MASTER COPY KEEP THIS COPY FOR REPRODUCTION PURPOSES

AD-A257 036

REPORT DOCUMENTATION PAGE

Form Approved
OMB No. 0704-0188

1. AGENCY USE ONLY *(Leave blank)*

2. REPORT DATE 9/10/92

3. REPORT TYPE AND DATES COVERED Final 15 Mar 89-14 Mar 92

4. TITLE AND SUBTITLE
~~Structure and Dynamics of Surfactant Stabilized Systems~~
See Title Page

5. FUNDING NUMBERS
DAAL03-89-K-0058

6. AUTHOR(S)
D. Fennell Evans

DTIC
ELECTE
OCT 22 1992
S B D

7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)
University of Minnesota
Office of Research & Technology Transfer Adm.
Suite 201, 1100 Washington Avenue S
Minneapolis, MN 55415

RFORMING ORGANIZATION PORT NUMBER

. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)
U. S. Army Research Office
P. O. Box 12211
Research Triangle Park, NC 27709-2211

10. SPONSORING/MONITORING AGENCY REPORT NUMBER
ARO 26296.7-CH

11. SUPPLEMENTARY NOTES
The view, opinions and/or findings contained in this report are those of the author(s) and should not be construed as an official Department of the Army position, policy, or decision, unless so designated by other documentation.

12a. DISTRIBUTION / AVAILABILITY STATEMENT
Approved for public release; distribution unlimited.

425680

92-27556

2198

13. ABSTRACT *(Maximum 200 words)*

We have determined micellar aggregation numbers for a number of single- and double-chain surfactants using time-resolved fluorescence quenching and small angle neutron scattering as functions of surfactant concentration, chain length and temperature.

The force between dialkyldimethylammonium bromide and acetate bilayers was measured with the surface forces apparatus as a function of added salt and temperature. Using atomic force microscopy we obtained images of normal and interdigitated bilayers.

We identified a new mechanism for emulsification in which a W/O microemulsion inverts to a O/W macroemulsion upon contact with water. We characterized high internal phase emulsions and related their structures to the HLB temperature of the surfactant.

We prepared the first reversed vesicles containing water shells separated by well-defined hydrocarbon interior and exterior phases. We demonstrated how both normal and reversed micelles can be prepared from the same oil/water/surfactant system near the HLB temperatures of the surfactant by simply varying the concentration of components.

14. SUBJECT TERMS Self-Assembly, Amphiphiles, Reversed Vesicles, Surface Forces Apparatus, Atomic Force Microscopy, High Internal Volume Phase Emulsions

15. NUMBER OF PAGES 21

16. PRICE CODE

17. SECURITY CLASSIFICATION OF REPORT	**18. SECURITY CLASSIFICATION OF THIS PAGE**	**19. SECURITY CLASSIFICATION OF ABSTRACT**	**20. LIMITATION OF ABSTRACT**
UNCLASSIFIED	UNCLASSIFIED	UNCLASSIFIED	UL

CHARACTERIZATION OF VESICLE AND MICROEMULSION MICROSTRUCTURES

FINAL REPORT

D. Fennell Evans

September 1992

U.S. Army Research Office

DAAL03-89-K-0058

University of Minnesota

Approved for Public Release:
Distribution Unlimited

TABLE OF CONTENTS

I. GOALS OF THE RESEARCH

This research focused on two main objectives (1) the relation between surfactant structure, intra- and intermolecular interactions that dictate aggregate microstructure and (2) properties of macro- and microemulsions with an emphasis on mew mechanisms of emulsion formation, high volume phase volume fraction emulsions and the relation between vesicles and bilayers formed in surfactant, oil and water systems.

II. AGGREGATE MICROSTRUCTURE

The unique ability of amphiphilic molecules to form organized assemblies such as micelles, vesicles, microtubules and bilayers has led to many important application of these aggregates. In micellar catalysis, the very high interfacial area per volume of small, spherical micelles or of microemulsions allows significant rate enhancements of reaction between water-soluble and -insoluble molecules. In biological systems nature utilizes the amphiphilic character of phospholipids to construct a variety of assemblies including cell membranes and endocytotic, pinocytotic and phagocytotic vesicles. In microemulsion systems complex bicontinuous microstructure can lead to ultralow interfacial tension that are important in enhanced oil recovery. In all cases aggregate size and shape determine function.

A major challenge in colloid science is to relate amphiphilic microstructure to molecular and field variables such as temperature, pressure, surfactant concentration and added salt. Double-chain surfactants offer a particular challenge because such compounds can assemble to form small spherical micelles, vesicles, microtubules or bilayers that constantly transform form one structure to another as temperature, counterions and concentration are varied. The apparent simultaneous coexistence of several structures constitutes an added complexity.

IIA. Micelle–Vesicle Equilibrium: The interplay between field variables and microstructure is most readily illustrated by the dialkyldimethylammonium surfactants such as didodecyldimethylammonium ($2C_{12}N2C_1$) acetate or bromide. At room temperature, the bromide forms turbid solutions containing large structures such as liposomes, vesicles and other bilayer structures. When a dilute $2C_{12}N2C_1Br$ solution is heated in a video enhanced microscope (VEM), the bilayer structures initially transform to a mixture of vesicles and micelles, which upon further heating form clear micellar solutions. These observations indicated a micellar-vesicle equilibrium at intermediate temperatures.

With $2C_{12}N2C_1$ acetate or hydroxide clear solutions are formed up to at least 0.5 M. Investigation of the $2C_{12}N2C_1OAc$ by VEM and cryo-transmission electron microscopy revealed the presence of small unilamellar vesicles in dilute aqueous solutions (0.001 to 0.5 M), but no such structures at higher concentrations. This implied a vesicle to micelle transformation with increasing surfactant concentration.

In order to obtain quantitative information on these micellar-vesicle transformations, we used time resolve fluorescence quenching (TRFQ) and small angle neutron scattering (SANS) to directly measure aggregation numbers and determine the relative concentrations of vesicles and micelles (D.D. Miller. L.J. Magid and D F. Evans, *J. Phys. Chem.* **1990**, 93, 323). We determined aggregation numbers for nine single chain and double chain ammonium bromides and acetate and mixture of zwitterionic phosphatidylcholines ($2C_6PC$ and $2C_{16}PC$) as functions of amphiphilic concentration, temperature and chain length.

Some of our results are summarized in Figures 1–4. Figure 1 compares the aggregation numbers, N, for $C_{16}N3C_1$ bromide and acetate as a function of temperature. With the bromide, N decreases substantially a results attributed to greater counterion dissociation as the temperature is increased. With acetate, N is almost independent of temperature reflecting that the initial degree of counterion binding is much less than with Br^-. With increasing temperature the values of N for both ions approach a common value.

