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13. ABSTRACT *(Maximum 200 words)*

The overall goal of this study was to understand variations in the surface elasticity of sea surface microlayer films and slicks in terms of their chemical composition. Microlayer and subsurface seawater samples collected in the Mid-Atlantic and California Bights were analyzed by pyrolysis-mass spectrometry. The mass spectra, representative of surfactant composition, were correlated with surface elasticity using multiple regression techniques. The mass spectra were found to contain sufficient information to predict static surface elasticity.

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Marine Surfactant Chemistry

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Long-term Goals

Sea-surface films modify the boundary conditions affecting important air-sea interfacial processes accessible by remote sensing. These processes include exchange of momentum and mass, bubble and foam stabilization, aerosol formation, and the absorbance and scattering of electromagnetic radiation. The long-term goals of this research are to relate the surface properties of natural sea-surface films to their chemical composition and to predict the probable range of surface viscoelasticity for different ocean provinces.

Scientific Objectives

(1) Characterize the molecular composition of organic matter in the surface microlayer using mass spectrometry.

(2) Determine how the elasticity of the microlayer changes with molecular composition.

Approach

Surface microlayers and underlying bulk seawater were collected using the SMS (Surface Microlayer Sampler, a rotating glass cylinder skimmer) for varying sea surface conditions. Two major sampling cruises were made on the R/V Cape Henlopen, deploying the SMS to skim the sea surface. Sampling was carried out in two seasons, during September-October, 1994 and May-June, 1995 along the same cruise track from Delaware Bay across the shelf and slope waters to the Sargasso Sea (Figure 1). The sampling involved collection of large volume surface microlayer and bulk seawater samples along a strong gradient of biological productivity and organic matter levels. Small volume samples were collected for assays of surfactant concentration, dissolved organic carbon (DOC) and chlorophyll and colored dissolved organic matter (CDOM) fluorescence. Microlayers included samples from unslicked surfaces, strongly banded slicks and diffuse slick regions in productive and oligotrophic waters. Thus, the sample suite included a variety of surface conditions. In addition, we participated in a third cruise of opportunity on the R/V New Horizon during the ONR-MBL experiment (April-May, 1995) involving the FLIP research platform, that was moored off Monterey Bay. Additional microlayer and bulk seawater samples were collected during this cruise in the area of Monterey Bay and the Santa Barbara Channel islands, expanding the sample suite to include organic matter from west coast microlayers.

Surfactants in the samples were isolated either by foam tower enrichment or solid phase adsorption. The complex microlayer surfactant mixtures were separated into fractions according to solubility and polarity, or analyzed directly by mass spectrometry. Mass spectrometry was used to make inferences regarding chemical class and composition, since mass spectral patterns reflect molecular structure. Fragmentation patterns were acquired by pyrolysis-mass spectrometry. Static elasticities of these fractions were measured using a Langmuir film balance and then correlated with molecular composition and molecular structure using multiple regression techniques.

