sharp triplet methyl resonance indicative of rapid ethyl group exchange on the NMR time scale. Coalescence temperatures for internal rotation were 85 °C for **1** and 78 °C for **2**. Activation energies for this process were 17.8 kcal·mol^{-1} for each isomer.[11] A similar hindered rotation has been noted for [*nido*-9-SMe_2-7,8-$C_2B_9H_{11}$]$^-$.[10c]

Formation of isomers in a 1:1 statistical ratio suggests a mechanism wherein diethyl sulfide is initially lost from $B_{10}H_{12}(SEt_2)_2$ and recaptured upon formation of **1** and **2**. This process may be related to the acid-catalyzed nucleophilic substitution reaction as it occurs in the formation of [M-($C_2B_9H_{11}$)($C_2B_9H_{10}SEt_2$)] (M = Fe, Co) upon reaction of diethyl sulfide with protonated [M($C_2B_9H_{11}$)$_2$]$^-$ (M = Fe, Co).[10d]

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Supplementary Material Available: Tables of positional and thermal parameters and interatomic distances and angles for **1** and **2** (16 pages). Ordering information is given on any current masthead page.

(11) Free energies of activation ($\Delta G^{\ddagger}$) were obtained at coalescence temperatures by means of the Eyring equation and the expression $k = \pi\Delta\nu/2^{1/2}$.

Use of a Polymeric Counterion To Induce Bilayer Formation from a Single-Chain Surfactant[1]

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In this paper we show that cetyltrimethylammonium bromide (CTAB), a common micelle-forming surfactant, is converted into a bilayer-forming polyelectrolyte when the bromide ion is replaced by poly(acrylate). This finding demonstrates the feasibility of using a polymeric counterion to control micellar/lamellar phase formation from a *single-chain surfactant* and establishes a new and unique class of surfactant vesicles.[3]

Although single-chain surfactants typically form micellar aggregates in aqueous media,[4] we sought to investigate whether single-chain surfactants paired with polymeric counterions might produce a lamellar phase. In particular, we reasoned that organic counterions, held in close mutual proximity along a polymer backbone, could promote (i) tight ion pairing, (ii) reduced electrostatic repulsion between (and hydration of) the head groups, and (iii) enhanced lateral interaction among the surfactant chains.[5]

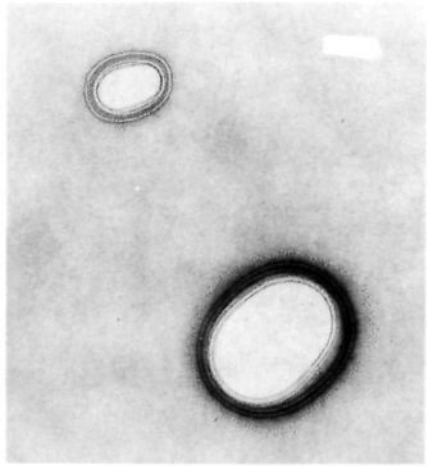

Figure 1. Transmission electron micrograph of an unstained dispersion of **1**; bar represents 1000 Å.

In terms of the packing of the molecules, we hypothesized that a reduction in the effective interfacial headgroup area might promote the formation of a lamellar phase. Further, given the low cost and ready availability of a wide variety of single-chain surfactants, together with the potential utility of surfactant vesicles for device applications,[6] such a finding would be of both theoretical and practical interest. In this report, we confirm this hypothesis by showing that bilayer vesicles are produced from common and inexpensive poly(acrylic acid) and CTAB precursors.

CTAB was converted into its hydroxide form via ion exchange (Amberlite IRA-400 (OH), Aldrich) and then combined with a stoichiometric quantity of poly(acrylic acid) (MW 2000, Aldrich) in methanol. Subsequent removal of solvent, and lyophilization from *tert*-butyl alcohol, afforded a 99% yield of poly(cetyltrimethylammonium acrylate) [**1**] as a white powder; analysis by IR (thin film on NaCl plates, deposited from a $CHCl_3$ solution) confirmed the complete disappearance of the carboxylic acid (1680 cm^{-1}) and the appearance of ammonium carboxylate groups (1570, 1400 cm^{-1}); thin layer chromatography [silica, $CHCl_3/CH_3OH$, 8/2 (v/v)] showed a single spot at the origin and the complete disappearance of CTAB (R_f 0.45).

$(CH_3)_3N^+(CH_2)_{15}CH_3$ $\quad$ $-[CH_2-CH\bar{O}_2-]_n$
1, $n_{av} = 28$

Rapid injection of 35 μL of a 0.124 M ethanolic solution of **1** into 1.5 mL of water produced a translucent dispersion.[7] Dynamic light scattering (Nicomp 200, 632.8 nm, 90° scattering angle) indicated particles having diameters ranging between 800 and 3500 Å; examination by transmission electron microscopy (TEM) as *unstained* samples (Philips 400) revealed particles of similar size, comprised of well-defined concentric membranes (Figure 1).[8] The apparent thickness of these membranes (dark rings) was 38 ± 5 Å, which is consistent with bilayer thicknesses found in other vesicles or liposomes.[9] Further examination of these particles using a through-focal series of micrographs confirmed that these images are due to a mass thickness contrast and are not derived from Fresnel fringe formation.