Figure 2 gives values of N for $2C_{12}N2C_1OAc$ and $2C_{14}N2C_1OAc$ as a function of concentration. The results are consistent with the formation of only micelles. Neither TRFQ or SANS indicate the presence of an detectable concentration of vesicles in these solutions.

Figure 3 gives TRFQ data for ditetradecyldimethylammonium aggregates with mixtures of acetate and bromide counterions. A_4 is a measured quantity which is independent of quencher concentration, η, for micelles, but increases with η for vesicles. With acetate counterions only micelles are present, but upon addition of bromide the fraction of micelles, f_m, decreases. With 50% Br^-, nearly 90% of the aggregates are vesicles and liposomes.

Figure 4 shows how adding a long chain phospholipid ($2C_{16}PC$) to a solution containing ($2C_6PC$) results in the transformation of micelles to vesicles. This illustrates how mixtures of surfactant with different chain lengths can control curvature at the aggregate-water interface.

As part of our program to characterize amphiphilic microstructures, we also developed a zeta potential cell for the video enhance microscope which permits direct visualization of vesicles and liposomes which cannot be detected using regular zeta potential instrument equipped with a light microscope. Zeta potential measurements on surfactant aggregates of $2C_{14}N2C_1$ Br-OAc mixtures were made (T. Kaneko, D.D. Miller and D.F. Evans, *J. Solution Chem.* **1990**, 19, 457). This apparatus has since been used by a number of other groups to characterize surfactant and colloidal aggregates.

IIB. Temperature Dependent Interaction Forces Between Amphiphilic Aggregates: In the previous grant period (1986–1989), we determined critical micelle concentrations, CMC, and aggregation numbers, N, for tetradecyltrimethylammonium bromide in water over the temperature range of 25 to 160°C. We found that the CMC increased by a factor of eight while the aggregation number decreased from 70 to 8. These results can be understood in terms of intra surfactant interaction within a given micelle. Increasing temperature decreases counterion binding which leads to increased head group repulsion and a corresponding decrease in N.

During this grant period, we extended these studies to include characterization of the interaggregate interactions which drive the bilayer → vesicle → micelles transitions. We

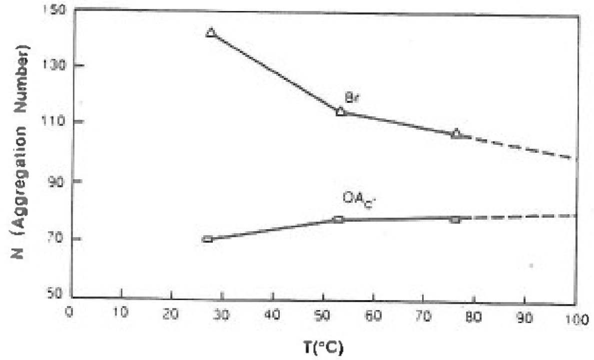


Figure 1. Aggregation numbers of 0.05 M $C_{16}N3C_1Br$ and $C_{16}N3C_1OAc$ as a function of temperature.

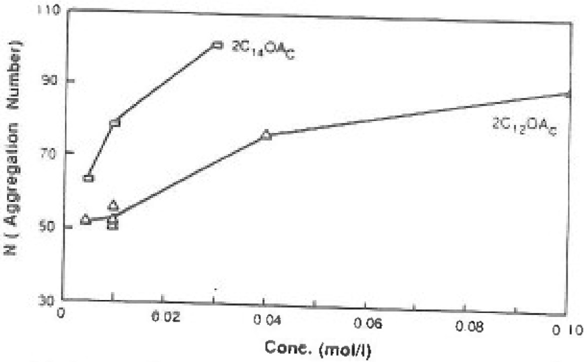


Figure 2. Aggregation numbers of double-chained acetate surfactants (by.TRFQ) as a function of surfactant concentration ($2C_{14}OAc$ = ditetradecyldimethylammonium acetate, $2C_{12}OAc$ = didodecyldimethylammonium acetate).

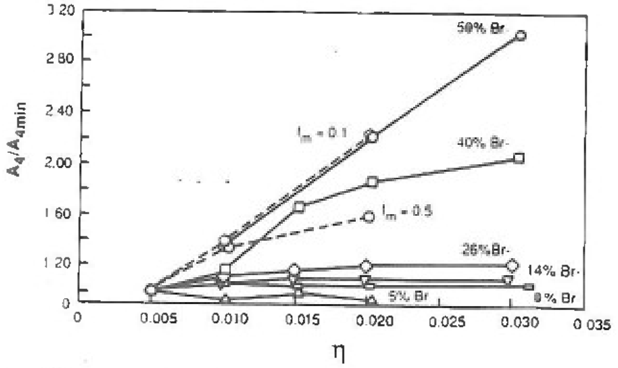


Figure 3. Plot of $A_4/A_{4_{min}}$ vs η for ditetradecyldimethylammonium aggregates with mixtures (acetate and bromide) counterions. Also shown (dashed lines) are values of A_4 for simulated data with $f_m = 0.1$ (90% vesicles) and $f_m = 0.5$ (50% vesicles). Note that the proportion of surfactant in vesicle form increases with increased bromide ion. With 50% bromide, nearly 90% of the aggregates are vesicles, liposomes, and other large aggregates.

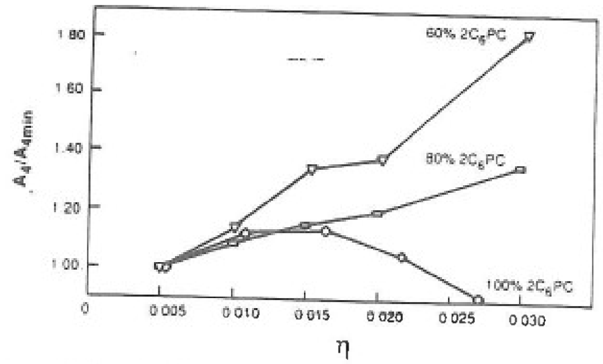


Figure 4. Plot of $A_4/A_{4_{min}}$ vs η for mixtures of dicaproylphosphatidylcholine ($2C_6PC$) and dipalmitoylphosphatidylcholine ($2C_{16}PC$) at 53 °C. The increased dependence of A_4 on η with decreased $2C_6PC$ indicates that the proportion of surfactant in vesicles and liposomes is also increasing. With 100% $2C_{16}PC$, there is no evidence for micellar aggregates and thus all the phospholipid has aggregated into large structures.

used the surfaces forces apparatus to directly measure interaction forces between dihexadecyldimethylammonium bilayers with acetate and bromide counterions as a function of temperature from 25 to 60°C (Y.-H. Tsao, S.X. Yang and D.F. Evans, *Langmuir* 1992, 8, 1188) Examples of the force curves obtained at 50°C as a function of added salt (NaOAc and KBr) are presented in Figures 5 and 6. The results can be interpolated in terms of increasing surface potentials leading to increased repulsion between head groups. This explains the bilayer to vesicle to micelles transformation described in the section above.