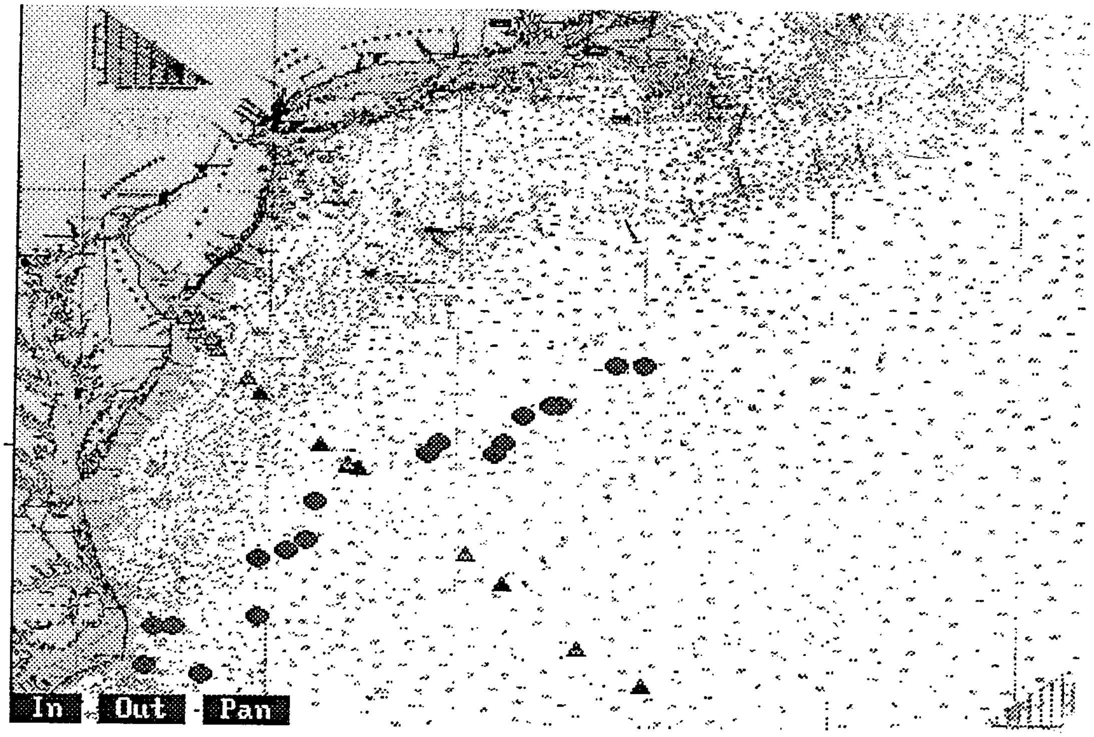

Figure 1 Chart of R/V Cape Henlopen microlayer cruises during September-October, 1994 and May-June, 1995. Triangles indicate the sampling stations; circles indicate the approximate location of western edge of the Gulf Stream.

Tasks Completed

The following tasks were completed during the project:

(1) *Small volume sample analysis*: Dissolved organic carbon (DOC), surfactant concentration, chromophoric dissolved organic matter (CDOM) fluorescence and carbon-nitrogen content were measured on the small volume samples from the Cape Henlopen and New Horizon cruises.

(2) *Large volume sample processing*: The large volume samples from all three cruises were processed by two methods: (1) foam enrichment and solvent extraction (adsorption on bubble surfaces) followed by successive extraction in three solvent systems and (2) by solid phase adsorption on C_{18}-SepPak cartridges followed by solvent elution of the adsorbed surfactants.

(3) *Mass spectrometric analyses*: The organic matter in the large volume samples (surface film and bulk seawater) has been analysed by mass spectrometry. Fragmentation patterns of the extracted surfactant mixtures were acquired in triplicate using pyrolysis-electron impact mass spectrometry (PY-MS) for use in a multiple regression analysis.

(4) *Static elasticity measurements*: Approximately 150 surface pressure-area isotherms have been measured for the various sample fractions. The isotherms have been processed to derive static film elasticity as a function of surface pressure. The elasticity data have been subsampled at fixed surface pressure intervals for input to the multiple regression analysis.

(5) *Multiple regression studies*: Linear discriminant analysis has been applied to a subset of the ~450 PY-MS spectra of microlayer and bulk surface seawater surfactants in our database. The LDA used a two-step principal component analysis to find mass descriptors (discriminant functions) that minimized and maximized the between-replicate and between-sample variance, respectively. The discriminant function scores for each spectrum were evaluated. The LDA scores were then correlated with the corresponding static surface elasticities measured for surface films of the materials. A quantitative description of microlayer films covering different dynamic and physical conditions in a variety of geographic and productivity regimes was thus developed.

Results

The R/V Cape Henlopen cruise tracks covered strong coastal-offshore concentration gradients in several chemical properties, including chlorophyll, dissolved organic carbon (DOC), surfactants, and colored dissolved organic matter (CDOM). Dissolved organic carbon levels decreased by nearly a factor of two in crossing the shelf and slope waters to the open ocean. Bulk seawater surfactant concentrations, as measured by static dropping mercury electrode (SDME) polarography, were shown to decrease by about a factor of twenty along the cruise transect. Colored organic matter or gelbstoff was a prominent component of the microlayer samples. Fluorescence emission spectra of discrete bulk seawater and microlayer samples taken during the fall 1994 cruise showed enhanced fluorescence in coastal waters relative to offshore waters and enhanced microlayer CDOM fluorescence relative to subsurface water. Overall, bulk seawater CDOM fluorescence levels decreased by a factor of twenty. A high degree of covariance between DOC, CDOM fluorescence and surfactant concentration was observed. Strong positive correlations between surfactant concentration and both DOC and CDOM fluorescence were demonstrated, consistent with similar measurements made during previous cruises in this area. Surfactant concentration was only weakly correlated with chlorophyll fluorescence as measured by the ship's SAIL system, probably because fluctuations in dissolved organic matter levels can be decoupled from primary production by such factors as riverine input, upwelling events and the phase lag between phytoplankton growth and production of surfactants.

