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MICELLE FORMATION UNDER UNUSUAL CONDITIONS AND
OPTIMIZING SOLUBILIZATION IN MICELLAR SOLUTIONS(U)
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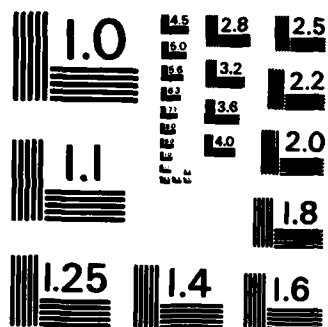
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20. ABSTRACT (Continue on reverse side if necessary and identify by block number) 1. Spontaneous thermodynamically stable vesicles were discovered. 2. Simple three-component microemulsions were formulated and their properties described. 3. Video enhanced contrast differential interference microscopy was applied for the first time to the characterization of colloidal material. 4. Micelle and liquid crystal formations were documented in ethylammonium nitrate and hydrazine and used to reinterpet hydrophobic effects in aqueous solution.		

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MICELLE FORMATION UNDER UNUSUAL CONDITIONS
AND OPTIMIZING SOLUBILIZATION IN MICELLAR SOLUTIONS

Final Report

D. Fennell Evans

August 28, 1984

U.S. Army Research Office

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DAAG-81-K-0099

University of Minnesota

A. STATEMENT OF THE PROBLEM STUDIED:

1. Spontaneous thermodynamically stable vesicles were discovered.
2. Simple three-component microemulsions were formulated and their properties described.
3. Video enhanced contrast differential interference microscopy was applied for the first time to the characterization of colloidal material.
4. Micelle and liquid crystal formations were documented in ethylammonium nitrate and hydrazine and used to reinterpret hydrophobic effects in aqueous solution.

B. SUMMARY OF THE MOST IMPORTANT RESULTS:

1. Spontaneously Formed Vesicles

Lecithin and dialkyldimethylammonium halides [12] form lamellar liquid crystalline phases upon contact with water. Upon sonification these compounds form vesicles, which always revert back to the lamellar form from which they emerged. The inability to form stable vesicles has been an inhibition in the use of these microstructures in controlled drug delivery, in photocatalysis and as models for biological membranes. There has been some debate as to whether vesicles can ever be stable.

We found that dilute solutions (10^{-3} to 10^{-4} M) of didodecyldimethylammonium hydroxide (DDAOH) spontaneously form vesicles, as demonstrated by VECDIM [4], QELS [13] and electron microscopy [14]. These vesicles are recovered after freeze-thaw cycles. The difference in the behavior of the halides and hydroxide results from how they affect surfactant aggregate curvature. Unlike the halide ions which nestle amongst the surfactant head groups, the extremely hydrophilic hydroxide sits away from the aggregate surface (model calculations indicate an average separation of 4Å) [15]. This produces an increased repulsion between the charged head groups and induces curvature. This explanation is consistent with our study of the single chain alkyltrimethylammonium hydroxides. The CMC's are twice as large as for the corresponding bromide reflecting increased surfactant head group repulsion. The aggregation numbers are only one-half as large as for the bromides reflecting increased curvature. Addition of acid to the dialkyl hydroxide vesicles results in a decrease of curvature with a corresponding increase in vesicle size. Complete neutralization results in the eventual formation of a lamellar phase, but the process can be slow requiring days or weeks.

More concentrated solutions of DDAOH (up to 0.2 M) are also clear, but vesicles are not found. Instead micelles with aggregation numbers of 45 are detected using the double exponential fluorescence lifetime technique. These results suggest an equilibrium between micelles and vesicles which is surprisingly rapidly attained (~60 sec) for DDAOH. This type of equilibrium is unusual because it involves aggregate size decreasing with increasing surfactant concentration. One of the goals of this research is to characterize the nature of this type of equilibrium.

The addition of salt generally causes surfactant aggregates to become larger and to eventually form gels or liquid crystalline phases. Upon addition of up to 0.5 M of sodium hydroxide, the DDAOH vesicular solutions remain clear with no evidence of large structures. This suggests new strategies for controlling spontane-



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ous microstructural aggregation.

We have found that a surprising range of dialkyldimethylammonium salts including carboxylate (formate through butyrate), fluoride, glycerate, tartrate and oxalate form vesicles with surprising ease. The micelle-vesicle equilibrium is evident in these systems; an initial estimate of the micelle aggregation number for 0.1 M DDAOAC is 80. Our subjective impression based on VECDIM results is that these vesicles are not formed as easily as the hydroxides. This suggests to us that there is a continuum in vesicle stability and ease of formation. At one end of the spectrum are the vesicles formed from lecithin, but only by sonication. At the other end are the hydroxides. We plan to explore this hypothesis in more detail in the proposed research.