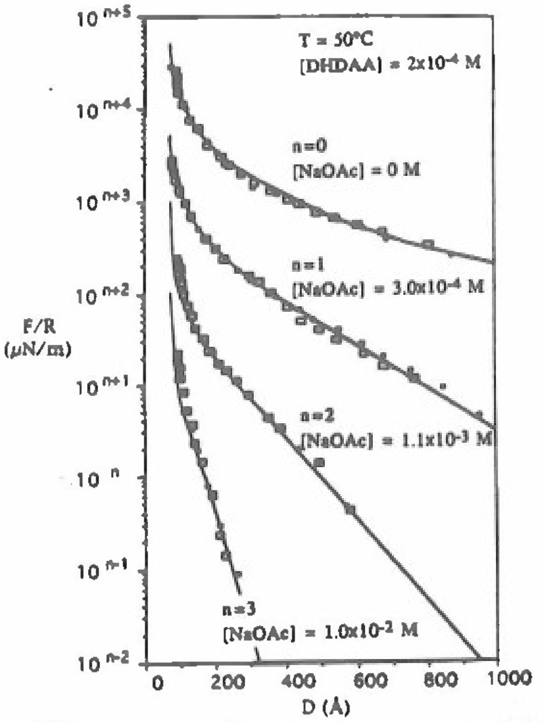


Figure 5. Forces measured between adsorbed DHDAA bilayers in 2×10^{-4} M DHDAA solution as a function of added NaOAc at 50 °C.

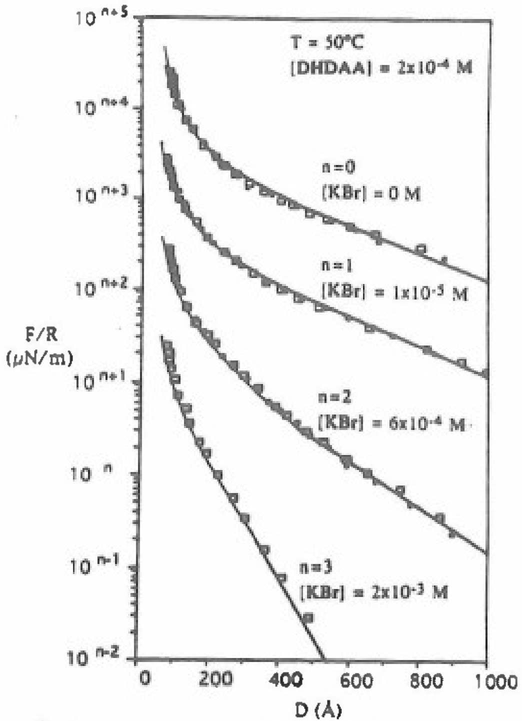


Figure 6. Forces measured between DHDAA bilayers with addition of KBr at 50 °C.

In addition we were able to obtain atomic force microscopy (AFM) images of the bilayers (Figure 7) which along the STM data confirmed the existence of two types of bilayer structures on mica which can be controlled by the method of deposition (Figure 8). If a solution of 2×10^{-4} M DHDAA is injected in the SFA containing bare mica a interdigitated bilayer forms. However, if a hydrophobic monolayer is first adsorbed onto the mica from a cyclohexane solution containing DHDAA and then assembled in the SFA and a DHDAA solution subsequently injected a normal bilayer forms.

By using the AFM as a micro-mechanical tester, i.e. varying the force between the AFM tip and the bilayer, we were able to detect a significant difference in the mechanical properties of the two bilayers. The interdigitated bilayer was robust and could be imaged over a considerable force range. The normal bilayer was more fragile, as expected from its structure, and could be only imaged at very small interaction forces. The ability to directly image surfaces at a molecular level which are used in other types of measurements constitute a powerful technique for characterizing interfacial systems.