Coherent slicks were observed in both coastal and oligotrophic waters, indicating that sufficient surface-active organic material was usually present to form localized surface features whenever organized water motions were favorable for concentrating organic material at the surface. The strong gradient observed for surfactant concentration suggests that surface roughness in the capillary-small gravity wave regime should be generally diminished in productive coastal waters relative to oligotrophic regions under similar physical forcing conditions, due to surfactant effects on wave generation and dissipation. This effect is important to interpretation of backscatter from airborne or space-based radar systems.

Significant variations in microlayer composition were observed spatially due to changing organic matter composition in the underlying bulk water. However, wind stress and subsurface water motions also played a strong role in controlling enrichment of the major surfactant classes that dominated microlayer surface elasticity. The mass spectra reflected significant compositional variations along the cruise transect and enrichments of specific organic compounds in the microlayer relative to the underlying water. The pyrolysis-MS spectra of extracts of a surface microlayer and a bulk seawater sample collected near the western edge of the Gulf Stream at 37°N 73°W are given in Figure 2. Enrichments of specific lipid compounds are directly evident from a comparison of the spectra. These include fatty acids (*e.g.* m/z 256, 270, 284), sterols and other tetracyclic/pentacylic lipids (m/z 370-470), carotenoids (m/z 536) and highly oxygenated compounds similar to poloxamers (m/z 58, 59, 160, 161, 333). Less apparent in the spectra are mass fragments that indicate the presence of peptide/protein components and a background of degraded polymeric (humic) materials that are the source of the CDOM fluorescence signal. Electrospray ionization mass spectra indicate that the bulk of the surface-active materials have molecular weights below 2000 Da, with a maximum abundance in the 700-1000 Da range.

With few exceptions, the mass spectra indicated that certain compound classes tended always to be enriched in microlayers regardless of spatial considerations (reflecting autochthonous marine sources), while enrichment of other compound classes depended strongly on distance offshore (reflecting both terrigenous and marine sources). In the Mid-Atlantic Bight, for example, the contribution from terrigenous organic matter (colored humic materials) to the spectra decreased strongly with distance from estuarine and terrestrial sources, progressing from Delaware Bay to the Sargasso Sea. The Mid-Atlantic Bight samples were very similar to those collected in the California Bight during the New Horizon cruise and during the SLIX 88/89 exercises in the same region. The predominant components identified in the SLIX 88/89 microlayers by linear discriminant analysis were also enriched in these microlayers, suggesting that a limited number of compound classes are dominant in microlayer films.

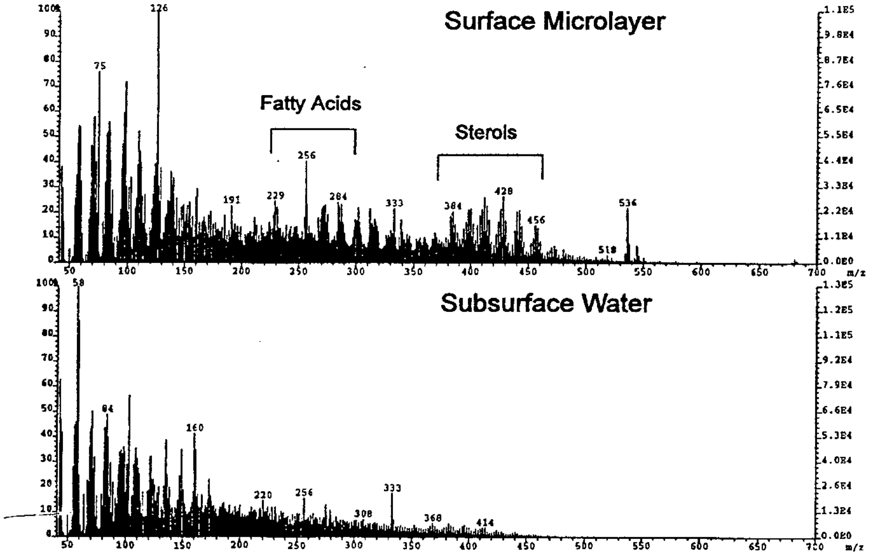

Figure 2 Comparison of PY-MS spectra of a marine microlayer extract with that of the underlying seawater. This chloroform/methanol fraction highlights microlayer enrichments of several classes of lipid compounds including fatty acids, sterol and carotenoids. Underlying these prominent components is a background of polymeric humic materials.