Passage of the dispersion through a Sephadex G-50 column afforded a 48% recovery in the void volume (nitrogen analysis).[5] In some preparations, a small amount of polymeric surfactant was detected beyond the void volume. Rechromatography of the vesicle fraction through a fresh Sephadex G-50 column afforded an 80%

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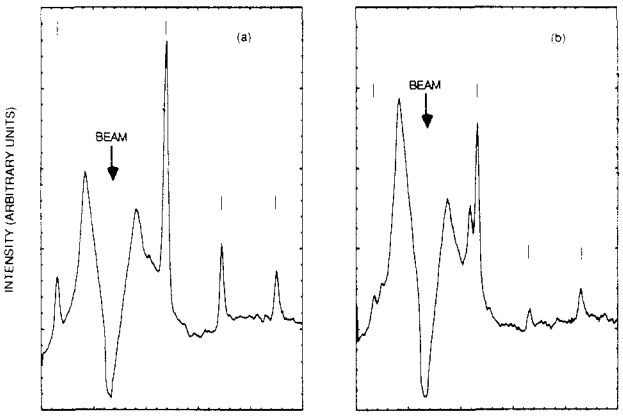

Figure 2. Radially integrated diffraction patterns for **1**. (a) Diffraction at 10 °C and 50% relative humidity; tic marks indicate the expected reflections for a lamellar lattice with basis length $d = 31.5$ Å. The arrow indicates the position of the main beam, blocked by a beam stop. (b) Diffraction at 10 °C and 80% relative humidity; tic marks indicate expected reflections for lamellar lattice of $d = 33.5$ Å. Note the appearance of the second lattice peak as described in the text.

recovery, without trailing of **1** on the column. These gel filtration results infer the presence of a nonvesicular component in the initial dispersion. Vesicles derived from **1** were stable for more than 48 h at ambient temperature (light scattering).

X-ray diffraction was used to demonstrate that dried, sedimented pellets of **1** form a lamellar phase when moistened in a stream of humidified gas. Specimens were prepared by depositing a drop of the vesicle dispersion onto a 12.5 μm thick mylar substrate, followed by overnight dehydration at 20% relative humidity at room temperature. This procedure is known to enhance macroscopic orientation and pseudoperiodic stacking of lamellae.[10] Specific methods used for sample preparation, humidity control, and X-ray analysis were similar to those previously described.[11-14] In the temperature range of −30 °C to 10 °C (20–50% relative humidity), a single lamellar lattice is clearly indicated (Figure 2a); above 50% humidity, a second lattice appears. However, too few diffraction lines are present to establish its structure. Figure 2b shows the diffraction pattern seen at 10 °C and 80% relative humidity, which clearly indicates a 33.5 ± 1.5 Å lamellar lattice coexisting with the second lattice. As the humidity is raised further, diffraction from the second lattice increases in intensity, while the original lamellar lattice loses intensity. Qualitatively, similar results were obtained at room temperature. Bulk (unoriented) dispersions of **1** also show two closely spaced lines, suggestive of two coexisting phases. In this case, a definitive phase assignment cannot be made because of the lack of higher orders of diffraction. In combination with the oriented specimen and electron microscope data, it appears likely that at least one of the phases is lamellar.

Studies which are now in progress are aimed at characterizing the permeability properties of these bilayers and at preparing analogous membranes from mixtures of single- and double-chain surfactants.[15] Results of these efforts will be reported in due course.

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A Model for the Chromophoric Site of Purple Acid Phosphatases

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The active sites of the purple acid phosphatases from bovine spleen and porcine uterus consist of a binuclear iron complex with two accessible oxidation states—a catalytically inactive, purple Fe(III)–Fe(III) form and an enzymatically active, pink Fe(II-I)–Fe(II) form.[1-8] The visible chromophore in these enzymes is associated with a tyrosinate-to-Fe(III) charge-transfer transition;[4,9] its persistence in both oxidation states and the similar extinction coefficients found for the chromophore in both states implicates a binuclear complex where tyrosine is coordinated to only one of the iron centers, the redox-inactive chromoporic site. Evidence for histidine coordination to both iron centers has been found in NMR[10] and pulsed EPR[11] studies. The oxidized Fe(II-II)–Fe(III) forms exhibit strong antiferromagnetic coupling[3,4,7,8] and Fe–Fe distances of 3.0–3.2 Å estimated from EXAFS studies.[2,6,12] Together, these observations suggest the presence of oxo and carboxylato units which bridge the iron atoms, as found for methemerythrin[2,13] and ribonucleotide reductase.[2,14,15] However, the absence of spectral features in the resonance Raman[4] and EXAFS[2,6] spectra that would corroborate the presence of the oxo group is troubling. We have therefore initiated an effort to model the active site of the purple acid phosphatases; our initial results are reported herein.

Treatment of a methanolic solution of $Fe(NO_3)_3 \cdot 9H_2O$ with the tripodal ligand *N*-(*o*-hydroxybenzyl)-*N*,*N*-bis(2-pyridylmethyl)amine[16] (L) and an equivalent of Et_3N gives rise to a

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