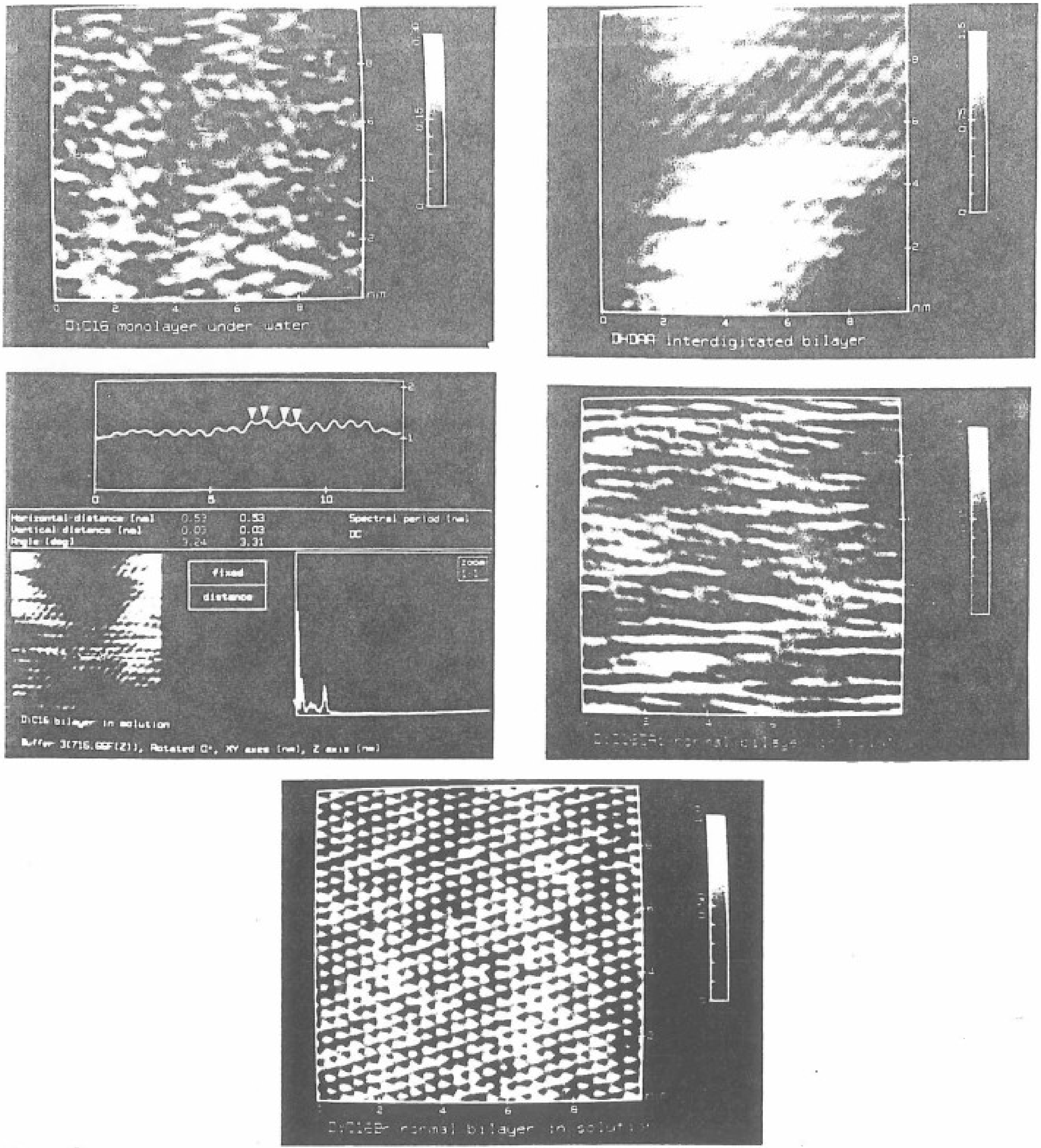


Figure 7. (a, top left) AFM images of a DHDA monolayer on mica in water at 25 °C. Individual methyl groups of the hydrocarbon chains can he identified. (h, top right) AFM image of a DHDAA interdigitated bilayer showing a set of well-defined peaks with an average area of 34 ± 4 Å^2, assumed to be equal to area of individual methyl groups of tha head groups. (c, middla left) Cross-section profile of AFM image of a DHDAA interdigitated hilayer. The two methyl groups associated with a DHDA molecula ara separated hy 5.5 Å. (d, middle right) AFM image of DHDAA normal hilayer giving an area per head group of 40 ± 2 Å^2. (e, bottom) AFM image of a DHDAA normal hilayer in 2×10^{-3} M KBr solution showing a headgroup area of 38 ± 2 Å^2. Addition of KBr produces AFM images which are more ordered.

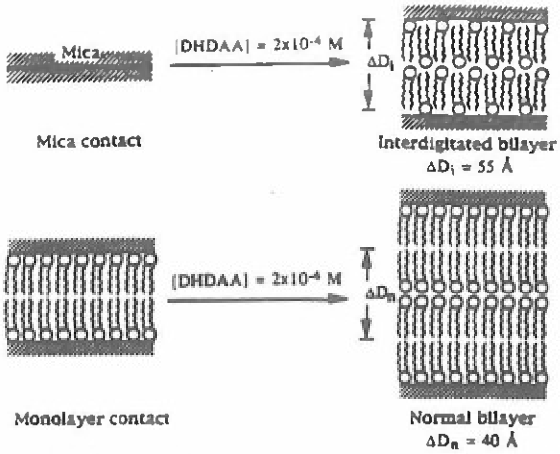


Figure 8. Schematic drawing of formation of interdigitated and normal DHDAA bilayers.

IIC. Summary of Related Studies: We characterized the properties of a large cationic counterion, tetraethanolammonium $(EtOH)_4N^+$, by measuring CMCs and aggregation numbers for tetraethanolammonium dodecylsulfate, $(EtOH)_4NDs$, as a function of added $(EtOH)_4NBr$ and compared the results to alkali metal and tetraalkylammonim dodecylammonium micelles. We also measured interaction forces between mica in the SFA as a function of added $(EtOH)_4N^+$ ion (M. Ueno, Y.-H. Tsao, J.B. Evans and D.F. Evans, *J. Solution Chem.* 1992, 21, 445).

Considerable interest has been generated by the claims that trehalose. a trisaccharide sugar, which is produced by several microorganisms upon dehydration, provides a special stabilizing effect on vesicles. We initiated a study of the effect of trehalose on stabilizing vesicles using video enhanced microscopy. However, we unable to discern any major difference between trehalose and other sugars such a sucrose. While our study was underway, we learned that the Parsegian and Rand had carried out osmotic stress measurements on bilayers using a number of different sugars. They where unable to detect any major difference which identified a unique role for trehalose. Based on these observations, we terminated this study.

As a tribute to K. Shinoda upon his 65th birthday, we published a paper proposing a new organizing framework for amphiphilic solutions. As shown in Figure 9, three idealized solutions, molecular solutions — dominated by lyophilic interactions, phase separated systems — dominated by lyophobic interactions, and organized solutions — dominated by lyophilic/lyophobic interactions, are proposed as limiting idealized models. The rest of the paper summarizes accomplishments achieved under the research support from the U.S. Army Office of Research.

We also investigated the properties of palladium-iodide surface complexes with a view to using these materials as substrates for scanning tunneling microscopy imaging of adsorbed surfactant monolayers and bilayers and of adsorbed macromolecules (B. Farrell, G. Lee and D.F. Evans, *Surface Science*, manuscript submitted).

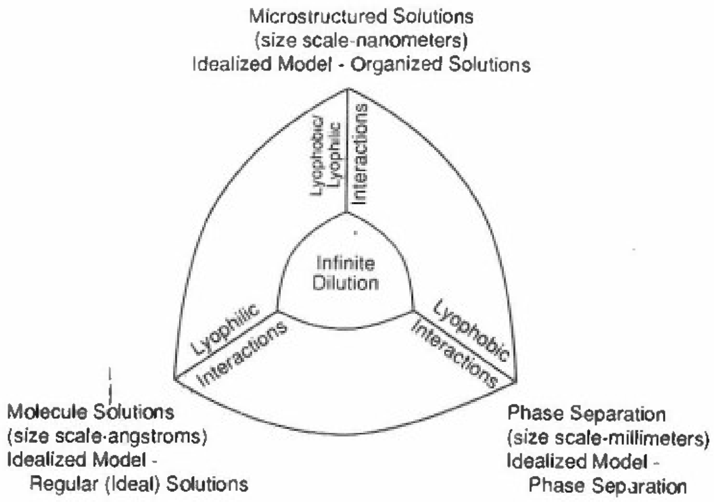
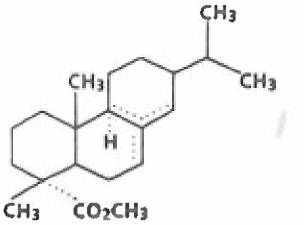


FIG. 9. Schematic of solute–solvent interactions leading to three idealized solution models: ideal solutions, phase-separated systems, and organized solutions. Associated with each of these solutions is a characteristic structural size.

III. MICRO- AND MACROEMULSIONS

IIIA. Spontaneous Formation of a Water-Continuous Macroemulsion from a W/O Microemulsion: Macroemulsions are thermodynamically unstable dispersions containing oil, water and an emulsifier such as a surfactant, polymer or small particles. Macro-emulsions contain water droplets in an oil continuum (O/W) or visa versa (W/O).