Previous field work (Bock and Frew, 1993) has suggested that sea-surface films exhibit a complex surface response to compressional-dilational straining, dependent on chemical composition. The particular mixtures of surfactant types present in the microlayers sampled in this study strongly influenced air-sea interfacial elasticity. Since the composition of natural mixed films was too complex to allow a rigorous model of elasticity based on individual component properties, an empirical approach was pursued, correlating elasticity with factors related to the hydrophilic-lipophilic balance of film components, chromatographic 'polar-nonpolar' behaviour, for example. A general correspondence between normal phase chromatographic retention index and static elasticity (ϵ) was observed, in which components with increasing chromatographic mobility (*i.e.* increasingly nonpolar, hydrophobic components) exhibited higher elasticity values at all surface pressures (π) compared to less mobile (more polar) components. This is illustrated by comparing the spectra of nonpolar and mixed nonpolar-polar thin layer chromatography fractions and their corresponding ϵ-π relationships (Figure 3). The presence of the polar components clearly resulted in lower film elasticities at a given film pressure. Components with low and high retention indices may be expected to make dominant contributions, respectively, to the elastic and viscous terms of the surface dilational modulus.

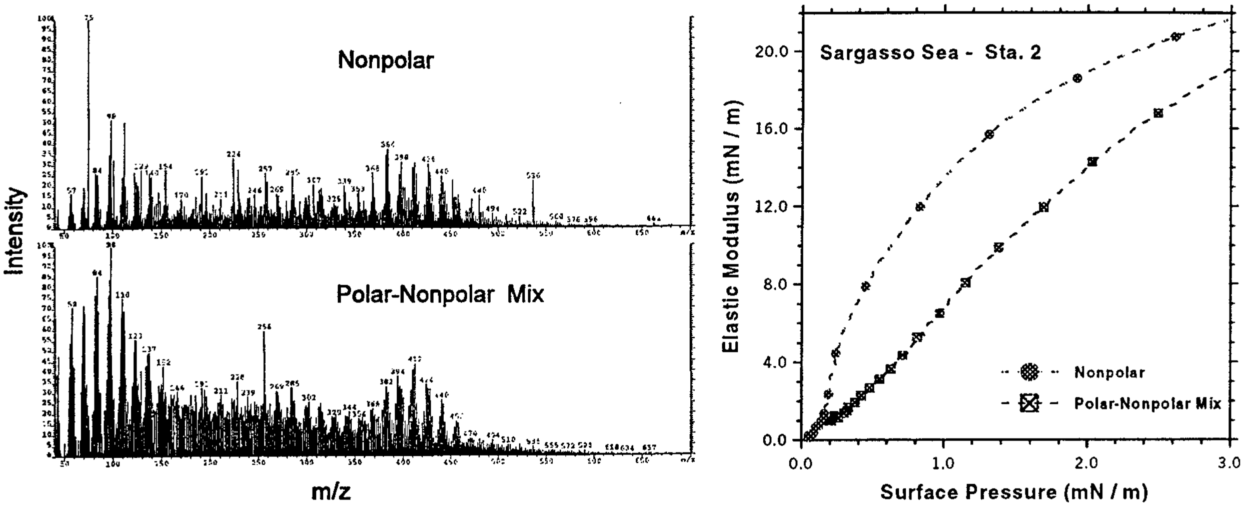

Figure 3 Mass spectra of nonpolar and mixed polar-nonpolar thin layer chromatography fractions of a marine slick and the elastic moduli of these fractions as a function of film pressure.

The strong influence of chemical composition on interfacial elasticity is further illustrated using representative microlayers collected in the Mid-Atlantic and southern California Bights (Figures 4-5). In Figure 4, mass spectra of three hexane/methylene chloride-extracted surfactant mixtures from (1) a surface bulk water sample, (2) an unslicked microlayer, and (3) a strongly slicked microlayer are presented. The spectrum of the bulk seawater sample is dominated by intense ions from only a few compounds, whose structures we have shown to be poloxamers (mixed ethylene oxide and propylene oxide polymers) possibly of anthropogenic origin. In the spectrum of the visibly unslicked microlayer, additional low intensity ions are observed in the 80-150, 200-300, and 350-470 m/z regions, representing the presence of small amounts of adsorbed lipid materials, primarily free and bound fatty acids, steroids, and terpenoids, along with the poloxamers. The spectrum of the third sample indicates that these lipid components, seen in minor amounts in the unslicked microlayer, are heavily enriched in the slicked microlayer relative to the poloxamers. The effect of this changing composition on interfacial elasticity is shown in Figure 5, in which measured static surface elasticities (ϵ) are plotted as a function of film surface pressure (π) for the same three samples. Film balance measurements of elasticities of poloxamers isolated and purified from natural seawater have shown that these compounds have intrinsically low elasticity at a given surface pressure. This is reflected in Figure 5 by the ϵ-π plot for the bulk water sample, which exhibits the lowest elasticities as a function of film pressure. Increasing amounts of the lipid components in the microlayer samples have a strong effect on surface elasticity, increasing it by as much as four-fold (Figure 5).

