the lowest amount of oil was added, which suggested that the addition of a small amount of oil did not significantly affect the packing of the surfactant in the interfacial region and that larger amounts of oil are needed to be added to see a significant penetration into this region. However, the interfacial area per surfactant molecule calculated was seen to increase with an increase in the amount of oil present, suggesting that penetration increased with increasing oil concentration. The area per surfactant molecule for microemulsions containing ethyl butyrate increased to the greatest extent, suggesting that the model of a central oil core was least applicable in this case. It has been reported that the addition of a small amphiphilic molecule such as heptane-1,2,-triol (HP) to C_{12}AO micelles caused a decrease in both aggregate size and surfactant aggregation number upon increasing the number of HP molecules, suggesting that HP was acting in the same way as a cosurfactant by replacing water molecules around the surfactant head group (12).

CONCLUSIONS

The findings in the present study suggest that the nature of the micellar aggregates and the molecular volume of an oil play an important role in determining the nature of its incorporation into the microemulsion droplet and its subsequent effect on aggregation behavior. In general, the larger molecular volume oils tend to locate in the center of the surfactant aggregate, and the smaller molecular volume oils, at least partially, locate in the interfacial surfactant region. However, the precise effect of the oil on the shape of the aggregate depends very much on the amount of oil present and shape of the original micellar aggregate, which in turn depends on the molecular structure of the surfactant.

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