Emulsions are prepared using two basic strategies. (1) Dispersion in which mechanical energy is injected to break up bulk phases and create the large interfacial area associated with emulsions. (2) Condensation in which chemical energy stored in the reactants transform bulk phases via surface driven instabilities to emulsion droplets.



Methyl Dihydroabietate
(3 Isomers Possible)
I

Figure 10

We have identified a new condensation mechanism. The process involves preparing an w/o microemulsion and contacting it with water under conditions that lead to phase inversion and production of a O/W macroemulsion. A specific example employs Hercolyn D (methyl ester of partially hydrogenated rosin acid, Figure 10) as the oil and potassium rosinate obtained by partial hydrolysis of Hercolyn D as the emulsifier (R.W. Greiner and D.F. Evans, *Langmuir* 1990, 6, 1793). The emulsion produced by this process is exceedingly stable and remains unchanged for at least five years.

In order to understand this process as illustrated in Figure 11, we must consider some specific properties of the initial microemulsion. At low water content, the microemulsion is nonconducting, consistent with the formation of inverted W/O spheres. Provided that the water content is less than 1.8 wt%, the microemulsion undergoes phase inversion to give an O/W emulsion with an unusually uniform droplet diameter of 225 nm. Bringing microemulsions containing more than 1.8 wt% water into contact with water results in unstable emulsions.

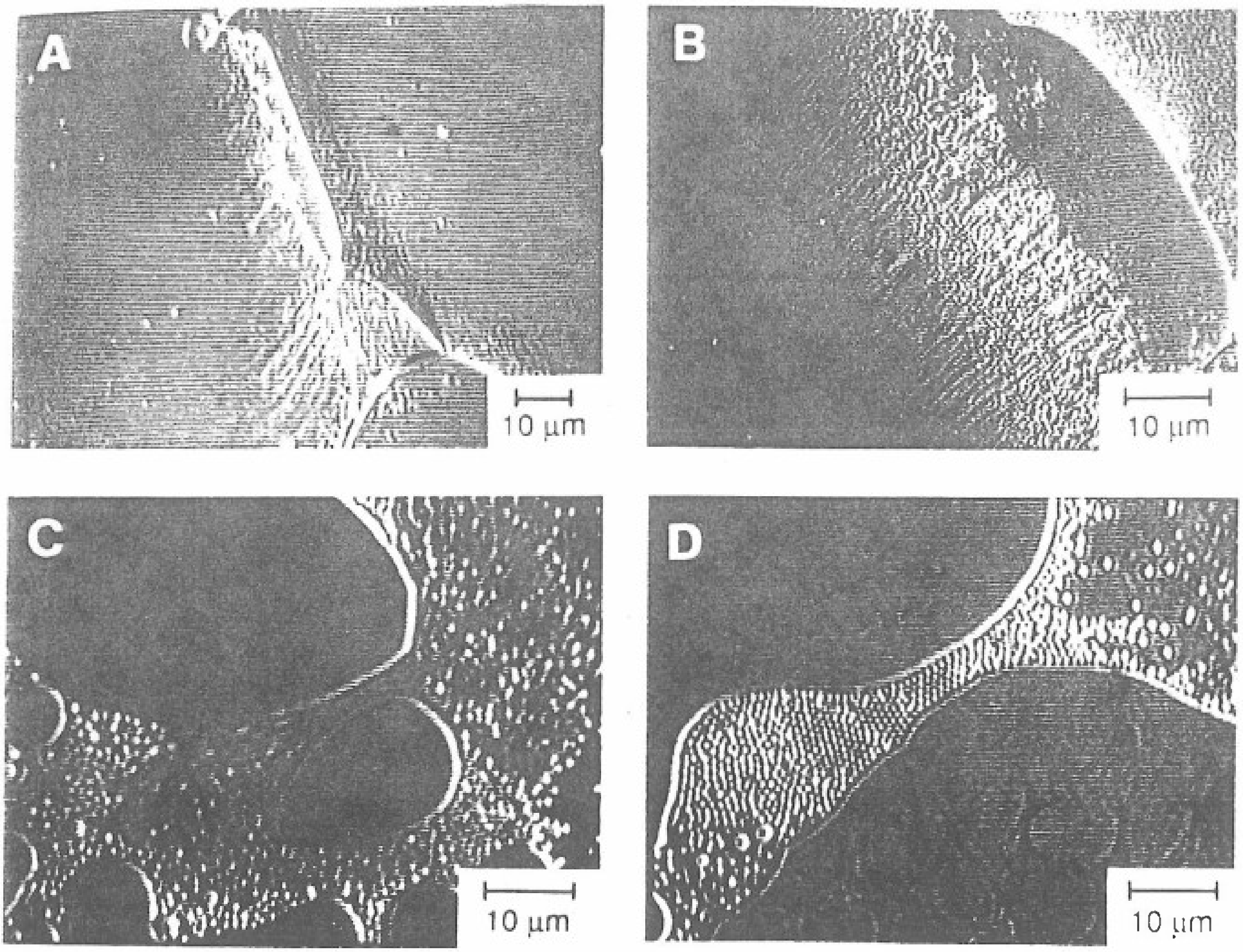


Figure 11. VEM images of spontaneous emulsification of Hercolyn D/potassium rosinate/water microemulsions with water: (A) approximately 25 s after contact; (B) approximately 40 s after contact; (C) 3–5 min after contact, explosive injection of oil phase droplets into water; (D) 3–5 min after contact, showing nearly uniform spheres of oil phase before injection into water.

If we titrate the 1.8 wt% microemulsion with water, the conductance initially increases, goes through a maximum, and then decreases. This reaction parallels the anti-percolation behavior observed with the DDAB microemulsions and suggests that adding water forms interconnected conduits that transform into spheres.

We can understand these observations as a result of the high concentration of counterions, which considerably lowers the osmotic pressure inside the inverted micelles contained in the microemulsion phase compared to that of the contacting water. Consequently, the inverted micelles imbibe water and grow. This process is equivalent to the titration path described above, but on a size scale confined to the interfacial region adjoining the two phases. Due to high viscosity of the medium and packing constraints, the micelles remain fixed as they grow, interconnect, and eventually invert. Initial microemulsion structure thus sets the constraints that determine the small, uniform size of the resulting emulsion drops. Immediately after the inversion process takes place, the emulsion droplets, stabilized by an anionic surfactant, behave as a concentrated colloidal dispersion. Electrostatic repulsion between droplets drives them apart and they move into the adjacent water phase.

If we replace the contacting water by a 2 M sucrose solution, we completely inhibit the emulsification process. This result is consistent with the role played by the difference in osmotic pressure. When we increase the water content of the microemulsion to the point at which interconnected conduits are present, then water from the aqueous phase simply fluxes into the oil phase and causes the formation of a coarse heterogeneous emulsion. In this situation, the difference in osmotic pressure provides the chemical energy to drive the inversion process leading to emulsion formation.