2. Three-Component Microemulsions

Microemulsions are used industrially where clear, transparent stable mixtures of oil and water of relatively low viscosity are desired (examples include food preparations, cosmetics, detergents, waxes, etc.). Microemulsions often have very low interfacial tensions against brine and oil rich phases and thus have possible importance in enhanced oil recovery. Microemulsions are typically composed of four or five components, oil, water; surfactant, a cosurfactant and sometimes salt. These systems are complex and much remains to be done to understand their behavior.

We have found that three-component microemulsions can be prepared using didodecyldimethylammonium bromide as the surfactant [17]. This surfactant is insoluble in both oil and water and thus is located at the oil-water interface. This is an important design feature since it means that the oil-water interface area is set by the surfactant concentration. It is a simplifying factor in understanding the behavior of these systems and consequently offers many advantages over the more widely studied aerosol AOT three-component system.

These microemulsions [18] show a number of unusual features: (i) there is considerable oil specificity (Fig. 6, the A-B lines mark initial formation of microemulsion upon addition of water); with hexane clear solutions are obtained upon addition of 4 volume % water (96% surfactant and oil) while for tetradecane 25% water is necessary. With the corresponding alkenes only $\sim 1/2$ as much water is required to form single-phase microemulsions. (ii) upon addition of more water (Fig. 6, lines CD) the conductance decreases by many orders of magnitude (Fig. 7), exhibits a percolation threshold (bicontinuous phases) and the microemulsion becomes oil continuous; still more water results in the formation of birefringent gels. If one follows the conductance down the AB lines of Fig. 6, the system remains conducting until just before the point designated B where the conductance rapidly decreases to the values characteristic of the oils. The tetradecane system is an exception to this behavior, it remains water continuous at all compositions studied (Fig. 7). (iii) along the AB lines the viscosities of the microemulsions are high. For example, the viscosity of the hexane microemulsion at point C is 70 times larger than the neat oil. Upon addition of water the viscosity decreases, goes through a minimum at point B (the percolation threshold) and subsequently increases.

NMR diffusion measurements give diffusion coefficients for surfactant and oil which are independent of concentration in the single microemulsion region. Thus,

the oil phase is always continuous. Diffusion coefficients for water decrease by a factor of twenty along the CD, C'D" lines indicated in Fig. 6 for all oils except tetradecane which remains virtually constant. The conductance and diffusion behavior is consistent and provides evidence for the formation of water discontinuous systems upon addition of water (a counterintuitive finding and an extreme departure from generalizations obtained from other microemulsion systems).

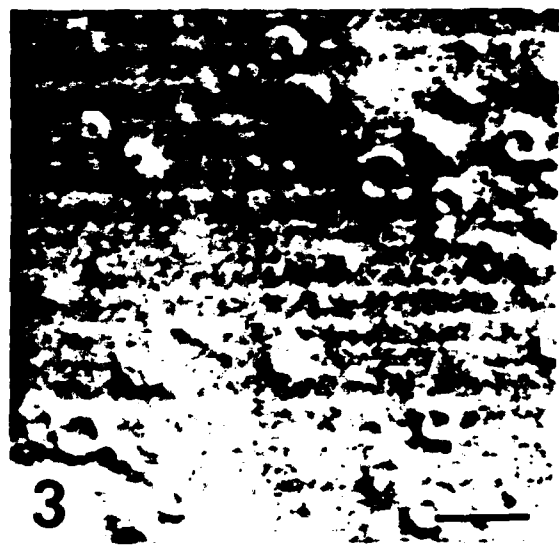
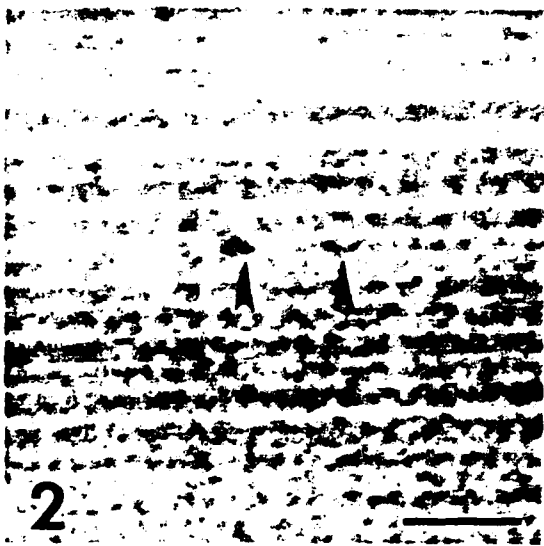
We believe that the microemulsion structures most consistent with these observations are as follows. Along the A down to just above the B, the microemulsions are bicontinuous. We envision the conducting water paths in this bicontinuous system in terms of chaotic interconnected conduits which are dynamic in nature. For hexane, the large value of v (high oil penetration) and the small value of a_0 (high bromide concentration in the water phase, Table I) results in conduits of small diameter ($v/\lambda_{ca_0} < 1$). The average conduit diameter can be roughly estimated as follows. If we assume that all of the surfactant is located at the oil-water interface with $a_0 = 40\text{\AA}^2$, the total oil-water interfacial area for 1 cm^3 of the hexane microemulsion (Table I, solution C) is $1.5 \times 10^6\text{ cm}^2$. The total volume of enclosed water plus bromide is 0.095 cm^3 if we assume $V(\text{Br}^-) = 2V(\text{H}_2\text{O})$. This gives an average conduit diameter of $\approx 25\text{\AA}$ and a total conduit length of 10^{12} cm . Addition of more water disrupts phase interconnected conduits. At a critical water concentration (point D, Fig. 2), the conducting paths have completely disappeared (percolation threshold) and water droplets immersed in oil result. As the chain length of the oil increases, more water must be added to obtain conduits with the minimum diameter compatible with the curvature dictated by the oil penetration. Notice that for each of the oils the percolation threshold points D, D', D" and B lie on almost a straight line. Extrapolation of this line to the w/s lines of Fig. 2 give estimates of the ratio of water to surfactant (specific for each oil) at which the system is completely converted to water spheres in an oil continuum. Within increasing oil chain length, the w/s ratio increases.