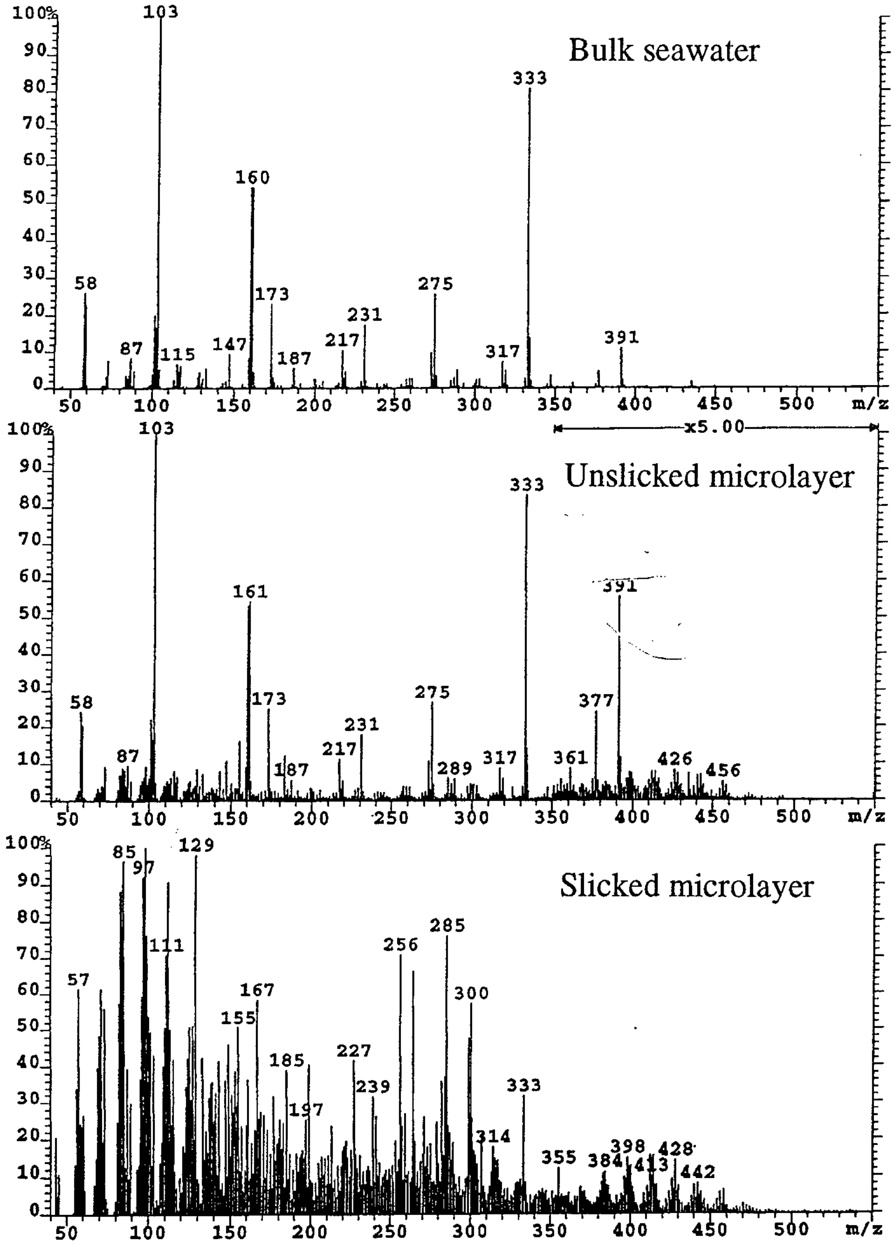

Figure 4 Mass spectra of hexane/methylene chloride extractable surfactants in bulk surface seawater (upper), unslicked surface microlayer (center) and slicked microlayer (lower). Spectra show dominance of poloxamer-like components in bulk water and increasing enrichments of more hydrophobic lipid surfactants in the microlayers.