Because of the unusual properties of this system, we decided to characterize both the microemulsion and macroemulsion formed by the Hercolyn D system. We found that the microemulsion phase region is very small suggesting that only spherical droplets are stable and that stable bicontinuous structures characteristic of many microemulsion systems do not form.

With the phase inversion emulsification process, it is possible to form Hercolyn D emulsions containing 50 to 60 vol % of the oil droplets. We found that these emulsion were quite stable and could be concentrated in an ultra centrifuge to 90 to 95 volume %. Examination of these concentrated emulsions by VEM showed that the droplets were polyhedra consistent with the high volume fraction of the internal phase exceeding the limiting value for close packing of undistorted spheres.

IIIB. High Internal Phase Emulsions: High internal phase ratio emulsions (HIPREs) are of intrinsic interest because of their extraordinarily large internal phase volume ($f =$ 0.95 to 0.99), their economical use of emulsifier, their unusual rheological properties and their translucent optical properties. We investigated a polyethyleneglycol n alkylether, oil and water system which could be formed as either a water rich W/O emulsion or as a oil rich O/W emulsion by by varying the length of the oil hydrocarbon chain and the temperature. In these emulsions the continuous phase was less than 3 volume %. (H. Kunieda, D.F. Evans, C. Solans and M. Yoshida, *Colloids and Surfaces* **1990**, 47 35).

Using video enhanced microscopy, we were able to obtain images of the emulsion structure (Fig. 12) which shows the expected polyhedral shape and to follow the collapse of the emulsion with increasing or decreasing temperature. The stability of the emulsions was related to the HLB temperature of the surfactant. The HLB temperature provides a measures of the surfactants hydrophobic-lyophilic interactions including the effect of oil penetration into the surfactant chains at the oil-water interface.

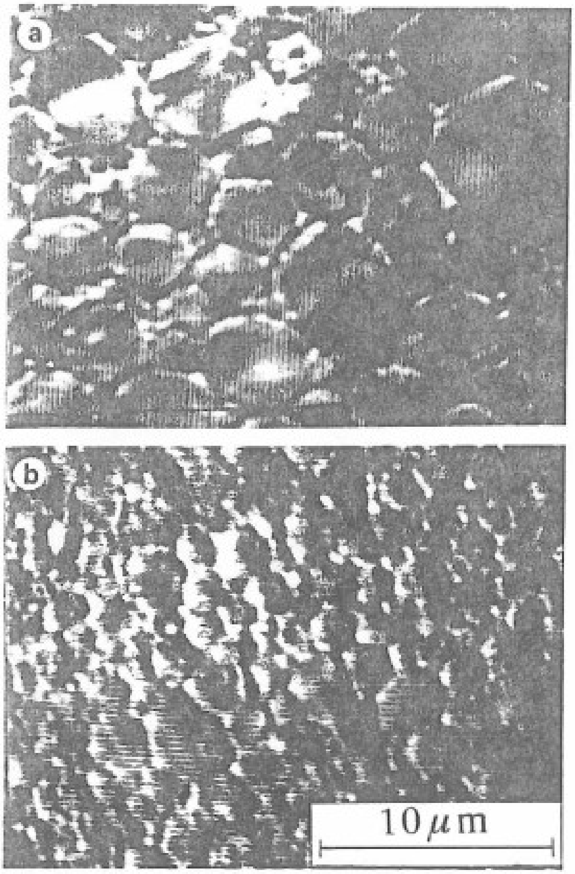


Fig. 12. VEM pictures for (a) O/W-type gel and (b) W/O-type gel in oil- and water-rich regions, respectively. Compositions; (a) water 3%: $R_{12}EO_6$ 1%: hexadecane 96%; (b) 5% NaCl solution 98.5%: $R_{12}EO_4$ 0.75%: decane 0.75%.

IIIC. Formation of Normal and Reversed Vesicles and Their Relation to Bilayer Structures in Three-Component Microemulsions: There is a symmetry among most self organizing structures in regard to the distribution of polar and nonpolar components. The formation of normal and reversed micelles, hexagonal liquid crystals, macro- and microemulsions and bicontinuous structures is well documented. One notable exception to symmetrical pattern was vesicles. Normal vesicles and liposomes possessing closed hydrocarbon shells separating well-defined aqueous interior and exterior phases have been extensively studied. However reversed vesicles had not been reported previously. We found a method to form reversed vesicles, i.e. water shells separated well defined hydrocarbon interior and exterior phases. We produced VEM images demonstrating the size and dynamic nature of reversed vesicles (H. Kunieda, K. Nakamura and D.F. Evans, *J. Am. Chem. Soc.* 1991, 113, 1051).

In a subsequent paper (H. Kunieda, K. Nakamura, H.T. Davis and D.F. Evans, *Langmuir* 1991, 7, 1915), we demonstrated the symmetrical nature of vesicle structures by forming both normal and inverted vesicle from the same oil/water/ surfactant system near the HLB temperature of the surfactant. This was accomplished by simply varying the concentration of components. This paper provides a general relationship between phase behavior, liquid crystals swollen with oil or water and the formation of normal or reversed vesicles, These results establish a guideline for when vesicles can be formed in amphiphilic systems.

III D. Summary of Related Studies: We continued to develop models to explain the phase behavior of the didecyldimethylammonium bromide (DDAB) microemulsions using Voronoi structures. We have defined phase boundary and modeled the percolation behavior which is characteristic of the DDAB systems. A manuscript is in preparation.

We also investigated a system which produces Voronoi tessellation structures as a result of spin-coating polymers onto silicone wafers (T.G. Stange, R. Yang, D.F. Evans and W.A. Hendrickson, *Langmuir* **1992**, 8, 920). The evolution of the Voronoi tessellation structures as visualized by STM or AFM measurements are shown in Figure 13.