The reason for the lack of a percolation threshold with tetradecane can be understood. If one takes the w/s ratio = 0.20 for dodecane and places this line on the tetradecane phase diagram, it lies below the limit of the one phase microemulsion region. Thus, the tetradecane system always consists of conducting water conduits.

3. Application of VECDIM to Characterization of Microemulsions

To illustrate the power of VECDIM, we show pictures on p. 4a (published in the Journal of Colloid and Interface Science 100, 287 (1984)) of latex spheres, vesicles, liposomes (liquid (liquid crystallites) and microemulsion debris [4,5]. The total magnification of the images given in the figure is 15,000X (the bar length in these figures = 20,000Å). The depth of field contained in an optical section is 2000Å and the square microscope field is $200 \times 200\text{ }\mu\text{m}$. It is important to realize that no still photograph can convey the quality of images of the particle dynamics seen on the T.V. screen.

The monodisperse latex spheres ($D = 2,300\text{\AA}$) are seen as rapidly moving due to a combination of Brownian motion and convection and give rise to the blurred images seen in Fig. 1. We also have pictures of latex spheres, $D = 800\text{\AA}$. The vesicles which form spontaneously from didodecyldimethylammonium hydroxide are smaller



and more difficult to see on a still photograph (Fig. 2). The growth of these vesicles upon neutralization with hydrobromic acid (Fig. 3) and their transition to microtubules can be followed directly and in real time. The slow dynamics of liposomes (having the expected structure of Dupin cyclides) formed from SHBS (sodium 4(1'-heptylnonyl)benzenesulfonate) have been observed (Fig. 4). The kinetics of liquid crystal bilayer formation upon destabilization of small spherulites of SHBS liquid crystals (acid form) upon addition of calcium chloride can be followed; as a dramatic illustration of the VECDIM technique, we made a 10 minute sequence in which vesicles and microtubules form, shrink, and fuse and then explode into liquid crystals, eventually ending up as large birefringent liquid crystalline debris attached to the microscope slide. The liquid crystalline structures resulting from decomposition of a three component microemulsion (didodecyltrimethylammonium bromide, tetradecane and water) made unstable by filtration are shown in Fig. 5. The pictures shown in Figs. 1-5 were selected from 8 hours of video tape which represent the characterization of over 120 samples. The tape was made during a two-day visit at the NIH lab. The study demonstrates the power of the VECDIM technique and represents the first application to the study of non-biological structures.

The motivation for developing this technique is that it is a powerful new tool for characterizing colloidal microstructure. While it will not replace other physicochemical methods, it complements them and by allowing direct visualization represents a significant advance.

In contrast, traditional physicochemical methods are slow and often indirect. Light scattering (both classical and QELS), low angle x-ray scattering, sedimentation, and viscosity measurements all require theoretical models to relate the measured variables to aggregate structure. Electron microscopy permits structures to be directly visualized, but requires extreme sample modification such as metal shadow casting, chemical fixation or thermal fixation with examination at liquid nitrogen temperatures. The information obtained by all of these techniques allows only an averaged static representation of microstructure to be inferred. Polydispersity presents a severe complication in interpretation of experimental measurements. The relationship between structure and reactivity remains obscure. When combined with emerging theories of mechanisms and types of microstructure described below, VECDIM will appreciably enhance our understanding of biological processes and our ability to design and control microstructures for practical applications.