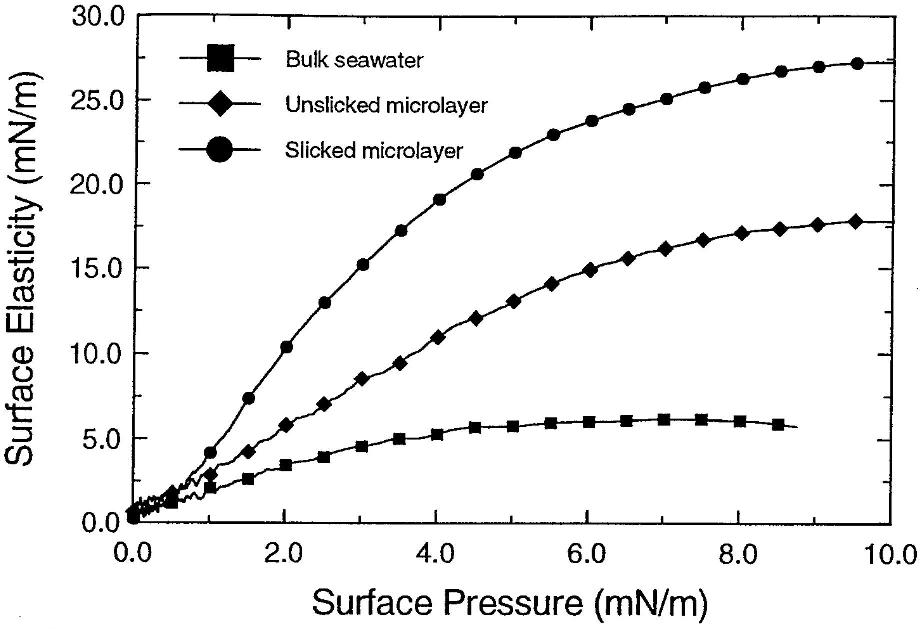

Figure 5 Variation of surface elasticity (ϵ) with film surface pressure (π) of air-water interfacial films corresponding to the compositions and mass spectra of Figure 4.

The mass spectra thus appeared to contain information not only about chemical composition, but also the surface elasticity. The surface physical properties of a surfactant are strongly dependent on molecular structure. Thus, it may be possible to use the spectra of microlayer organics not only to identify structural classes which control elasticity but also to predict elasticity. This hypothesis was tested by applying chemometric techniques to the mass spectra of a suite of 30 microlayer and bulk seawater samples. The sample spectra were loosely grouped according to their measured elasticities at 5 dyne/cm. A multivariate analysis technique (Linear Discriminant Analysis, LDA) was carried out in which discriminant functions were developed that distinguished each elasticity class from every other based on the spectra. The discriminant functions were evaluated for each spectrum to provide a discriminant score. Experimentally measured static elasticities for the samples were then compared with the discriminant scores to determine the degree of correlation between composition and surface elasticity. It was found that elasticities were strongly correlated with the scores of the first ranked discriminant, D1 and that the mass spectra contained sufficient information to predict film elasticities.

LDA results from one set of hexane/methylene chloride surfactant extracts are presented in Figures 6-8. The analysis demonstrates that mass spectral variations are strongly correlated with observed variations in elasticity. Five discriminant functions explained roughly 75% of the between-sample spectral variance. Figure 6 is the graphical representation of the first-ranked discriminant function (D1), representing 50% of the variance in the original spectral data. Here the intensities

