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# Three Component Ionic Microemulsions

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## ABSTRACT

Necessary design features of microemulsions formed from cationic surfactant without any requirement for cosurfactant are illustrated by a study of microemulsions formed from didodecyldimethylammonium bromide in various oils. Ease of purification, preparation and manipulation give this and related systems a considerable advantage over conventional systems in enhancing our understanding of microemulsions and emulsion behavior.

## INTRODUCTION

Most of the literature<sup>(1-11)</sup> on microemulsions containing ionic surfactants has dealt with systems which require alcohol or some other cosurfactant and/or salt for their formation and stability. An exception is work<sup>(12,13)</sup> on the anionic surfactant sodium di-ethylhexyl sulphosuccinate (AOT). The use of cosurfactant (or equivalently mixtures of double and single chained surfactants) injects considerable flexibility in inducing changes in structure. Cosurfactants provide an easy route to properties of interest like low surface tension. However there is no theoretical requirement for cosurfactant in general.<sup>(8)</sup> Further, experimental and theoretical difficulties associated with the manipulation of a four and (with salt) five component system pose formidable obstacles to progress. This circumstance provides a strong motivation for a search for other three component ionic systems. Ideally one requires an easily purified surfactant which admits the possibility of systematic studies of oil, cationic or anionic, and solvent specificity. An additional ideal requirement is that the surfactant head group be small so that attention can be focussed on the role of electrostatic curvature<sup>(14)</sup> effects due to salt in low surface tension phenomena.

We here report some preliminary results on three component cationic microemulsions which satisfy these requirements. The system forms spontaneous microemulsions at room temperature, is reversible to temperature cycles, and is apparently stable based on observation, for several months in northern and southern hemispheres.

A necessary, but not sufficient, elementary design characteristic<sup>(8)</sup> is that the surfactant hydrocarbon volume  $v$ , effective length  $l_c$  (in the presence of oil), and head group area  $a_o$  in a bilayer configuration

satisfy  $v/a \cdot l_c = 1$ . We have chosen for most of our work the surfactant didodecyldimethylammonium bromide  $((C_{12})_2DAB)$ .

## 2. EXPERIMENTAL

Two samples of  $(C_{12})_2DAB$  were used. The first was synthesized from dimethyldodecylamine and 1-bromododecane, twice recrystallized from ethyl acetate and dried in a vacuum oven at 50°C. The second sample was purchased from Eastman Kodak, dissolved in acetone, filtered through a fine fritted glass filter to remove particulate matter, precipitated from ether, recrystallized from ethyl acetate and dried in a vacuum oven. In order to check for purity, NMR N-methyl spectra (Nicolet N-T 300) of samples of the surfactant in deuterobenzene with and without added dimethyldodecylamine were measured. The complete absence in the surfactant sample of the sharp methyl amine peak (which is displaced from the broad quaternary ammonium methyl peak) established that amine impurities were less than 0.03 mole%. Infrared analysis of a surfactant-KBr pellet gave no detectable evidence for either N-H or O-H bonds.

The hydrocarbon oils were Aldrich Chemical Company gold label quality (filtered, doubly distilled). We have investigated the behavior of systems containing the oils cyclohexane, toluene, and the even numbered n-alkanes hexane through hexadecane. The microemulsions were usually prepared by titrating a well stirred mixture of oil and surfactant with water until a clear solution was obtained. The resulting microemulsions were characterized by visual inspection, microscopy in a polarizing microscope, quasi-elastic light scattering, x-ray analysis, viscosity and conductivity measurements. We were unable to form microemulsions with toluene.

We have also carried out preliminary measurements using the unsymmetrical dialkyldimethylammonium compounds  $C_{10}C_{12}$  DAB and  $C_8C_{12}$  DAB. These surfactants exhibit similar behavior, to that of the symmetrical surfactant. However their purification poses difficulties which have been addressed by Zana.<sup>(15)</sup>

## RESULTS

We list below examples of typical preparations which demonstrate the diversity of microemulsion properties which can be obtained.

Hexane. Addition of 0.25 ml of water to a stirred suspension containing 0.5 g surfactant and 5 ml of  $C_6H_{14}$  yields a clear solution. Beyond about 0.3 ml of water the solution becomes turbid and upon standing a water phase containing surfactant debris separates. Addition of more surfactant clears the solution. The stable one-phase microemulsion can be diluted with oil. At minimum water content the microemulsion is highly viscous, reminiscent of cubic phase microemulsions, becoming less viscous on further addition of water. The system is conducting even at lowest water content, and appears to have a critical temperature close to 20°C. Cyclohexane also forms microemulsions.

Octane. Similar to hexane. However the minimum water content is higher for the one phase system, and the volume fractions of water to oil over which the microemulsion exists is extended.

Decane. (a) A clear freely flowing phase is obtained when 1.2-2 ml of water are added to 5 ml of  $C_{10}H_{22}$  and 0.5 g surfactant. Excess surfactant results in a separation into two clear phases with a flat meniscus between them. A solution containing 2 ml of water can be diluted by at least a factor of ten with oil.

(b) With 0.47 g ( $\approx 10^{-3}$  Moles) surfactant and 2.5 ml decane, a single clear viscous phase appears at 0.4 ml  $H_2O$ , gradually tending towards characteristic middle phase bluish hued solution up to addition of 2.5 ml of water where phase separation occurs.

(c) With 0.47 g surfactant and 5 ml decane, the surfactant can be solubilized on heating to 50-60°C. Minimum water content for onset of a clear stable viscous phase is about 0.5 ml of  $H_2O$ , half that required for preparation (a). These decane phases studied are non-conducting.