4. Origins of Hydrophobic Effects in Water

In the classic paper on hydrophobic hydration by Frank and Evans [22], the thermodynamics of transfer of rare gases and hydrocarbons from the vapor phase to water were analyzed. An example is given in Table I (line 3) for the transfer of argon to water from cyclohexane, which is used as a reference solvent instead of the vapor phase. Frank and Evans attributed the surprising enthalpy and entropy changes to an increase of structured water around nonpolar groups. As applied to microstructure formation, this approach leads to the conclusion that an important driving force for aggregation is the release of structured water from around the surfactant hydrocarbon chain upon association. It is the juxtaposition of the enthalpy-entropy behavior in water compared to other solvents that appears to make water completely different.

TABLE I
THERMODYNAMIC FUNCTION FOR TRANSFER OF ONE MOLE OF ARGON
FROM CYCLOHEXANE TO WATER AND TO HYDRAZINE

STEP	ΔG^0 (Kcal mol ⁻¹)	ΔH^0 (Kcal mol ⁻¹)	ΔS^0 (Kcal mol ⁻¹ deg ⁻¹)
(1) Ar($X_2=1$ in C ₆ H ₁₂) = Ar($X_2=1$ in H ₄ N ₂)	2.84	2.27	-1.9
(2) Ar($X_2=1$ in H ₄ N ₂) = Ar($X_2=1$ in H ₂ O)	-0.36	-4.95	-15.4
(3) Ar($X_2=1$ in C ₆ H ₁₂) = Ar($X_2=1$ in H ₂ O)	2.48	-2.68	-17.3

TABLE II COMPARISON OF HYDRAZINE AND WATER		
Property	N ₂ H ₄	H ₂ O
M.P. (°C)	1.69	0.00
B.P. (°C)	113.5	100.0
T _c (°C)	380	374.2
P _c (atm)	145	218.3
Density (25°C, g cm ⁻³)	1.0036	0.9971
η (25°C, cp)	.905	.890
γ (25°C, dyn cm ⁻¹)	66.67	72.0
ΔH_f (M.P., cal mol ⁻¹)	3025	1440
ΔS_f (M.P., cal mol ⁻¹)	11	5.3
ΔH_{vap} (BP, cal mol ⁻¹)	9760	9720
ΔS_{vap} (BP, gbs mol ⁻¹)	25.2	26.1
M (gas, Debye)	1.85	1.85
ϵ (25°C)	51.7	78.3
n_D	1.4644	1.3325
C _p (liq, cal mol ⁻¹ K ⁻¹)	23.62	17.98
C _p (S, cal mol ⁻¹ K ⁻¹)	15.3	8.9

An alternative interpretation of the origin of hydrophobic effects in water has recently been proposed by Frank. He suggested that the transfer process shown in Table I, line 3 be divided into two steps. The first step, consists of transferring argon into water which is an "inhibited" state. This can be viewed as the equivalent of making a hole in water, inserting the argon, but preventing the water from reorienting or responding to the presence of the nonpolar group. In the second set, the restrictions on inhibited water are relaxed.

Frank suggested that hydrazine be used as a model for inhibited water. In Table II, the physical properties of hydrazine and water are compared. There is a remarkable similarity between the two pure liquids [23]. Densities, melting and boiling points, entropy and enthalpy of vaporization are nearly identical. Other properties such as molar expansivity, although quite different at low temperatures ($H_4N_2 = 2.57 \times 10^{-4} \text{ K}^{-1}$ and $H_2O = 8.93 \times 10^{-4} \text{ K}^{-1}$, 25°C), become very similar even at only moderately high temperatures ($H_4N_2 = 1.03 \times 10^{-3} \text{ K}^{-1}$ and $H_2O = 1.14 \times 10^{-3} \text{ K}^{-1}$, 150°C).

Water and hydrazine differ dramatically at lower temperatures in just those properties which are abnormal for water. Hydrazine has no volume decrease on melting, no temperature of maximum density, no compressibility maximum at least to 80°C. The unusual

behavior of the expansivity is absent in hydrazine and the heat capacity per atom at lower temperatures is about one-half of the value for water. The differences reflect one or more unusual features of water which are generally attributed to the high degree of three-dimensional order available to water, but not to hydrazine. These similarities and differences suggest that hydrazine can be viewed as a "nonaqueous or inhibited water" in the sense that it has all the important properties of water except the ability to promote structure around hydrocarbon or other non polar groups.

TABLE III
THERMODYNAMICS OF MICELLE FORMATION IN HYDRAZINE AND WATER

	Surfactant	T	N	ΔG_{HP}	ΔH	ΔS
Hydrazine	C ₁₂ OSO ₃ Na	35	60	8.6	-14	-18
	C ₁₂ TAB	35	45	7.0	-11	-13
H ₂ O	C ₁₄ TAB	25	70	-10.5	- 3	25
		54	60	-11.1	- 5.6	16
		95	50	-11.5	-12.4	- 3
		135	30	-11.1	-15.6	-11
		166	20	-10.6	-15.6	-12

As can be seen from Table I (line 1), the transfer of argon from cyclohexane to hydrazine has an unfavorable free energy resulting from a large positive enthalpy and a negligible entropy. The enthalpy can be associated with the energetics of creating a cavity in a polar medium. In the second step, the restraints on "inhibited" water are removed and water reorganizes around the argon molecules. This corresponds to the transfer of argon from hydrazine to water (Table I, line 2). The free energy for this process is small and negative. However, the changes in enthalpy and entropy are large and negative and almost completely compensated.