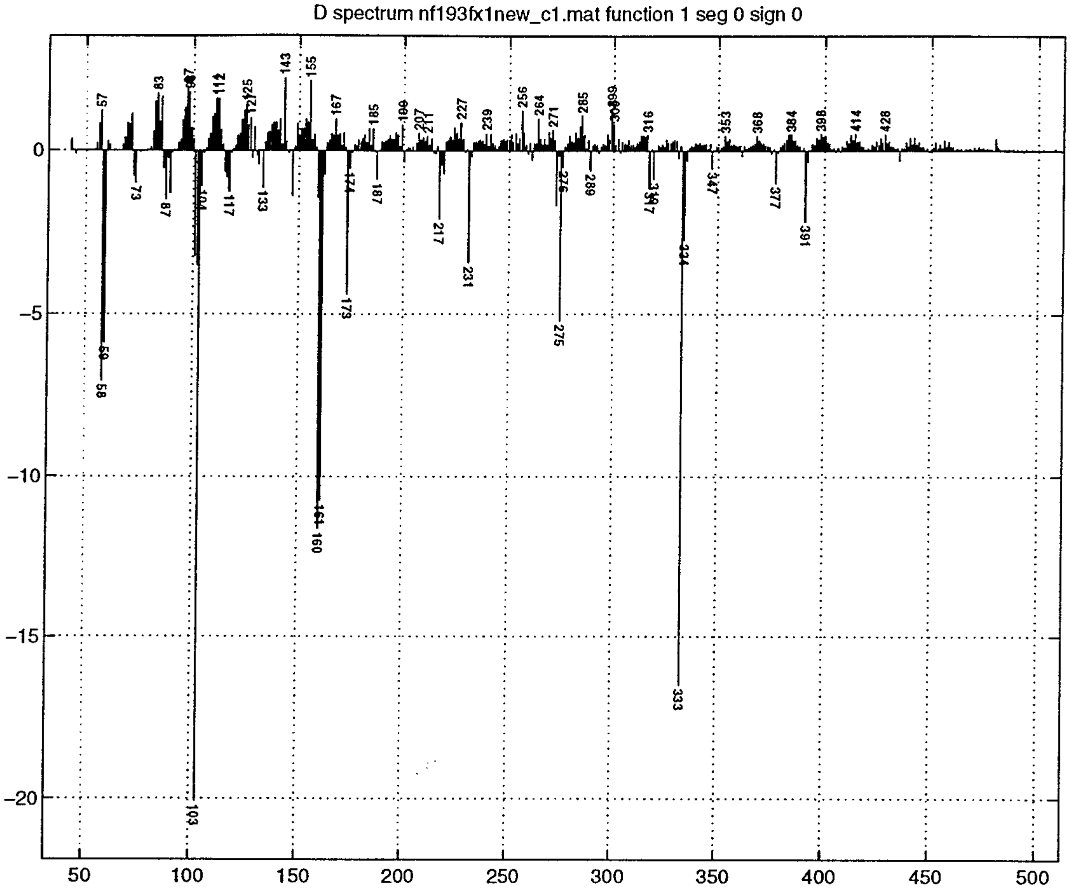

Figure 6 Graphical representation of discriminant D1 derived in the chemometric analysis of microlayer film mass spectra. Intensities at each mass value represent loadings for that particular mass used to calculate discriminant scores. Prominent masses include those representative of fatty acids, acyl lipids, sterols, poloxamers and humic compounds.

represent the loadings for each particular mass-to-charge ratio (m/z) used to calculate scores from individual sample spectra. The positive portion of D1 (D1+) was dominated by lipid components, particularly free fatty acids (e.g. m/z 256, 270, 284), bound acyl lipids, including wax esters and glycerides (m/z 227, 239, 271, 285, 299), and sterols (m/z 368, 384, 398, 412). The negative portion of D1 (D1-) was dominated by highly oxygenated poloxymers (m/z 160, 161, 333, 391). The D1 scores for a set of 30 of these sample extracts are plotted against corresponding surface elasticities in Figure 7. A strong linear correlation is evident. Microlayers enriched in D1+ components had higher elasticities than those enriched in D1- components. In Figure 8, we demonstrate that the D1 scores and the resulting regression relations can be used to predict surface elasticities at a given surface pressure reasonably accurately (to within 20%). Deviations of the predicted elasticities from the measured values are mainly due to the fact that only D1 was used in the prediction, thus ignoring information in lower ranked discriminants.