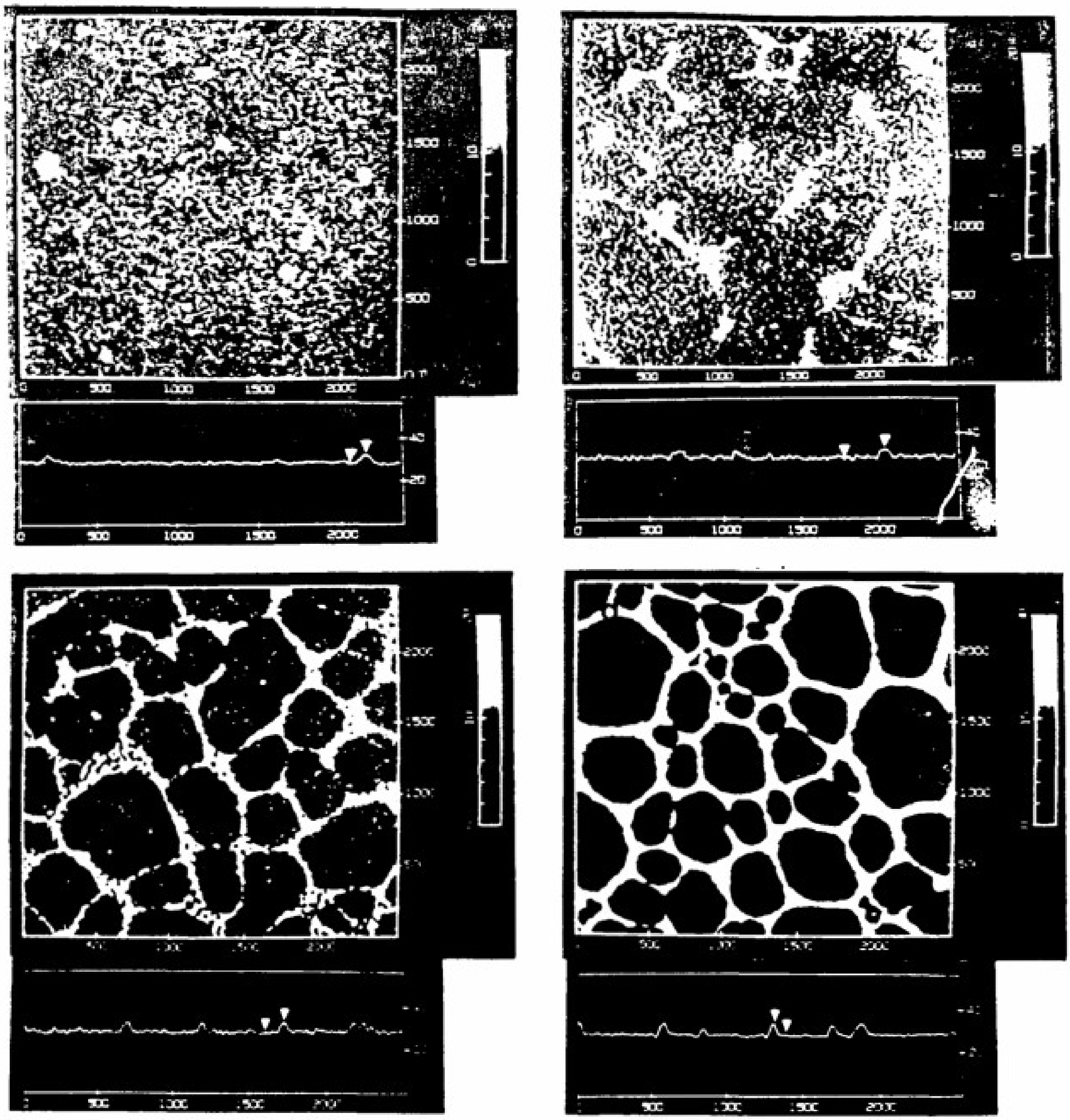


Figure 13.STM images and random cross-sectional profiles of spin-coated polystyrene at various concentrations: (a) molecular and monomolecular particles at 0.0005 wt %, vertical distance between markers 4.35 nm; (b) 0.003 wt %, vertical distance between markers 4.66 nm; (c) 0.01 wt %, vertical distance between markers 4.74 nm; (d) Voronoi tessellation pattern and 0.025 wt %, vertical distance between markers 4.81 nm. M_w of polymer was 990 000 g/mol.

ABSTRACTS OF ALL PUBLICATIONS

"Determination of the Zeta Potential of Surfactants with Mixed Counterions Using a Video Enhanced Microscopy Electrophoresis Cell," T. Kaneko, D.D. Miller and D.F. Evans, *J. Solution Chem.* **1989**, 19, 457.

The zeta potential of 2 mM solutions of didodecyldimethylammonium and ditetradecyldimethylammonium surfactants containing a mixture of acetate and bromide are reported. The measurements were made using new electrophoretic cells which can be used with a video enhanced microscope. This permits the simultaneous visualization and zeta potential characterization of vesicles and microtubule surfactant solutions. With increasing acetate molar fraction, the zeta potential increases. These results are interpreted in terms of the charge density at the shear plane of the aggregate interface.

"Fluorescence Quenching in Double-Chained Surfactants. 2. Experimental Results," D.D. Miller, L.J. Magid and D.F. Evans, *J. Phys. Chem.* **94**, 5921 (1990).

The aggregation behavior of single- and double-chained ionic surfactants ($C_{16}N3C_1Br$, $C_{16}N3C_1OAc$, $C_{14}N3C_1Br$, $2C_{10}N2C_1Br$, $2C_{12}N2C_1OAc$, $2C_{12}N2C_1Br$, $2C_{14}N2C_1Br$, $2C_{14}N2C_1OAc$, and $2C_{16}N2C_1OAC$) and zwitterionic phospholipids (dicaproyl- and dipalmitoylphosphatidylcholine ($2C_6PC$ and $2C_{16}PC$, respectively)) is investigated by time-resolved fluorescence quenching and small-angle neutron scattering measurements as a function of surfactant concentration, salt, and temperature. The double-chain surfactans with acetate as counterions form micelles whose aggregation number increases with surfactant concentration but is relatively independent of temperature. The transformation of the corresponding bromide surfactant from liposomes to micelles with increasing temperature is delineated; at intermediate temperatures, the solution contains mixtures of micelles and vesicles. Mixtures of zwitterionic surfactants transform from liposomes to micelles as the mole fraction of $2C_6PC$ increases, with a vesice–micelle equilibrium at intermediate values. The aggregation numbers for the single-chain acetate and bromide surfactants, which at low temperatures differ by a factor of 2, appear to approach one another at higher temperatures. These observations are analyzed in terms of specific counterion headgroup interactions and their variation with the field variables.

"The Structure of Gel-Emulsions in a Water/Nonionic Surfactant/Oil System," H. Kunieda, D.F. Evans, C. Solans and M. Yoshida, *Colloids and Surfaces* **47**, 35 (1900).

Gel formation in an oil-rich region was studied in water/nonionic surfactant/oil systems. The gel consists of an aqueous micellar solution phase and excess oil phase. It is necessary that the surfactant is hydrophilic enough to produce gels in an oil-rich region. This result is opposite to that of gels in a water-rich region; a surfactant must be lipophilic to form the gel. Gels in water-rich regions are W/O type whereas those in oil-rich regions are O/W type concentrated emulsions. The shape of droplets is not spherical but polyhedral because the volume fraction of the internal phase exceeds the limiting value of close packing of undistorted spheres. The effect of temperature on the stability of the O/W gel (in an oil-rich region) was also investigated in a water/$R_{12}EO_8$/hexadecane system by VEM. With an increase in temperature, the coalescence of droplets in the gel is started at a temperature about 25–30°C lower than HLB temperature. It is considered that this phenomenon is related to the stability of ordinary O/W type emulsions in nonionic surfactant systems.