Thus, the unfavorable free energy associated with the transfer of argon from cyclohexane to water can be interpreted in two alternative ways. Using only step 3, one focuses on the large negative entropy. Using steps 1 and 2, the free energy in step 3 is dominated by step 1 and is attributed to the large positive enthalpy change.

The Gibbs energy for transfer of argon from hydrazine to water varies with temperature from -660 to 60 cal/mole. The negative free energies at the lower temperature suggest that the solubility of argon, and by inference other nonpolar groups, is actually increased as the consequence of the water-nonpolar interactions. Shinoda [24], reached the same conclusion from an analysis of the solubility of hydrocarbons and alcohols in water over an extended temperature range. At high temperatures, plots of $\ln X_{\text{solute}}$ vs. $1/T$ give straight lines which when extrapolated to room temperature gave predicted solubilities which are a factor of 3 or 4 times too low.

(1) Micelles in hot water and in other solvophobic solvents. The idea implicit in Table I suggested to us the usefulness of characterizing "hydrophobic" processes in water over an extended temperature range and in other polar solvents. We have determined the CMC of the alkyltrimethylammonium bromides in water up to 160°C [25,26] and of surfactant in hydrazine at 25, 35 and 45°C [23]. We have obtained the thermodynamics of transferring the surfactant hydrocarbon chain from the solvent to the oil-like interior of the micelle using eq. (1-3) [15]. The change in ΔG_{HP} for C₁₄TAB with temperature (25 to 166°C) and the relative contribution of g_s and $RT\ln X_{CMC}$ are shown in Fig. 8, on page 9. The maximum at 95°C in ΔG_{HP} indicates a minimum in the solubility of the hydrocarbon chain in water.

The entropy and enthalpy associated with micelle formation in H₂O and H₄N₂ are strikingly different while the Gibbs energies are similar. In hydrazine, the enthalpy change is large and negative and reflects the ordering accompanying the transfer of surfactant tail to the confines of the micelle. Thus the formation of micelles in hydrazine is entirely a consequence of favorable energy change.

In water at low temperatures, the enthalpy changes are considerably less negative than those observed for hydrazine, and the entropy changes are large and positive. Clearly, the entropy change accompanying micelle formation in water must be a composite of two processes which parallel that given in Table I. In the first process, a large positive entropy change accompanies the removal of structured water from around the hydrocarbon chain. In the second, a large negative enthalpy change accompanies the transfer of surfactant to the micelle. This second step is analogous to what is seen in hydrazine for micelles. The enthalpy change must also be the sum of these two processes with opposite signs. The removal of structured water will be endothermic and the transfer of hydrocarbon out of water will be exothermic. The results for water at high temperatures are similar to those determined for hydrazine at room temperature.

We have also continued an investigation of hydrophobic processes in ethylammonium nitrate, a low melting fused salt [27,28]. We have obtained micelle aggregation numbers (first data on a solvent other than water) [29], characterized liquid crystals [30] in EAN and investigated enzyme activity in EAN-H₂O mixtures [31]. The aggregation numbers for micelles in EAN are only 1/3 of those obtained for the same surfactants in water. There are two possible interpretations of this result, either small classical micelles are formed or else mixed micelles are formed in which the ethylammonium ion is incorporated into the micelle as a cosurfactant. In this concentrated salt solution (11 M) coulombic repulsion between the cationic surfactants and the ethylammonium ion at the micelle surface would be negligible.

We have just completed precise density and heat capacity measurements on EAN-H₂O mixtures and are preparing a manuscript for publication. Plots of density and heat capacity vs. X_{EAN} are surprisingly linear across the composition range. Considering the components involved, we find the boring nature of the results extraordinary.

C. LIST OF ALL PUBLICATIONS

1. VECDIM

"Rapid Characterization of Colloidal Systems by Video Enhanced Light Microscopy," B. Kachar, D. F. Evans, and B. W. Ninham, J. Colloid & Interf. Sci. **99**, 593 (1984).

A new microscopy technique, Video Enhanced Contrast-Differential Interference Contrast Microscopy, is used to characterize colloidal systems by direct visualization on a T.V. screen. This method allows rapid characterization of colloidal surfactant aggregates and other macromolecules in the size range 500-10,000Å and offers a number of advantages over classical methods.