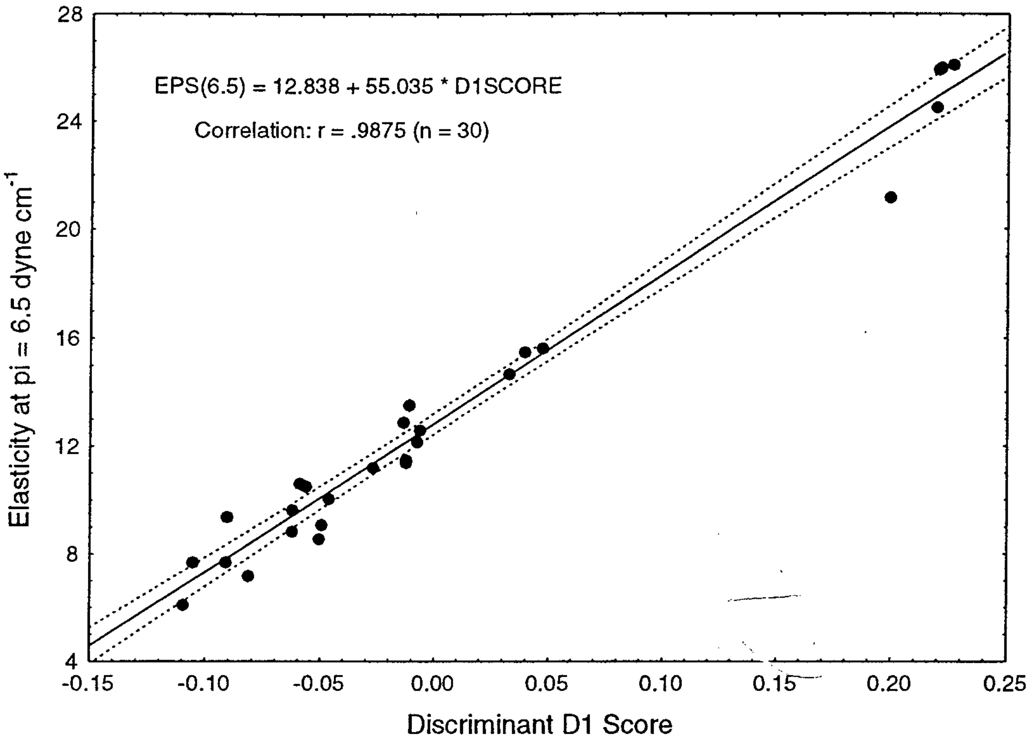

Figure 7 Correlation of surface elasticity (ϵ) at a film surface pressure of 6.5 dyne cm^{-1} with discriminant D1 scores for a suite of 30 films formed from microlayer and subsurface seawater surfactant extracts.

Impact/Application

A method for relating the composition and molecular structure of complex natural surface films to interfacial physical properties has been demonstrated. The PyMS-LDA method combines chemical and structural data with statistical analysis. The advantage of this approach is that it facilitates identification of the end-member components in complex mixtures that determine the elasticity of microlayer films. The mass spectra of microlayer organics can be used to predict elasticity from the spectra. This approach could be applied to *in situ* mapping of slick composition and surface elasticity by coupling our recently acquired benchtop mass spectrometer, which is capable of detecting and measuring individual film components in unresolved mixtures using multistage MS (MS^n), with a microlayer sampler.

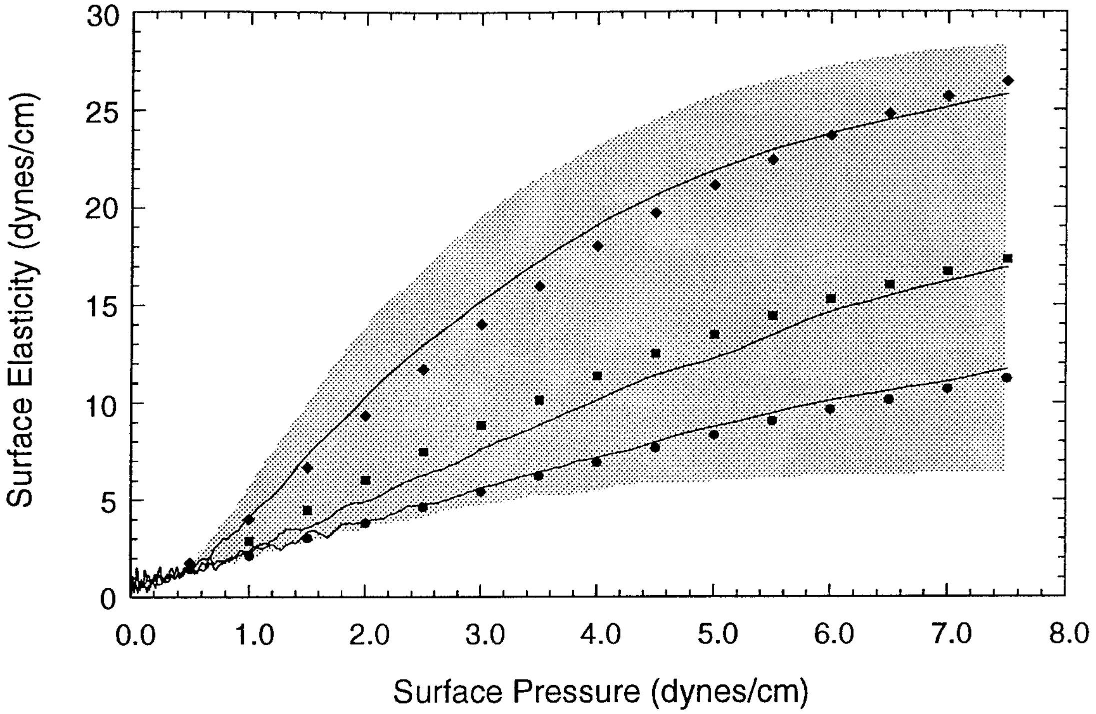

Figure 8 Measured surface elasticity as a function of film surface pressure for 3 surface microlayer films (solid lines). Shaded area indicates the overall range of elasticity observed for films from 30 microlayer and subsurface samples. Solid symbols are elasticity values predicted for the 3 films from their mass spectra using LDA-derived D1 score-elasticity relationships.

Related Projects

This project has relevance to those ONR-funded projects investigating (1) oceanic and atmospheric processes that modulate small scale waves and air-sea fluxes and (2) remote sensing imagery of the ocean surface using passive and active microwave sensors.

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