Some preparations exhibit extraordinary viscosity. E.g. a 50/50 mixture of surfactant and decane diluted with water becomes one phase at 15% water content and increases in viscosity until at 63% water content the still clear microemulsion is a rigid gel.

Tetradecane. Over a narrow range of surfactant-water ratios tetradecane forms a clear bluish single phase, and at higher water/surfactant ratios two phases appear, the upper clear, and the lower clear blue. In the range  $\sim 28-45^\circ C$ , the upper phase disappears.

Single phase regions of the phase diagram are reminiscent of the aerosol-O-T, p-Xylene, water system. <sup>(6)</sup>

Dodecane. Dodecane is intermediate in behavior between decane and tetradecane, forms colorless, single phase microemulsions over a narrower water range, than the former, and wider than the latter.

Hexadecane. We were unable to form a single phase microemulsion. However two phase systems are easily formed. Mixtures of hexadecane and decane in excess, and/or decane with added salt and surfactant gave three phase systems. The meniscus between upper and middle phases is quite flat. In the only sample tried, we were able to remove the middle phase for characterization by QELS, and it remains stable. The meniscus is here clearly of very low surface tension. All microemulsions reported exhibit

an upper consolute point on heating to  $\sim 60^{\circ}\text{C}$ , become cloudy, but rapidly clear again on cooling. All lower phases were examined for liquid crystals and no birefringence was found.

Preliminary measurements using QELS, x-ray analysis and viscosity measurements give the results listed in Table 1.

The "radii" obtained in these three component systems are comparable to or much larger than those reported on more complex microemulsions. X-ray data for hexane cannot be interpreted in terms of water-in-oil spheres as the data indicate extreme polydispersity if such a model is adopted. Decane and dodecane samples could be consistent with monodisperse water-in-oil spheres. The QELS scattering data for hexane and octane are completely inconsistent with any picture involving small water-in-oil spheres, as would have been expected for such small volume fractions. This is evident from elementary geometric considerations. <sup>(8)</sup>

Those viscosity measurements reported do seem to indicate a correlation between the number of water molecules/surfactant molecule and viscosity. Microemulsions of low w/s ratios appear to have very high viscosities ( $\sim 50$  times bulk oil values at 5% w/o). The viscosities decrease to "normal" values compatible with the Einstein equation once "bound" water requirements of the surfactant molecules are satisfied.

Hexane data might well be consistent with a structure reminiscent of cubic phase, or some bicontinuous phase, with thin water sheets separating two surfactant head group layers. In any event these microemulsions do not admit an easy interpretation (see e.g. Kaler and Prager<sup>(16)</sup>). In the higher oils the observed behavior is reasonably consistent with large water-in-oil drops with maximum uptake of water dictated by close packing. <sup>(8)</sup>



## DISCUSSION

$(C_{12})_2$  DAB forms unilamellar vesicles on sonication in water.<sup>(17,18)</sup> These are stable for some months. Hence the surfactant parameter satisfies the principal requirement  $1/2 < v/a_o l_c < 1$ . This can easily be verified by calculation ( $v \sim 800\text{\AA}^3$ ,  $a_o =$  typically  $50\text{\AA}^2$ ,  $l_c = 16\text{\AA}$  (maximum)). Theoretical and experimental studies of lecithin bilayers establish<sup>(19,20)</sup> that alkanes can penetrate amongst surfactant chains. The area per head group does not change on uptake of hydrocarbon. Hence the volume per surfactant increases. The degree of penetration is a maximum for smaller alkanes, decreasing quite sharply when the alkane chain length exceeds that of the surfactant. We would expect that in the presence of hexane  $v/a_o l_c$  increases to around 1.5-2, decreasing towards and below unity for tetradecane and hexadecane. Such correlations have already been observed for non-ionic microemulsions.<sup>(8)</sup> Elementary theoretical expectations are then that inverse structures are formed for hexane and octane with smaller water uptake than for decane and dodecane. For decane the very wide variation of possible water to oil ratios confirms the expected compatibility of this hydrocarbon and the surfactant. Oil penetration decreases rapidly for higher chains, so that normal, rather than inverse structures are preferred for tetradecane and hexadecane. With changes of counterion, and ionic strength it is possible to dictate the forces operating and reduce or enhance forces due to associated water structure and double layer effects<sup>(21)</sup> so that collapse to a lamellar state is not allowed. We remark in passing that the nature of the anion affects both micellar and microemulsion behavior quite dramatically. We shall report on these aspects in later publications.

TABLE I

Characteristics of microemulsions

oil (5ml)	$\frac{\text{moles water}}{\text{moles surfactant}}$	5-6% water/oil dilutions		H <sub>2</sub> O(ml)	Hydrodynamic radii $r_h$ (A) 25°C	35°C	"radii" of gyration (A)	viscosity centi-poise	conductance
		surfactant(g)	MW = 460						
hexane	14	.55	0.30	200	130	29A	14(25°) (polydisperse)	conducting	
octane	15	.42	0.25	300	195	-	8.5(35°)	-	
decane	54	.12	0.25	105	105	-	-	nc	
decane	28	.26	0.30	200	135	68	6(25°) 3.9(35°)	nc	
dodecane	21	.36	0.29	42	40	74	-	-	

Higher water/oil ratios for hexane, decane, tetradecane gave  $r_h$  values of 246A, 127A and 622A respectively.

At 35°C, tetradecane value was 196A. 50/50 ratios of decane-water microemulsions are not conducting.

Note that some of these data are certainly not consistent with simple geometric interpretations such as spheres in a continuum.

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