"Video Enhanced Contrast Differential Interference Microscopy, A New Tool for the Study of Association Colloids and Pre-biotic Assemblies," B. Kachar, D. F. Evans and B. W. Ninham, J. Colloid & Interface Sci. **100**, 287 (1984).

Progress in our understanding of molecular forces enables some rules to be formulated for design of surfactant systems. Competition between electrostatic and hydration head group forces, hydrocarbon chain interactions, associated oil penetrability, and interaggregate forces can be put to work to dictate prescribed curvature and other properties of association colloids. Such aggregates can be visualized directly and quickly by a new light microscopy technique. The power of this technique which complements QELS, neutron scattering, electron microscopy and other methods is illustrated by a study on several surfactant-water systems.

2. Relation between Surfactant Structure and Aggregation Size and Shape

"Spontaneous Vesicles Formed from Hydroxide Surfactants — Evidence from Electron Microscopy," Y. Talmon, D. F. Evans, and B. W. Ninham, Science **221**, 1047 (1983).

Dialkyldimethylammonium hydroxide surfactants are highly soluble in water and form spontaneous stable vesicles. These vesicles can be grown to size with added acid, and appear to provide an ideal analogue membrane mimetic system for the study of fusion and ion transport. The existence of these phenomena is a consequence of strong hydration forces, not necessarily limited to the hydroxide ions. These forces can be put to work to design a variety of model systems. The observations are in direct contrast to the behavior exhibited by most double chained surfactants whether natural lipids or manufactured ionic compounds like didodecyldimethylammonium bromides which form insoluble liquid crystalline phases in water, and unstable vesicle suspensions on prolonged sonication.

"The Curious World of Hydroxide Surfactants: Spontaneous Vesicles and Anomalous Micelles," B. W. Ninham, D. F. Evans and G. J. Wei, J. Phys. Chem. **87**, 4538 (1983).

Double chained cationic surfactants typified by didodecyldimethylammonium bromide are insoluble in water, forming lamellar liquid crystal phases. They form vesicles only on prolonged sonication. If the halide ion is replaced by a hydrox-

ide, the resulting surfactants are highly soluble and form spontaneously a clear solution which appears to comprise a mixture of small micelles and fairly monodisperse vesicles. The distribution of particle size changes with added base or with partial titration with acid (HBr, HCl, HF) which can sometimes yield vesicles with an initially unsymmetric distribution of anions. Evidence for these structures from quasi-elastic light scattering and viscosity measurements and an account of their extraordinary properties is presented.

"Unusual Behavior of Hydroxide Surfactants," S. Hashimoto, J. K. Thomas, D. F. Evans, S. Mukherjee and B. W. Ninham, J. Colloid & Interface Sci. **95**, 594 (1983).

Critical micelle concentrations, aggregation numbers, and degree of ion binding are reported for the single-chained surfactant tetradecyltrimethylammonium hydroxide in the presence of excess sodium hydroxide. Contrary to the usual structures with bromides or chlorides, where micelles undergo a rapid increase in size with added counterions, hydroxide micelles remain substantially unchanged up to high salt. The results indicate the existence of, and quantify, strong hydration forces associated with the hydroxide radical at a micellar surface which are also observed with corresponding double-chained vesicle-forming hydroxides.

"Spontaneous Vesicles" J. E. Brady, D. F. Evans, B. Kachar and B. W. Ninham, J. Amer. Chem. Soc. **106**, 4279 (1984).

Video Enhanced Differential Interference Contrast Microscopy (VEDICM) confirms spontaneous vesicle formation by a wide range of didodecyldimethylammonium salts. Didodecyldimethylammonium (DDA) fluoride, formate, acetate, propionate, butyrate, glycinate, acrylate, tartarate (dianion), and oxalate (dianion) yield clear, isotropic, low to moderate viscosity solutions to at least 0.1 M. VEDICM reveals vesicle formation by the fluoride and carboxylate surfactants at 10^{-5} to 10^{-3} M surfactant concentration. Spontaneous vesicle formation by DDA glycinate, tartarate (-2), and oxalate (-2) is anticipated. DDA acrylate vesicles are polymerizable (via addition of H_2O_2) to yield polymer stabilized vesicles. Sonication prior to polymerization does not appear to influence vesicle size. DDA trifluoroacetate, trichloroacetate, bromoacetate, benzoate, octanoate, oxalate (monoanion) and perfluorobutyrate yield cloudy solutions (bilayer dispersions) at 10^{-5} to 10^{-3} M. With the exceptions of DDA benzoate and DDA octanoate the vesicle forming surfactants are the DDA salts of weak acids (pK_a 3.4-9.8).

"Three Component Ionic Microemulsions," L. R. Angel, D. F. Evans and B. W. Ninham, J. Phys. Chem., **87**, 538 (1983).

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.