"Spontaneous Formation of a Water-Continuous Emulsion from a W/O Microemulsion," R.W. Greiner and D.F. Evans, *Langmuir* **6**, 1793 (1990).

A new mechanism for spontaneous emulsification is proposed which involves inversion of a highly viscous W/O microemulsion, formed from the methyl ester of partially hydrogenated rosin containing 5 wt% of the potassium salt of partially hydrogenated rosin acid and small amounts of water, by a quiescent adjacent water phase. Inversion leads to the formation of stable, rather homogeneous O/W emulsions containing oil droplets as small as 150 nm. The proposed mechanism involves osmotically driven swelling of inverted micelles in the W/O microemulsion which remain fixed in a small volume element because of the high viscosity of the oil phase. The inverted micelles interconnect as they grow and eventually invert. They are then driven apart by electrostatic repulsion and move into the adjacent water phase. It was found that 2 M sucrose and 1 N solutions of 1:1 electrolytes in the quiescent water phase completely inhibit emulsification. This process contains a number of features which are not accounted for by the spontaneous emulsification mechanisms previously described in the literature.

"Formation of Vesicles and Microemulsions in a Water/Tetraethylene Glycol Dodecyl Ether/Dodecane System," H. Kunieda, K. Nakamura, H.T. Davis and D.F. Evans, *Langmuir* **7**, 1915 (1991).

Phase equilibria in a water/nonionic surfactant/hydrocarbon system are symmetric in a relatively dilute region at the hydrophile-lipophile-balanced (HLB) temperature (~ 25°C), at which an isotropic surfactant phase (so-called middle-phase microemulsion) coexists with excess water and oil phases. Correlation between the phase behavior and types of aggregates were investigated in a water/tetraethylene glycol dodecyl ethe/dodecane system at the HLB temperature. Lamellar liquid crystal containing a large amount of water coexists with an excess water phase in the water-rich region in which normal vesicles form. On the other hand, lamellar liquid crystal swelling a large amount of oil coexists with an excess oil phase in the oil-rich region in which reversed vesciles form. The inside and outside of the reversed vesicles are oil. The shapes of the reversed vesicles are dependent on the oil content in lamellar liquid crystals. Consequently, the aggregation number of surfactant molecules is infinite over a wide range of water/oil ratio at the HLB temperature but the structures are dependent on the following water/oil ratios; normal vesicles in the water-rich region, reversed vesicles in the oil-rich region, and bicontinuous surfactant phase (microemulsions) at the medium water/oil ratio.

"Scanning Tunneling Microscopy and Atomic Force Microscopy Characterization of Polystyrene Spin-Coated onto Silicon Surfaces," T.G. Stange, R. Mathew, D.F. Evans and W. Hendrickson, *Langmuir* **8**, 920 (1992).

Scanning tunneling and atomic force images of polystyrene spin-coated onto silicon surfaces as a function of polymer molecular weight and concentration are presented. At low polymer concentrations (0.0005 wt%) individual polymer molecules are visualized; their apparent size increases with molecular weight. At concentrations above 0.05 wt% continuous films are seen. At intermediate concentrations, polymer molecules aggregate to form two-dimensional Voronoi tessellation-like networks. These are discussed in terms of a specific failure mechanism leading to film rupture in spin-coating processes.

"Formation of Reversed Vesciles, H. Kunieda, K. Nakamura and D.F. Evans, *J. Am. Chem. Soc.* **1991**, 113, 1052.

No Abstract.

"Aggregation Behavior of Mixed-Counterion Double-Chained Surfactants," D.D. Miller and D.F. Evans, *Surfactants in Solution*, Vol. 11, K.L. Mittal and D.O. Shaw (Eds.), Plenum Press (1991) p. 141.

The aggregation behavior of dilute solutions of the dietetradecyldimethylammonium surfactant cation with mixtures of bromide and acetate counterion were studied using video enhanced microscopy, cryo-transmission electron microscopy, and time-resolved fluorescence quenching. Large liposomal aggregates of the bromide surfactant are gradually transformed into micellar aggregates by the addition of the acetate surfactant. Stable, equilibrium, unilamellar vesicles predominate at intermediate concentrations (40–60% Br^-), while small, spherical micelles coexist with, and gradually replace, vesicles as the bromide content is further reduced. Similar behavior is seen with long chain–short chain phospholipid mixtures. These results are analyzed in terms of free energy minimization and bilayer assymetry arguments.

"Tetraethanolammonium Counterions in Surfactant and Classical Colloidal Systems," M. Ueno, Y.-H. Tsao, J.B. Evans and D.F. Evans, *J. Solution Chem.* **21** 445 (1992).

Interaction forces between mica surfaces as a function of added tetraethanolammonium bromide, $(EtOH)_4NBr$, were determined using surface forces measurements and critical micelle concentrations and aggregation numbers were determined for tetraethanolammonium dodecylsulfate, $(EtOH)_4NDS$, using surface tension and fluorescence probe-quencher measurements. The properties of the large hydrophilic counterion, $(EtOH)_4N^+$, are compared to those of the hydrophobic analogue, Pr_4N^+.

"A Reevaluation of Temperature-Dependent Bilayer Interaction Forces as Determined by Surface Forces and Atomic Force Microscopy Measurements," Y.-H. Tsao, S.X. Yang and D.F. Evans, *Langmuir* **8**, 1188 (1992).

Direct force measurements on dihexadecyldimethylammonium bilayers in the presence of sodium acetate at 25, 40, 50 and 60°C and KBr at 40 and 50°C were carried out using a modified surface forces apparatus (SFA) with temperature control. The data were analyzed using the DLVO theory combined with hydration force terms. With increasing temperature, surface potential increases and counterion binding decreases. Under comparable ionic strength conditions, the degree of counterion binding is larger for bromide than acetate. The change in surfactant aggregation with temperature is discussed in terms of the SFA data.

"Organized Solutions and Their Manifestations in Polar Solvents," D.F. Evans and D.D. Miller, *Organized Solutions: Surfactants in Science and Technology*, Vol. 44, S.E. Friberg and B. Lindman, (Eds.), Marcel Dekker, New York (1992) p. 33.

No abstract.

LIST OF SCIENTIFIC PERSONNEL

Beth Trend	09/01/89–02/15/90
Roy Mathew	09/01/89–03/31/90
Howard Doumaux	12/16/89–11/30/91
Terry Stange	12/16/89–06/15/91
Brenda Farrell	05/14/90–02/28/92