"Properties and Structure of Three-Component Ionic Microemulsions," S. J. Chen, D. F. Evans and B. W. Ninham, J. Phys. Chem. **88**, 1631 (1984).

Partial phase diagrams, conductivity and viscosity of cationic microemulsions, formed from didodecyldimethylammonium bromide in various alkanes with water are reported. In the one-phase region the microemulsions are conducting at low water content, and exhibit a percolation type transition to a nonconducting state with increasing water. Parallel behavior is exhibited by the viscosity of these systems. At very high water content the one phase system becomes a rigid gel. The behavior is virtually the obverse of that usually observed for microemulsions which require cosurfactant, and shows that the distinction between microemulsions and emulsions is tenuous. A high and systematic degree of oil specificity is observed. The data are analyzed and are consistent with simple pictures of microemulsion structure based on mainly geometric considerations. Characteristic sizes ranging from 50Å up to 2000-5000Å can be achieved.

"Structure and Dynamics in Three-Component Microemulsions," F. D. Blum, S. Pickup, B. Ninham, S. J. Chen and D. F. Evans, J. Phys. Chem., accepted.

NMR self-diffusion coefficients are reported for three-component microemulsions formed from didodecyldimethylammonium bromide/water/alkane. For hexane through tetradecane the oil diffusion coefficients are approximately half as large as those of the bulk oils and independent of composition. Therefore the systems are oil continuous through the entire one-phase region. The diffusion coefficients for the surfactant are small and independent of composition. The water self-diffusion coefficients decrease with added water for hexane through dodecane, and change in a manner consistent with the abrupt conducting-nonconducting transition, known to occur in this system. The microemulsions are bicontinuous in the conducting region, and disconnected water-in-oil droplets in the nonconducting region of the phase diagram. The phenomena reported clearly demonstrate the interplay between forces due to oil penetration and those due to head group interactions which control curvature and therefore microemulsion structure.

"Roles of Oils and Other Factors in Microemulsion Design," B. W. Ninham, S. J. Chen and D. F. Evans, J. Phys. Chem., accepted.

The role of oils in prescribing microemulsion formation and structure is illustrated by a comparison of three-component microemulsions formed from water, the double-chained surfactant didodecyldimethylammonium bromide, and alkanes or alkenes. The alkenes (1-hexene through 1-tetradecene) form water continuous microemulsions at a considerably lower water (~3% for hexene) than the corresponding alkanes.

3. Origin of Hydrophobic Effects

"Liquid Crystals in a Fused Salt: β,γ -Distearoyl Phosphatidylcholine in Ethylammonium Nitrate," D. F. Evans, E. W. Kaler and W. J. Benton, J. Phys. Chem. **87**, 533 (1983).

The formation of liquid crystals of β,γ -distearoylphosphatidylcholine (DSPC) in N-ethylammonium nitrate, a low-melting fused salt, has been documented with polarizing microscopy and small-angle X-ray scattering. The $L_{\beta'} \rightarrow P_{\beta'} \rightarrow L_{\alpha}$ transitions with increasing temperature are present in analogy with the behavior of DSPC in water. For a 1:1 (by weight) mixture the d spacing for the L_{α} phase is 63Å and the surfactant head group area is 76Å².

"Micelle Size in Ethylammonium Nitrate as Determined by Classical and Quasi-Elastic Light Scattering," D. F. Evans, A. Yamauchi, G. J. Wei and V. A. Bloomfield, J. Phys. Chem., **87**, 3537 (1983).

Aggregation of surfactants to form micelles in ethylammonium nitrate, a low melting fused salt, was investigated by classical and quasi-elastic light scattering. For tetradecylpyridinium bromide and hexadecylpyridinium bromide the following data were obtained: critical micelle concentrations 8.0×10^{-2} and 2.0×10^{-2} mol kg⁻¹, micellar aggregation numbers 17 and 26, second virial coefficients 1.64×10^{-3} and 1.30×10^{-3} mol-cc g⁻² and hydrodynamic radii 14Å and 22Å respectively. The results are consistent with either a small classical spherical micelle containing only surfactant or a spherical mixed micelle containing surfactant and ethylammonium ions as a cosurfactant. The measured second virial coefficients are almost equal to those calculated for hard spheres and reflect highly screened electrostatic interactions in the totally ionized solvent.

"The Activity and Stability of Alkaline Phosphatase in Solutions of Water and the Fused Salt Ethylammonium Nitrate," D. K. Magnuson, J. W. Bodley and D. F. Evans, J. Solution Chem., accepted.

The fused salt ethylammonium nitrate has several properties which resemble those of the biologically important solvent water. In order to shed light on the role of solvent in determining protein structure we have examined the influence on ethylammonium nitrate on the activity and stability of the enzyme alkaline phosphatase. Significant, although reduced enzymatic activity was observed in ethylammonium nitrate solutions up to 60% (v/v) in water while the enzyme was stable to brief exposure to solutions as high as 80% (v/v) in the fused salt.

"Critical Micelle Concentrations for the Alkyltrimethylammonium Bromide in Water Over the Temperature Range 25 to 160°C," D. F. Evans, M. Allen, B. W. Ninham, and A. Fouda, J. Solution Chem., **13**, 87 (1984).

Critical micelle concentrations were determined by conductance measurements for the decyl, dodecyl, tetradecyl and hexadecyl trimethylammonium bromides in water at 25, 60, 95, 130 and 160°C. The results are discussed in terms of the

equilibrium model and the nonlinear Poisson-Boltzmann model for micelle formation. The free energies of transferring a methylene group out of water and into the oil-like interior of the micelle are found to be -781 (25°C), -796 (60°C), -819 (95°C), -815 (130°C) and -787 (160°C) cal mol⁻¹.

"Why Micelles Form in Water and Hydrazine: A Reexamination of the Origins of Hydrophobicity," M. Ramadan, D. F. Evans and R. Lumry, J. Phys. Chem. **87**, 4538 (1983).

Micelle formation, a typical "hydrophobic process" in water, has been studied in hydrazine. The standard free energies, ΔG_0 , for micellization are similar in the two solvents (-9.6 Kcal mol⁻¹ for water and -7.8 Kcal mol⁻¹ for hydrazine for sodium dodecylsulfate). The corresponding ΔH_0 values (-6.1 Kcal mol⁻¹ and -13.3 Kcal mol⁻¹, respectively) and ΔS_0 values (11 gib mol⁻¹ and -18 gib mol⁻¹ respectively) are dramatically different. The differences between hydrazine and water are attributed to a large positive increment to both ΔH_0 (H₂O) and ΔS_0 (H₂O) accompanying the transfer of the surfactant hydrocarbon chain out of water. These increments nearly compensate each other and thus make only a small contribution to the free energy in the temperature range 25-45°C. This interpretation is bolstered by the almost identical free energy of transfer of a methylene group from water (-0.76 Kcal mol⁻¹) and hydrazine (-0.71 Kcal mol⁻¹) to the micelle. These results suggest that the lipophobic properties of water and hydrazine are very similar and that the unique structural properties of water do not play a dominate role. The critical micelle concentrations are reported for sodium octyl-, decyl- and dodecylsulfate and decyl- and dodecyltrimethylammonium bromide in hydrazine at 25, 35 and 45°C.

"Micelle Formation in Hydrazine-Water Mixtures," M. Ramadan, D. F. Evans, R. Lumry and S. Philson, submitted.

Critical micelle concentrations for sodium dodecylsulfate in hydrazine-water mixtures ($X_{H_4N_2} = 0.20, 0.35, 0.50, 0.60, 0.75, \text{ and } 0.85$) at 25, 35 and 45°C are analyzed with the equilibrium model for micelle formation to give the thermodynamics of transfer of hydrocarbon chains from the solvent mixture to the oil-like interior of the micelle. In going from water to hydrazine, ΔG , ΔH and ΔS vary almost linearly from -9.7 to -7.9 Kcal mol⁻¹, -4.1 to -13 Kcal mol⁻¹ and 11 to -18 cal mol⁻¹ °C⁻¹ respectively. No indication of a dramatic change from the compensated enthalpy-entropy behavior characteristic of water to the polar liquid behavior characteristic of hydrazine is observed.

"Ion Binding and the Hydrophobic Effect," D. F. Evans and B. W. Ninham, J. Phys. Chem. **87**, 5025 (1983).

Two apparently opposing interpretations of ionic surfactant aggregation are reconciled. Phenomenological constants ascribed to ion association at micellar surfaces are reinterpreted and shown to emerge naturally from a treatment of electrostatic head group interactions via an explicit approximate solution of the nonlinear Poisson-Boltzmann equation. Given critical micelle concentrations and

aggregation numbers, the free energies, enthalpies and entropies of micellization can be calculated. Enthalpy-entropy compensation is studied with water as solvent, and earlier conclusions based on the phenomenological model confirmed. Hydrazine exhibits very different behavior. By removing one parameter from consideration, the theory shows considerable light on the nature and importance of chain interactions in determining micellar structure, and on the validity of fluid-interior models for micelles.

"Ion Binding and Dressed Micelles," D. F. Evans, D. J. Mitchell and B. W. Ninham, J. Phys. Chem, accepted.

Analytic expressions for electrostatic curvature free energy derived from the nonlinear Poisson-Boltzmann equation are used to construct a theory of ionic micelles. The thermodynamics implicit in the ion-binding model is shown to emerge naturally without resort to Stern layers. Reconciliation of the two apparently opposed theories allows one to discriminate between real "ion binding" due to specific ion interactions, and that due to adsorption excesses.

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